A STUDY OF THE THERMAL DECOMPOSITION OF THE CARBONATES AND OXALATES OF SOME RARE EARTH ELEMENTS BY DIFFERENTIAL THERMAL ANALYSIS

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By

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To my Wife

VITA

The author was born in Bamberg, South Carolina, on August 30, 1932. He received his secondary and high school education in the Bamberg schools, graduating from Bamberg High School in June, 1950. The author received the Bachelor of Science degree from Clemson A. and M. College with a major in Chemistry.

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ABSTRACT

A STUDY OF THE THERMAL DECOMPOSITION OF THE CARBONATES AND OXALATES OF SOME RARE EARTH ELEMENTS BY DIFFERENTIAL THERMAL ANALYSIS.

by Carl Barnes Bishop

The thermal decomposition of the carbonates and oxalates of lanthanum, cerium, neodymium, praseodymium, samarium and yttrium was studied by the differential thermal analysis technique.

A description for the construction and operation of equipment for differential thermal analysis was given.

The carbonates were prepared by decomposing solutions of the trichloroacetates of the elements studied. Only yttrium indicated a stable hydrate. The other carbonates were anhydrous after air drying for forty-eight hours. The carbonates generally decompose as indicated by the equation

$$R_2(CO_3)_3 \text{ —— } R_2O_3\cdot CO_2 \text{ —— } R_2O_3$$

The oxalates were precipitated from hot dilute nitrate solutions by dilute oxalic acid. Decahydrates were formed for all the rare earth oxalates studied. Lanthanum also formed a hexahydrate which would decompose to a tetrahydrate. Intermediate hydrates were identified from the decahydrates of neodymium, samarium and yttrium. The oxalates generally decomposed as indicated by the equation

$$R_2(C_2O_4)_3 \text{———} R_2O_3\cdot 2CO_2 \text{———} R_2O_3\cdot CO_2 \text{ ------ } R_2O_3$$

A reversible crystal conversion at 960°C was found for praseodymium oxide (Pr_6O_{11}).

X-ray powder diffraction patterns, chemical analysis, and microscopic photography were used to identify the compounds.

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INTRODUCTION

The decomposition of oxygen-containing anion salts such as carbonates, oxalates, sulfates, nitrates, etc. of the rare earth elements has been studied for many years.

In the past, two techniques, the measurement of pressure created by the reaction products and the determination of weight loss as the temperature of the salt was increased, have been used primarily. These techniques required very slow heating rates to allow equilibrium to be maintained. Differential thermal analysis was used in this study to detect thermal changes which accompany decomposition reactions or crystalline inversion. X-ray powder diffraction patterns were used in conjunction with chemical analyses to identify the intermediate compounds formed during decomposition.

The purpose of this study was to determine the intermediate products of the decomposition and the temperatures of decomposition of the oxalates and carbonates of yttrium, lanthanum, cerium, praseodymium, neodymium and samarium.

HISTORY

Differential Thermal Analysis

Le Chatelier [1] has been given credit for first using temperature measurements in 1887 to study thermal reactions. Only one thermocouple was used in a sample which was heated at a rather rapid and uniform rate. At short intervals, galvanic readings were taken and compared with readings taken when no sample was present. Variations in the readings indicated that a thermal reaction had taken place in the sample.

In 1899 Roberts-Austen[2] devised a simple differential thermocouple circuit for measuring the difference in the temperatures of a sample and an inert reference material thereby determining when a thermal reaction occurred. This technique was used extensively in metallurgy. In 1913 in a study of silica minerals, Fenner [3] was the first to use this newer technique to study thermal reactions outside of metallurgy.

This technique, called differential thermal analysis, can be described as a method by which thermal reactions in a material can be studied by determining the differences1 in the temperatures of that material and some thermally inert standard while both are being heated to higher temperatures at a rather rapid constant rate. The differential thermal analysis curves, which are usually plots of the temperature difference between the sample material and the inert standard versus the temperature of the inert standard or the surroundings in the furnace is a record of the dynamic thermal reactions taking place within the sample material.

The curves obtained during differential thermal analysis may exhibit peaks on one or both sides of the base line. (The base line is the line indicating the differential temperature values obtained when no reactions occurred. The base line may drift away from a horizontal line if the sample and the inert standard material differ greatly in specific heat or conductivity of heat). These peaks above or below the base line represent endothermic or exothermic reactions depending upon the arrangement and electrical wiring of the thermocouples. Figure 1 shows a typical curve obtained in this study.

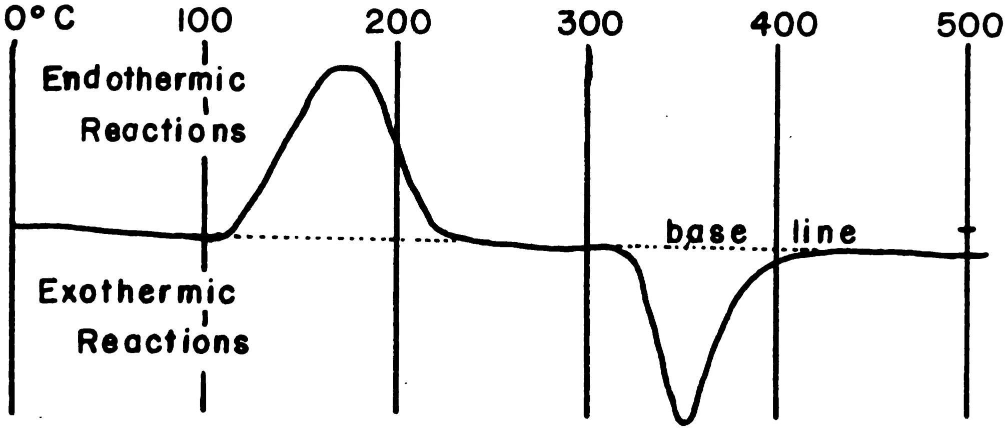


FIGURE 1

TYPICAL DIFFERENTIAL THERMAL ANALYSIS CURVE

Gruver [4] found that heat effects could be caused by the liberation of absorbed water, water of hydration, or water of crystallization; by the dissociation of a radical such as carbonate, sulfate, nitrate, etc.; by crystallographic inversions; or by chemical reactions such as oxidations.

Much study has been made of the components of the equipment needed for the procedure. The equipment includes a specimen holder, thermocouples, a furnace, a controlled power supply and a recording mechanism.

Sample Holder

Pask and Warner [5] pointed out two important features of a specimen holder; (1) the sample holder should be large enough to hold enough sample to give thermal activity but small enough to prevent the occurrence of temperature gradients in the sample; (2) the walls of the holder should be thick enough to act as a heat stabilizer but thin enough so as not to absorb all the heat of the reaction.

The sample holder should be a material which will not react with the sample to be studied.

Le Chatelier [1] and others [4,13] used platinum crucibles as sample holders. More recently nickel or ceramic holders have been used. Norton [6] suggested the use of a heavy nickel block to eliminate thermal gradients around the sample. Gruver [7] claimed that thin walled platinum holders had the advantages of possessing a high conductivity of heat which allowed the sample to quickly reach the furnace temperature and also of possessing a lower heat capacity which would not tend to decrease the intensity and sharpness of some thermal reactions.

Herold and Planje [8] combined the ceramic block with special platinum-platinum rhodium cups which served both as the sample holder and as the differential thermocouple. The bottom half of the cups and the thermocouple leads from the bottom were platinum (90%) rhodium (10%) alloy and the tops of the cups and the connecting wire were platinum. This construction had the advantage of allowing the thermocouple to be cleaned easily when certain samples shrank and sintered into hard residues but had the disadvantage of not having the thermocouple in contact with the sample after it began to shrink.

After comparing the properties of nickel and alumina sample holders, Webb [9] reported that although a nickel block gave sharper peaks than an alumina block the peaks were less intense and began at higher temperatures. The porous nature of the alumina block allowed gaseous products to diffuse away more rapidly and thus allowed the reaction to be completed quickly. When a silica liner was used in the alumina block to prevent corrosion, it also cancelled this increase in reaction rate. Gordon and Campbell [10] used a steel block with the sample holes lined with borocilicate tubes.

Kerr and Kulp [11] have described a holder of chrome nickel-steel in which six different samples could be analyzed in one run.

Thermocouples

Thermocouples should be made from material which will withstand corrosion by the sample. The wire should be small enough so as not to conduct heat to or from the sample rapidly but yet large enough to have physical strength so it could be easily cleaned without damage. Wire ranging from 24 to 28 B and S gauge has proven to be satisfactory.

Several thermocouple circuits which have been used have been reported by Grim [12] (Figure 2, page 6). Circuit no. 1 has become the most popular because of the better reproducibility of results. A slight variation of this (circuit no. 3) will be used in this study so that all thermocouple junctio will be equal distance from the heating zone.

Pask and Warner [5] grounded the thermocouple with a 100 m.f.d. electrolytic 50 volt D.C. condenser to filter out any A.C. pickup.

Early investigators used platinum-platinum (90%) rhodium (10%) thermocouples and these alloy combinations are still being widely used. Chromel-alumel thermocouples have been used satisfactorily with some materials up to 1000°C. In lower temperature work, iron-constantan thermocouples are used to take advantage of the larger e.m.f. characteristic of these thermocouple elements. Kracek [13] used a gold-platinum versus platinum-rhodium thermocouple which produced about fifty microvolts per degree centigrade at high temperatures.

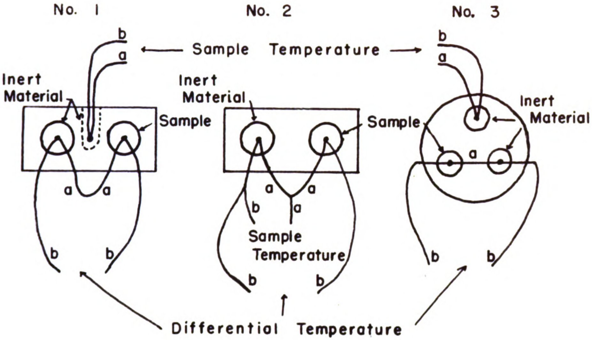


FIGURE 2

THERMOCOUPLE CIRCUITS.
NUMBER 1 AND NUMBER 2
CIRCUITS GIVEN BY
GRIM[12] AND NUMBER
3 USED IN THIS
STUDY.

Furnace Design

The furnace must be designed to give a uniform heating zone and have a heating capacity large enough to allow the specimen to be heated at a controlled uniform rate.

Pask and Warner [5] observed that heating elements of nichrome wire were satisfactory up to 1000°C, of Kanthal wire up to 1300°C, and of platinum-rhodium wire up to 1500°C.

Several types of furnaces have been reported. Grim [14] used a horizontal furnace mounted on rollers so that it could be easily rolled over the sample holder. This permitted easy access to the sample and reproducible positioning of the sample in the furnace. Gruver [7] has contended that the horizontal furnace reduced thermal currents and thermal gradients in the heating zone. Kracek [13] used a vertical furnace and lowered the sample and thermocouples through the top. Baffles were placed in the furnace tube to reduce convection currents. Herold and Planje [8] used a vertical furnace and inserted the sample holder through the bottom.

Furnace Temperature Control

The control must be tailored for each furnace to give the desired heating rate. Several "homemade" or commercial automatic program controllers have been made which give reproducible uniform heating rates. Autotransformers driven slowly by motors through gear reducers have been used to continuously increase the voltage. Controls which give heating rates from 6 to 20 degrees per minute have been used but a rate of about 12 degrees per minute is most common. Any sudden change in the heating rates will be reflected in the differential thermocouple potential.

Norton [6] has shown that a heating rate which is too slow produces broader peaks which occur at lower temperatures. The heating rate has to be fast enough to cause sharp reactions but slow enough to prevent the overlapping of the differential thermal peaks.

Thermocouple Potential Recording Equipment

Early workers [1,13] measured at regular intervals the e.m.f. of the differential thermocouples by a potentiometer and plotted these data against time or furnace temperature.

The first continuous recorders were photographic recorders in which a beam of light reflected from the mirror of a galvanometer was focused on photographic paper moving slowly on a drum. This method required elaborate preparations such as a dark box, a dark room and developing equipment and had the disadvantage of not allowing the investigator to watch the recording as it was made.

Gruver [7], Kerr and Kulp [11], and Gordon and Campbell [10] have described automatic recording devices which were satisfactory. Grim [12] was of the opinion that a recording device should give about a two inch deflection for a one tenth millivolt potential. He also suggested placing variable resistances in the thermocouple circuit to vary the sensitivity of the recorder when necessary.

Calibration of Reactions

The α-β crystal inversion of quartz which occurs at 575°C has been used by Berkelheimer[15,16] to establish a known temperature in calibrating the sample temperature. Faust[17] described a method of using quartz as an internal temperature standard in a sample. Prasad and Patel[18] in their study of manganese dioxide calibrated the sample temperature thermocouple with synthetic pyrolusite which gave peaks at 620° and 990°C.

Barshad[19] has made an excellent study of calibrating reactions and has reported fourteen compounds which give sharp peaks of crystal inversion or melting points which cover temperature ranges from 32°C to 961°C.

Inert Thermal Standards

Any material, which will not undergo any thermal reaction over the temperature range being studied, can be used as the standard reference material around one junction of the differential thermocouple. If there is a large difference in the heat capacities of the standard reference material and the sample, the base line, which is the plot of the readings of the differential thermocouple potential when no reaction is taking place, will drift away from zero potential due to the uneven heating of the differential thermocouple junction.

Calcined aluminum oxide (Al_2O_3) has been used most commonly as the reference material.[11,12,17,20]

Applications of Differential Thermal Analysis

Speil, Berkelheimer, Pask and Davies[21] developed a method which could be used quantitatively (± 5%) to determine the mineral constitution of mixtures whose prime constituents could be obtained and analyzed individually to establish standard peaks. The method could be used semiquantitatively (± 10%) or qualitatively to study the mineral constitution of natural clay or other aluminosilicate formations.

Berkelheimer[16] reported that the endothermic peak of the α-β inversion of quartz can be detected in a sample containing as little as 1% quartz. The area under the peak was reproducible to a maximum variation of 5% independent of the size of the quartz pieces. More than 15% calcium carbonate present in a sample when the quartz was less than 20μ in size resulted in loss of quartz by chemical reaction.

Barshad[19] described a procedure to measure the heats of reaction of compounds by comparing the area under the thermal peaks with peak areas which resulted from reactions of compounds having known heats of reaction.

OXALATES

Preparation of Oxalates

In a study of the precipitation of the oxalates of neodymium, praseodymium, yttrium and certain other rare earths, Baxter and Griffin[22] reported that in neutral or nearly neutral solutions these oxalates had high tendencies to carry down ammonium oxalate which was being used as the precipitating agent. They suggested adding a strong acid and decreasing the ammonium oxalate concentration as a means of preventing this phenomenon.

Later Baxter and Daudt[23] found only a trace of ammonium oxalate carried down when the solution was acidified with two equivalents of nitric acid. Sodium oxalate was carried down only by samarium oxalate in neutral solution. Yttrium occluded alkaline oxalates to almost the same degree in acid or neutral solutions. Oxalic acid was not carried down when used as the precipitating agent.

Wirth[24] reported that the precipitation of the rare earths with oxalic acid was best in a 5.5 N sulfuric acid solution and that excess oxalic acid greatly decreased the solubility of the oxalate.

Wylie[25] reported two hydrates (hexa- and di-) were formed when lanthanum nitrate solution was precipitated with 10% oxalic acid solution and digested. The hexahydrate was converted to the dihydrate at 180°C. Cerium (III) and neodymium formed only interstitial hydrates while yttrium formed a hexahydrate when heated for seven hours at 98°C in water.

Homogeneous precipitations of thorium and the rare earths with methyl oxalate were studied by Willard and Gordon[26]. Later Gordon, Brandt, Quill and Salutsky[27] used the hydrolysis of methyl oxalate to separate lanthanum and cerium (III) and also lanthanum and praseodymium.

Wendlandt[28] formed the oxalates of lanthanum, cerium (III), praseodymium, neodymium, samarium, europium, gadolinium and holmium by homogeneous precipitation with methyl oxalate and by drying with 95% ethyl alcohol and reported the decahydrate in all cases. Yttrium formed a nine hydrate while erbium formed a hexahydrate. Lower hydrates were formed when these were heated as indicated in Table I, page 12.

TABLE I

I. $\mathrm{Sc_2(C_2O_4)_3 \cdot 6H_2O} \xrightarrow[50^\circ-185^\circ C]{-H_2O} \mathrm{Sc_2(C_2O_4)_3 \cdot 2H_2O} \xrightarrow[220^\circ-635^\circ C]{-CO_2,\ -H_2O} \mathrm{Sc_2O_3}$

II. $\mathrm{Y_2(C_2O_4)_3 \cdot 9H_2O} \xrightarrow[45^\circ-1\text{[illegible]}0^\circ C]{} \mathrm{Y_2(C_2O_4)_3 \cdot 2H_2O} \xrightarrow[\text{[illegible]}]{} \mathrm{Y_2(C_2O_4)_3}$

$\xrightarrow[410-735^\circ]{} \mathrm{Y_2O_3}$

III. $\mathrm{La_2(C_2O_4)_3 \cdot 10H_2O} \xrightarrow[55-380^\circ C]{} \mathrm{La_2(C_2O_4)_3} \xrightarrow[380-550^\circ C]{} \mathrm{La_2O_3 \cdot CO_2}$

$\xrightarrow[735-800^\circ C]{} \mathrm{La_2O_3}$

IV. $\mathrm{Ce_2(C_2O_4)_3 \cdot 10H_2O} \xrightarrow[50-205^\circ C]{} \ ? \ \xrightarrow[300-360^\circ C]{} \mathrm{Ce\ O_2}$

V. $\mathrm{Pr_2(C_2O_4)_3 \cdot 10H_2O} \xrightarrow[40-420^\circ C]{} \mathrm{Pr_2(C_2O_4)_3} \xrightarrow[420-790^\circ C]{} \mathrm{Pr_6O_{11}}$

VI. $\mathrm{Nd_2(C_2O_4)_3 \cdot 10H_2O} \xrightarrow[50-250^\circ C]{} \ ? \ \xrightarrow[250-445^\circ C]{} \mathrm{Nd_2(C_2O_4)_3} \xrightarrow[445-735^\circ C]{} \mathrm{Nd_2O_3}$

VII. $\mathrm{Sm_2(C_2O_4)_3 \cdot 10H_2O} \xrightarrow[45^\circ C]{} \underset{140^\circ C}{\text{Several}} \ \underset{190^\circ C}{\text{Breaks}} \xrightarrow[300^\circ C]{} \mathrm{Sm_2(C_2O_4)_3}$

$\xrightarrow[410-735^\circ C]{} \mathrm{Sm_2O_3}$

Decomposition of Oxalates

From data of pressure measurements between 130-170°C, Wobbe and Noyes [29] proposed the probable equation for the decomposition of oxalic acid to be

$$(COOH)_2 \longrightarrow HCOOH + CO_2$$

Herschkowitsch [30] decomposed ferrous oxalate in a vacuum and found the residue to be about half metallic iron, half ferrous oxide and a small amount of carbon. A mixture of carbon monoxide and carbon dioxide was evolved. Nickel oxalate was decomposed and the residue was almost pure nickel with traces of the oxide and carbonate. The gases evolved were mainly carbon dioxide with a little carbon monoxide.

From this, Herschkowitsch proposed that the primary decomposition products of all oxalates were carbon dioxide and the metal, but the easily oxidized metals reduced half the carbon dioxide to give final products of carbonate and carbon monoxide. Part of the carbon dioxide could be reduced to carbon, and, as a consequence, a small amount of oxide remained also. Less readily oxidizable metals such as iron and lead reduced only part of the carbon dioxide and the result was the metal and the oxide.

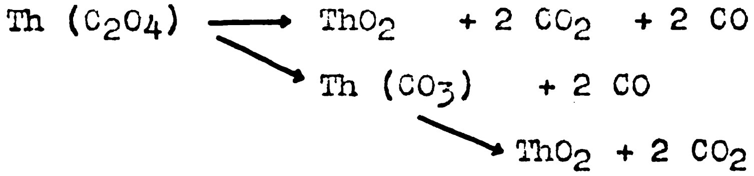
Švéda [31] decomposed lead (II) oxalate in a vacuum and reported the residue to be a mixture of lead oxide and lead. The ratio of lead oxide (PbO) to lead was found to be proportional to the carbon dioxide found.

In the decomposition of calcium oxalate monohydrate studied by Moles and Villamil [32], carbon dioxide, carbon monoxide, carbon, calcium carbonate, and traces of formic acid were the products. The oxalate decomposition began at 380°C and followed this primary reaction.

$$CaC_2O_4 \longrightarrow CaCO_3 + CO$$

Ugav^{33} determined the final products, the temperature of dehydration, and the decomposition of some divalent metal oxalates thermographically. The results are shown in Table II.

Thorium oxalate precipitated by ammonium oxalate and dried at 105°C was reported by D'Eye and Sellman^{34} to give a pentahydrated oxalate while precipitation by oxalic acid gave a dihydrated oxalate. When samples of these oxalates were heated in a quartz boat in a stream of water vapor of carbon dioxide-free nitrogen the water of hydration was lost readily at 270°C. Above 320°C the decomposition gave a mole ratio of carbon monoxide to carbon dioxide slightly greater than one. Carbon was formed in the reaction and D'Eye and Sellman believed it was formed by the disproportionation of carbon monoxide into carbon and carbon dioxide. The reaction may have proceeded simultaneously by two paths as shown in the following equations.



$$\begin{tikzcd}
Th\ (C_2O_4) \arrow[r] \arrow[dr] & ThO_2 + 2\ CO_2 + 2\ CO & \\
& Th\ (CO_3) + 2\ CO \arrow[dr] & \\
& & ThO_2 + 2\ CO_2
\end{tikzcd}$$

Centola ^{35} decomposed gadolinium oxalate tetrahydrate and measured vapor pressures with a tensimeter from 128° to 260°C. At 129°C the tetrahydrate began converting to the

TABLE II

	Temperature of		
Compounds	Dehydration &	Decomposition	Product
$H_2C_2O_4 \cdot 2H_2O$	96-99	191-196	
$NiC_2O_4 \cdot 2H_2O$	275-95	400-405	Ni
$CoC_2O_4 \cdot 2H_2O$	219-330°	400-409	Co
$FeC_2O_4 \cdot 2H_2O$	200-219	371-379	Fe
$MnC_2O_4 \cdot 2H_2O$	93-125	384-412	MnO
$ZnC_2O_4 \cdot 2H_2O$	183-230	414-426	ZnO
$MgC_2O_4 \cdot 2H_2O$	196-212	421-419 (super heat)	MgO
$CdC_2O_4 \cdot 3H_2O$	106-118	368-393	Cd + CdO
PbC_2O_4		354-413	PbO
SnC_2O_4		342-350	SnO_2
$CaC_2O_4 \cdot H_2O$	105-110	263-285	$CaCO_3$
$SrC_2O_4 \cdot H_2O$	122-164	182-194	$SrCO_3$
BaC_2O_4		226-246	$BaCO_3$
HgC_2O_4 (exotherm.)		233-320	Hg + HgO
$CuC_2O_4 \cdot 2H_2O$ (exotherm.)	140-171	320-376	Cu + CuO

dihydrate and continued to the monohydrate at 166°C. The anhydrous oxalate began to decompose at 195°C to give a final product of gadolinium oxide. No intermediate compounds were reported.

Günther and Rehaag [36] decomposed neodymium oxalate in a vacuum and found carbon monoxide and carbon dioxide evolved. They reported the primary product to be a peroxydioxalate instead of a carbonate. The oxalates of sodium, barium, calcium and thorium were reported to show this behavior. Carbon dioxide was believed to be formed by the disproportionation of carbon monoxide to carbon dioxide and carbon. The carbon was colloidal and easily oxidized by strong oxidizing agents.

Wylie[25] reported that slow decomposition of lanthanum oxalate occurred above 280°C.

Fornoff [37] reported in a study of the decomposition of cerium compounds that a 10.3 hydrate of cerous oxalate began losing water almost as soon as it was heated but reached a stable compound corresponding to a 0.8 hydrate between 130°C and 230°C. A sharp break occurred in weight loss at about 250°C to form a material which had a molecular weight of approximately 456 atomic weight units. Then at about 290°C a second sharp break occurred as the material went to the oxide.

Somiya and Hirano[33] studied the decomposition of the oxalates of lanthanum, cerium (III), praseodymium, neodymium and samarium by thermogravimetric techniques. The decomposition of lanthanum, praseodymium, neodymium or samarium oxalate is generalized by the following equation.

$$(C_2O_4)_3 \cdot n\ H_2O \longrightarrow R_2(C_2O_4)_3 \longrightarrow R_2(CO_3)_3 \longrightarrow R_2O_3 \cdot 2CO_2$$

$$\longrightarrow R_2O_3 \cdot CO_2 \longrightarrow R_2O_3$$

The temperature of decomposition of $R_2O_3 \cdot CO_2$ to R_2O_3 rose accordingly as the oxide became more basic.

A summary of their results is given in Table III.

Table III

I

$$Sm_2(C_2O_4)_3 \cdot 10H_2O \xrightarrow{70-150^\circ C} Sm_2(C_2O_4)_3 \cdot 3H_2O \xrightarrow{170-250^\circ C} Sm_2(C_2O_4)_3$$

$$\xrightarrow{365-400^\circ C} Sm_2(CO_3)_3 \xrightarrow{400-530^\circ C} Sm_2O_3 \cdot CO_2 \xrightarrow{740-750^\circ C} Sm_2O_3$$

II

$$Nd_2(C_2O_4)_3 \cdot 10H_2O \xrightarrow{70-170^\circ C} Nd_2(C_2O_4)_3 \xrightarrow{360-410^\circ C} Nd_2(CO_3)_3$$

$$\xrightarrow{415-545^\circ C} Nd_2O_3 \cdot CO_2 \xrightarrow{820-835^\circ C} Nd_2O_3$$

III

$$Ce_2(C_2O_4)_3 \cdot 9H_2O \xrightarrow{40-125^\circ C} Ce_2(C_2O_4)_3 \xrightarrow{295-330^\circ C} CeO_2$$

IV

$$La_2(C_2O_4)_3 \cdot 7H_2O \xrightarrow{35-110^\circ C} La_2(C_2O_4)_3 \cdot 3H_2O \xrightarrow{120-205^\circ C} La_2(C_2O_4)_3$$

$$\xrightarrow{370-505^\circ C} La_2O_3 \cdot 2CO_2 \xrightarrow{525-545^\circ C} La_2O_3 \cdot CO_2 \xrightarrow{945-960^\circ C} La_2O_3$$

V

$$Pr_2(C_2O_4)_3 \cdot xH_2O \longrightarrow Pr_2O_3 \cdot CO_2 \xrightarrow{910-920^\circ C} Pr_2O_3$$

Wendlandt[28] studied the decomposition of 90-100 milligrams of some rare earth oxalates in a thermobalance. Table III gives part of the interpretation of the data by Wendlandt. Several breaks in the weight loss curves were not explained.

Carbonates

Rare earth carbonates have been prepared by a variety of methods. Precipitation by the addition of alkali carbonates or bicarbonates[39] to rare earth salt solutions produced a material usually contaminated with alkali ions. Preparations made by passing a stream of carbon dioxide[40] through suspensions of rare earth hydroxides always contained some of the hydroxide as an impurity. Salutsky and Quill[41] prepared the normal carbonates by decomposing the trichloroacetates of rare earth metals on a steam bath. The procedure liberated carbon dioxide and chloroform and left no positive metal ions to contaminate the precipitate.

A number of hydrates were reported for the normal carbonates. Preiss and Dussik[42] prepared the normal carbonates of cerium, lanthanum, neodymium and praseodymium by precipitation from bicarbonate solutions with carbon dioxide. The octahydrate was formed when air dried. The dihydrate was produced when dried over concentrated sulfuric acid and the monohydrate resulted at 100°C. Anhydrous normal carbonate resulted when heated for weeks at 200°C in a current of carbon dioxide.

Salutsky[43] reported some normal carbonates prepared by the trichloroacetate method to be $La_2(CO_3)_3 \cdot 5.51\ H_2O$, $Nd_2(CO_3)_3 \cdot 2.5\ H_2O$ and $Sm_2(CO_3)_3\ 3H_2O$.

Hallander[44] prepared the normal lanthanum carbonate by the same procedure and obtained two hydrates $La_2(CO_3)_3 \cdot 6.11\ H_2O$ and $La_2(CO_3)_3 \cdot 7.78\ H_2O$.

Mono-, tri-, and octahydrates for lanthanum carbonate have been reported in the literature[45].

The carbonates were reported by Paul, Brinton and James[46] to undergo hydrolysis. The rate of hydrolysis was used to determine the order of basicity. It was noted that the rate of hydrolysis increased usually with increasing atomic weight.

Jaquith[47] prepared europium carbonate to study the effect of hydrolysis during the preparation of the carbonates by the method of Salutsky and Quill[41] and found the effect to be very small.

In a study of the optical properties of lanthanum and neodymium, Engel[48] determined the crystalline system of lanthanum carbonate to be biaxial negative monoclinic. The refractive index at 24°C was found to be 1.6533 ± 0.0003 for the α axis, 1.6895 ± 0.0003 for the γ axis, and the β axis was nearest the γ axis. Neodymium carbonate was orthorhombic and the refractive indexes were 1.6045 ± 0.0005 for the α axis, and 1.6570 ± 0.0005 for the γ axis. The β index was undetermined.

MATERIALS AND METHODS

Construction of Equipment

The equipment for differential thermal analysis was designed and assembled by the author. The equipment consisted of a sample holder, a furnace, three thermocouples, two recording potentiometers and a controlled power supply.

Sample Holder (Photos 1 and 2)

The sample crucible was shaped from a block of Norton Alundum cement (RA 1142) with overall dimensions, one and one-half inches high and one and three-fourths inches in diameter. The crucible was composed of three sections; the lid (A), the center (C), and the base (E) (Figure III). The lid (A) was a solid disk, one and three-fourth inches in diameter and one-fourth inch thick. The center (C) was one-fourth inch thick with the bottom edge notched one-eighth inch to fit as the male joint into the base. The base (E) was one and three-eighth inches high and one and three-fourth inches in diameter with a one-eighth inch rim to fit as the female joint with the center (C). This type joint was used to keep the holes aligned and to prevent radiation of heat through the seam which would cause the sample to be heated unevenly. Three five-sixteenth inch diameter holes were drilled through the center section into the base for an overall depth of one-half inch. These holes were arranged in an equilateral triangle with their centers one-half inch from the edge of the block. Holes one-fourth inch in diameter and three-

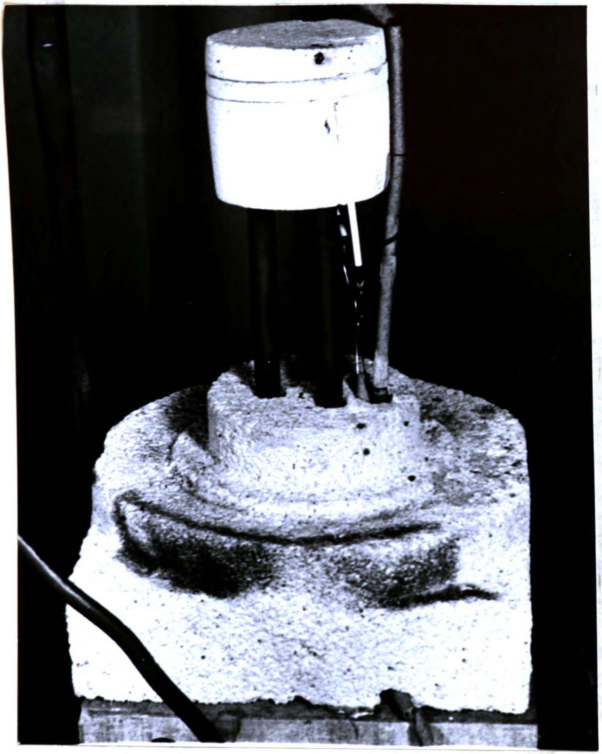


PHOTO 1. CLOSE VIEW OF SAMPLE CRUCIBLE, NICKEL TUBE SUPPORTS, DIFFERENTIAL THERMOCOUPLE LEADS, INSULATED CHRONOTROL CONTROL THERMOCOUPLE BESIDE AND ABOVE THE CRUCIBLE, AND FIRE BRICK PLUG. AT THE LEFT REAR IS SHOWN ONE OF THE FURNACE GUIDE RODS.

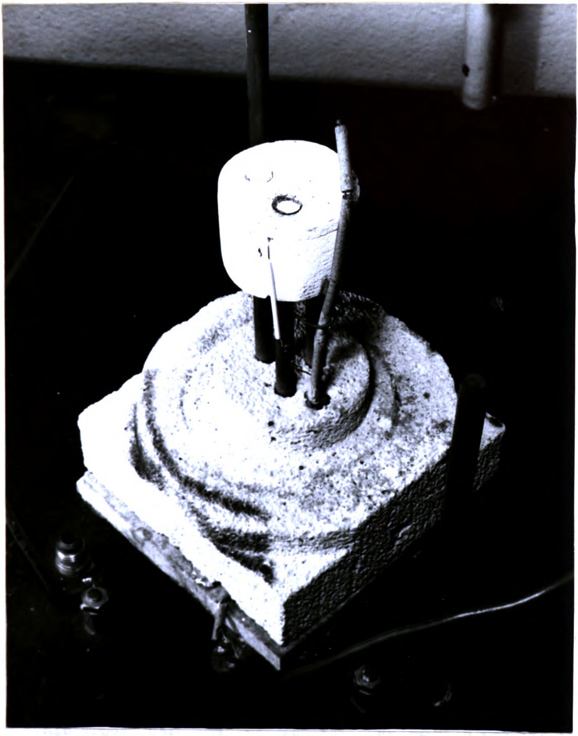


PHOTO 2. AN ANGLE VIEW OF THE SAMPLE CRUCIBLE WITH THE LID REMOVED TO EXPOSE THE SAMPLE HOLES. THE CHRONOTROL CONTROL THERMOCOUPLE, THE DIFFERENTIAL THERMOCOUPLE LEADS AND FIRE BRICK PLUG ARE SHOWN. ACROSS THE BOTTOM FROM LEFT TO RIGHT IS ONE WATER CONNECTOR, FURNACE POWER LEAD AND BINDING POST, DIFFERENTIAL THERMOCOUPLE BINDING POST, ANOTHER FURNACE POWER LEAD AND BINDING POST, AND A FURNACE GUIDE ROD.

eighth inch deep were drilled in the base directly below the crucible holes to receive the support tubes. A hole, one-thirty second inch in diameter was drilled with a paper clip wire to connect the support tube holes and the crucible holes.

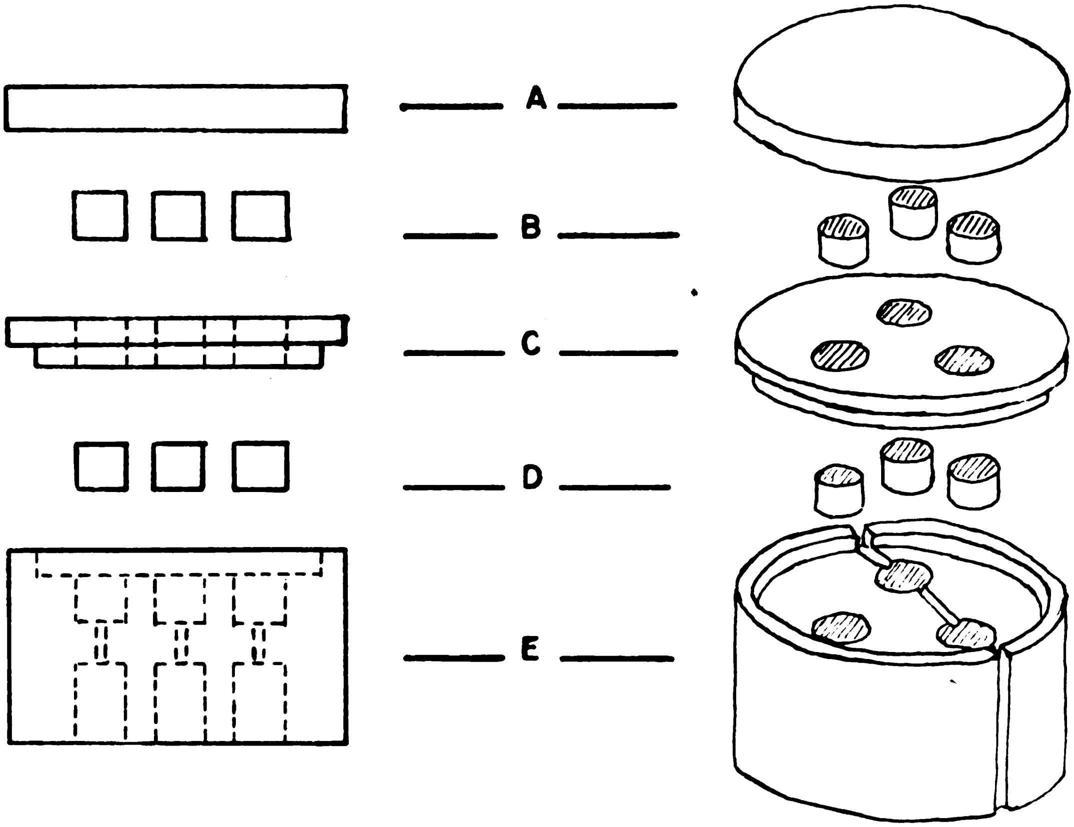


FIGURE III

A SIDE VIEW AND A SKETCH OF THE PARTS OF THE SAMPLE CRUCIBLE. A-LID, B-PLATINUM RINGS, C-CENTER SECTION, D-PLATINUM CUPS, E-BASE.

A groove was cut diagonally across the top of the base section (E) through the center of two of the crucible holes. This groove held the differential thermocouple and its insulation in place between the base and the center section.

The crucible holes in the base section (E) were fitted with platinum cups (D) and the center section (C) holes were filled with platinum rings (B). The cups and rings were fabricated from a twenty-eight gauge platinum sheet by fitting the parts over a steel rod, nine-thirty second inches in diameter, heating the seams with an oxygen-acetylene torch and tapping gently with a small hammer to fuse the joints. The top edges of the rings were flared to prevent them from falling out when the center section was removed from the base.

The alundum cement parts were heated to 1200°C for two hours to harden them.

Thermocouples

Three thermocouples were necessary in this equipment design. One was a differential thermocouple used to detect thermal changes in the sample and was connected to a sensitive high speed recorder which recorded these electrical impulses. A second thermocouple was used for measuring the sample reaction temperatures, and a third thermocouple actuated the rate-of-heating program apparatus.

The differential thermocouple was made from No. 24 B gauge platinum (87%)-rhodium (13%) wire in the center section and platinum in the outer leads. The fused junctions were 17mm. apart. The wires were held in position by the jig shown in Figure IV and were fused by heating with an oxygen-acetylene torch and tapping lightly with the punches. Single hole spaghetti ceramic insulators (one-sixteenth inch in outside diameter and one-thirty second inch in inside diameter) were used to insulate the thermocouple leads where they passed between the platinum rings and cups.

The sample temperature was measured with a chromel-alumel thermocouple made of No. 18 B&S gauge matched wire. The furnace control thermocouple was constructed of the same material. The leads of both thermocouples were insulated with two hole spaghetti insulator one-eighth inch outside diameter.

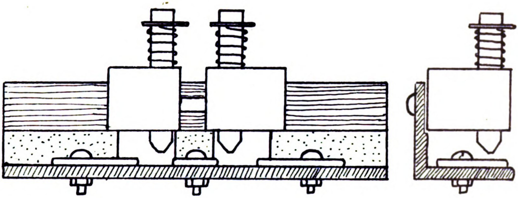


FIGURE IV

A FRONT VIEW AND END VIEW OF THE JIG USED IN MAKING THE DIFFERENTIAL THERMOCOUPLE. THE DISTANCE BETWEEN THE PUNCH TIPS WAS ADJUSTABLE. THE WIRE COMPONENTS OF THE THERMOCOUPLE WERE HELD IN PLACE BY THE METAL PLATES ON THE BASE. SPRINGS HELD THE PUNCHES UP WHILE THE WIRES TO BE FUSED WERE HEATED. (ACTUAL SIZE)

The sample temperature thermocouple was passed up through the nickel tube into the alundum crucible to the third sample hole and the junction was packed in Al_2O_3. The junction of the furnace control thermocouple was placed about three-fourth inches above the sample crucible and the insulated leads passed beside the crucible through a fire brick plug out to the binding post on the furnace base (Photos 1 and 2).

Furnace Base

The furnace was mounted on a cast iron base twelve inches by twelve inches by one-half inch which was supported by a one inch angle iron frame six inches high. Because of the difficulty of welding or silver soldering to cast iron, all fittings on the base were mounted by threading the fitting with tapered pipe threads and screwing the fitting into the furnace base from the bottom side, Figure V. Three one-fourth inch nickel tubes, seven inches long, were silver soldered into brass plugs and mounted in the furnace base in a manner to fit into the holes in the base of the crucible. A four inch by four inch by two and one-half inch fire brick was cut on a lathe to form a circular plug, two and one-fourth inches in diameter and three-fourths inches high, on one square side to close the end of the furnace (Photos 1 and 2). Three one-fourth inch diameter holes were drilled through the plug to allow the brick to slip over the three crucible support tubes. Two more holes, one-eighth inch in diameter, were drilled diagonally through the top of the plug to the lower edges of the fire brick for the furnace control thermocouple leads and differential thermocouple leads. A four inch by four inch by one-half inch asbestos board was cut with corresponding holes and was placed between the iron base and the fire brick plug to raise the plug to fit tight in the furnace end. Two brass water connector fixtures (Figure V)

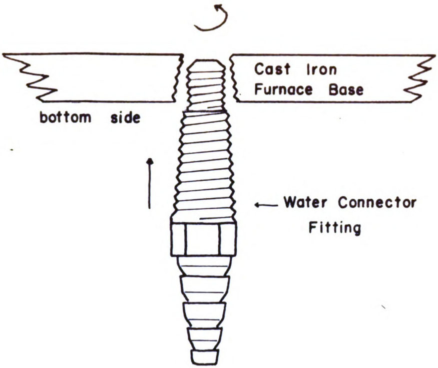


FIGURE V

SIDE VIEW OF THE TECHNIQUE FOR MOUNTING FIXTURES IN THE FURNACE BASE. THE WATER CONNECTOR FITTING EXTENDED THE TOP THREADS ABOVE THE BASE TO CONNECT TO THE FLARED WATER COOLING TUBES. THE TAPPERED PIPE THREADED SECTION HELD THE FITTING FIRMLY IN THE FURNACE BASE. THE BOTTOM SECTION CONNECTED TO A RUBBER HOSE.

constructed to serve as the male parts of flared one-fourth inch copper tube joints were mounted through the furnace base and connected to a tap water source and to a drain by rubber hoses. Soft rubber washers cut as cross sections from a one-fourth inch rubber hose were used in the flared joints to prevent leaks. Binding posts for the differential thermocouple, the furnace control thermocouple, and the furnace power leads were made from phenol resin round stock and fitted with brass bolts which served as connecting conductors.

Two steel rods, one-fourth inch in diameter and seven inches long, were silver soldered in brass plugs and mounted perpendicular to the base about three inches from opposite sides of the crucible to guide the furnace over the crucible.

Furnace

The heating element was made from twenty-six and one-half feet of No. 13 B&S gauge nichrome wire covered with one-eighth inch fish spine ceramic insulators. To wind the furnace non-inductively, the insulated wire was doubled back on itself with one section of wire three and one-half feet longer than the other. The wire was wound around a collapsible wood and metal form (Figure VI), two and three-fourth inches in diameter, starting with the looped end of the wire about four and one-half inches from the top of the dome. The doubled wire was wound four turns per inch. The left-over section of the longer bend of the wire was coiled over the dome of the form and held in place with straight pins. This noninductive winding technique which caused the current to flow in alternate wires along the sides in opposite directions was used to decrease any A.C. induction effects in the thermocouple leads to a minimum. The leads were tripled and twisted from the heating zone to the binding post. A mold made from a ceramic tube, three and five-eighth inches in inside diameter and six inches high, was fitted around the

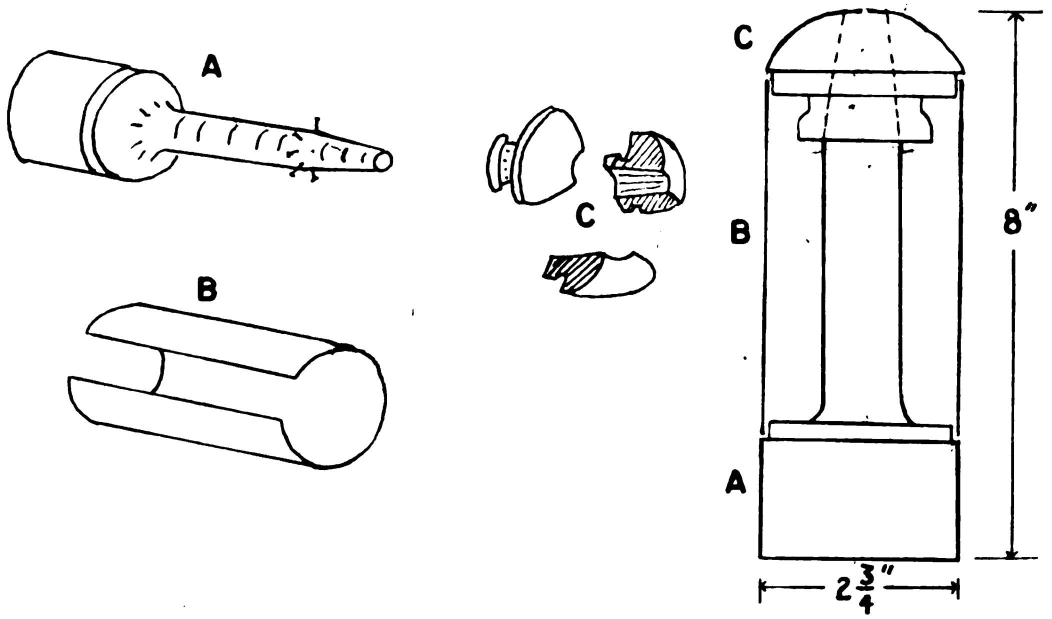


FIGURE VI

COLLAPSIBLE CORE FOR MAKING FURNACE HEATING ELEMENT. A- CENTER WOODEN KEY PIN, B- METAL WALL JACKET, C- THREE PIECE COLLAPSIBLE WOODEN CAP.

windings and filled with Norton alundum cement (R.A. 1162). After the cement was dried in an oven at 115°C so that it held the windings in place, the pins were removed from the dome and the core was collapsed and removed from the windings. The mold was removed and any holes in the cement were patched. The unit was ignited to 1000°C to harden the alundum cement case.

A copper cylinder six and one-half inches in diameter and seven and one-half inches high, was constructed from one-thirty second inch copper sheet. A circular copper sheet six and one-half inches in diameter with a hole three inches in diameter in its center was soldered to the bottom end. The top was closed with a solid, circular copper cover which was attached with sheet metal screws so that it could be removed. To prevent the solder used to construct this jacket from melting and to keep the outside of the jacket cool enough to handle, thirteen feet of one-fourth inch copper tubing was coiled and soldered around the container starting with a loop on the top and winding both ends around the sides to the bottom. The ends of the copper tubing were flared to be attached by nuts as the female section of a standard one-fourth inch flare connection to the water fixtures in the base. The copper tubing was cut at the top seam and connected with rubber tubing.

With the top of the cooling jacket removed, a ceramic tube three and five-eighth inch inside diameter by six inches long was placed in the center of the container over the hole in the bottom and packed in place with asbestos cement. The heating core was slipped into the ceramic tube and the leads were soldered to copper binding post made from one-fourth inch brass bolts which were drilled lengthwise with a one-eighth inch drill bit. Large brass nuts electrically insulated from the cooling jacket walls by asbestos sheet held the binding posts in place. An asbestos pad, three-fourths inch thick was placed on top of the heating core, thus completing the thermal insulation.

Two brass tubes, six inches long by three eighth inches inside diameter were soldered to the cooling coils on opposite sides of the furnace jacket to slip over the guide rods mounted on the base and to direct the furnace heating coils down over the crucible (shown in Photo 2).

Power Supply and Control

A current controlling device for the furnace consisted of a variable transformer and a Chronotrol. The positioning of the transformer was brought about by a motor-gear reducing assembly which responded to controls from the Chronotrol.

A 115 volt-60 cycle, 300 r.p.m. Bodine motor, type KYC-23RB was connected to a 1:150 gear reducer. This drive shaft was then connected to a 1:150 worm gear reducer by a universal joint. A 120 tooth gear secured by winged screws to this shaft was meshed with a 130 tooth gear on the rotor of a variable transformer, 15 ampere-120 volt powerstat made by Superior Electrical Company, type 2 PF1126. These connections gave the powerstat a rotating speed of 2/165 r.p.m. (Photo 3).

The Bodine motor on the power supply reacted to the signals from a Wheelco Chronotrol (Model 72241). Desired heating rates were obtained by preparing appropriate templates for the Chronotrol. The furnace temperature was measured by a chromel-alumel thermocouple and compared by the Chronotrol to the prescribed heating program. When the furnace temperature dropped below the program temperature, the Chronotrol relay was activated to turn on the Bodine motor which in turn increased the current to the furnace.

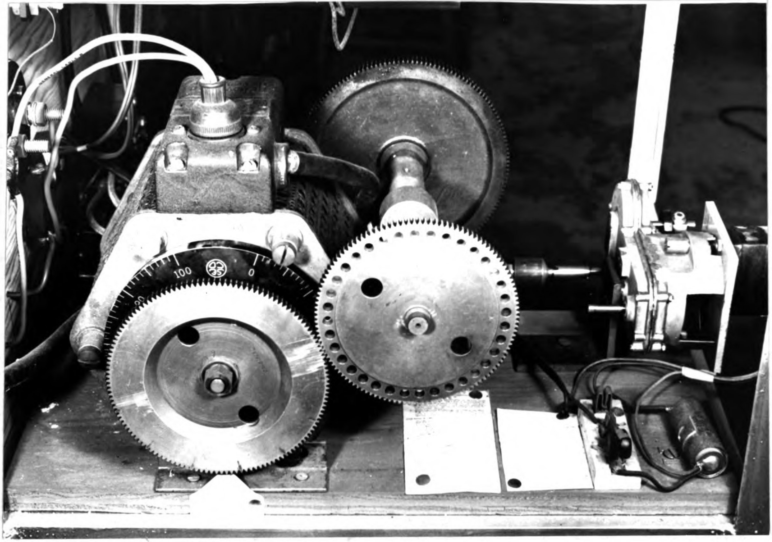


PHOTO 3. POWER SUPPLY CONTROL. FROM LEFT TO RIGHT IS SHOWN THE POWERSTAT, THE SPEED REDUCING TRAIN, AND AT THE EXTREME RIGHT THE DRIVING MOTOR. A MANUAL KNIFE SWITCH IN THE MOTOR CIRCUIT IS ALSO SHOWN IN THE LOWER RIGHT HAND CORNER.

The shape of the template for a heating program was determined by heating the furnace and manually turning on the Bodine motor to approximate a desired heating rate. The Chronotrol thermocouple temperature and the length of time the motor was on were recorded and plotted on a recording of the sample temperature. Second approximations for the motor control were made from this plot to correct for any deviations in the desired heating rate. This procedure was repeated until the heating rate was uniform. A program template was marked to correspond to the furnace temperature indicated by the thermocouple of the Chronotrol. To force the motor to turn on at the correct time, small humps indicating sudden increase in temperature were marked on the program template covering the period of time the motor should be operating. The operating program template was cut out with a band saw and a hand file and smoothed with emory paper. This program template was used and checked against the corrected manual program. Final corrections were made with a hand file and emory paper.

Recorders

Two recorders were necessary for the temperature measurements, one to record differences in temperature when thermal changes occurred and the other to record the reaction temperatures. The differential temperature was recorded with a one millivolt full scale Bristol wide strip Dynamaster (Model 560) D.C. potentiometer.

The cross-chart pen speed was two seconds; the chart speed was twelve inches per hour. A helipot was installed to allow continuous adjustment of the zero pen position to any place across the chart. Bristol chart paper R.5049 was used in this instrument.

The sample temperatures were recorded with a Bristol wide-strip Dynamaster (model 560) D.C. potentiometer adjusted to record from 0 to 1200°C using a chromel-alumel thermocouple. The cross chart pen speed was three seconds and the chart speed was twelve inches per hour. In this instrument, Bristol chart paper R.1292 was used.

Control Panel

A master switch and a microswitch on the Chronotrol operated a relay which controlled a power circuit for the furnace and a power circuit for the recorders and Chronotrol. The microswitch could be set to cut off all the power and end a thermal analysis at any chosen time. Individual switches for the recording charts and the Chronotrol program were available so that these instruments could be warmed up before an analysis without having the charts moving. The control panel also included a switch in the power circuit for the furnace, an A.C. voltmeter, and an A.C. ammeter to measure furnace power.

Assembly

The differential temperature recorder, the sample temperature recorder, the power supply, the control panel, and the Chronotrol were mounted in a vertical rack, twenty-one and one-half inches square and six feet high, made of one inch angle iron. The rack was mounted on three inch castors to facilitate moving the equipment.

The thermocouple leads and furnace power leads were approximately five feet long to reach the connections on the furnace base located on a nearby work bench (Photo 4).

A schematic electrical wiring diagram is shown in Figure VII.

Operation

To operate the equipment and to insure reproducible results for differential thermal analysis, a procedure was carefully followed. Beginning with the dissembling of the apparatus to put in a sample, the procedure followed is:

1. The valve which controls the water flow in the cooling jacket of the furnace was closed.
2. All electrical equipment was turned off with the master switch on the control panel.
3. The power leads to the furnace were disconnected at the binding posts on the cooling jacket.
4. The connecting nut of the flared joint of the intake water was unscrewed and the furnace was tipped slightly to allow the water to syphon from the cooling coils into the drain.

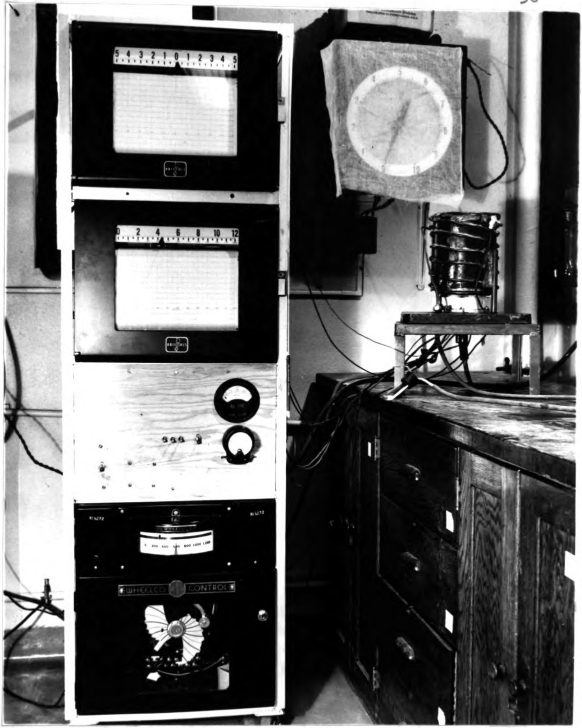


PHOTO 4. ASSEMBLY OF DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT. IN THE VERTICAL MOUNT ON THE LEFT FROM THE TOP DOWN IS THE DIFFERENTIAL TEMPERATURE RECORDER, THE SAMPLE TEMPERATURE RECORDER, THE CONTROL PANEL, AND THE WHEELCO CHRONOTROL. ON THE WORK BENCH AT RIGHT IS THE FURNACE AND FURNACE BASE.

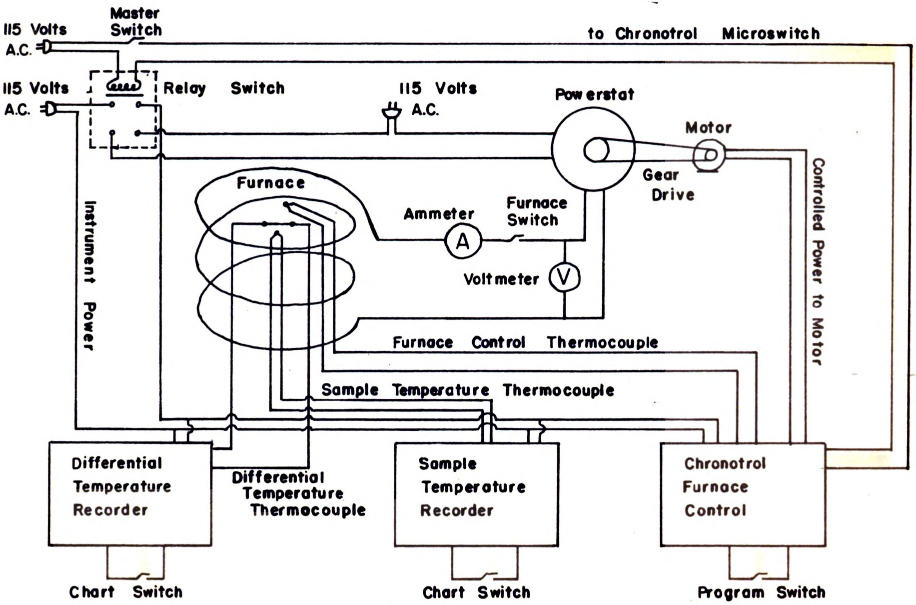


Figure VII —Electric wiring diagram for differential thermal analysis equipment.

5. The connecting nut of the flared joint of the outlet water was unscrewed and the furnace and cooling jacket were lifted off the guide rods. The furnace was left standing upside down.

6. The crucible lid was removed to expose the platinum lined sample holes.

7. A residue bottle (Figure VIII) and a gentle vacuum were used to remove the sample residue from the sample hole.

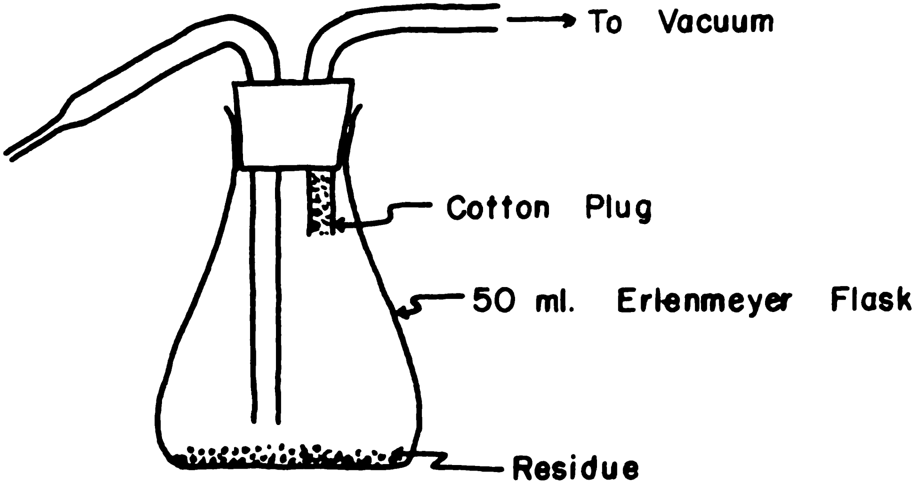


FIGURE VIII

VACUUM BOTTLE USED TO REMOVE SAMPLE RESIDUES FROM THE SAMPLE HOLE.

If compounds of a different element were to be used next and it was important to prevent contamination, the next five steps were included in the procedure.

8. The platinum ring lining in the center section was removed with small tweezers. The hole was cleaned again with the vacuum residue bottle.

9. The differential thermocouple was exposed by removing the center section carefully.

10. The differential thermocouple was loosened by straightening the leads to give more length or was disconnected from the leads. The thermocouple was moved to one side to allow the platinum cup to be removed for cleaning the hole with the vacuum bottle.

11. The platinum liners were cleaned with 10 N nitric acid, rinsed with distilled water and acetone, and air dried.

12. The crucible block was reassembled by reversing the preceding steps, taking care to center the junctions of the differential thermocouples in the sample holes, to replace the insulators to prevent shorting between the thermocouple and the platinum liners, and to repack the Al_2O_3 around the sample temperature thermocouple and the reference thermocouple.

13. When the sample crucible was satisfactorily cleaned, the sample to be studied was packed in the platinum lined sample hole using a small funnel made from an index card and a glass rod as a tamper. A different funnel was used for compounds of each element.

14. The crucible lid was replaced. Then the furnace guides were slipped over the guide rods and the furnace lowered over the crucible.

15. Rubber washers cut from one-fourth inch rubber hose were placed in the flared copper tube joints to prevent leaks and the connecting nuts were tightened by hand.

16. The cooling water control valve was opened slowly until a flow rate of approximately one quart per minute was obtained. This rate was estimated by the length of the water jet from the one-fourth inch drain hose. A jet of approximately three-fourth inch from a hose horizonal on the bottom of the sink was indicative of this flow rate. Any leaks in the cooling system were corrected at this time.

17. The furnace power leads were connected to the binding posts on the cooling jacket and were made secure with the brass nuts.

18. The winged screws which held the drive gear meshed with the gear on the powerstat were loosened to allow the powerstat rotor to be set on zero voltage.

19. While the template rider was held away from the temperature program template in the Wheelco Chronotrol, the program template and microswitch trip arm were rotated clockwise to reset the template rider below 20°C using the ten degree per minute template.

20. The master power switch was turned on.

21. The chart switches were turned on and the charts were allowed to advance until the recording pens were on the same relative time lines of the charts. This aided positioning the charts when the charts were overlaid to determine the temperature of the differential curves.

22. The Chronotrol template switch was turned on and the template was allowed to advance to 20°C.

23. The powerstat was reset by turning the drive gear so that the voltmeter read 54-55 volts and was secured again with the winged screws. This voltage setting was always approached from the low voltage side to remove slack in the gears and to insure reproducibility.

24. The knife switch in the Bodine motor circuit was checked to be sure it was closed.

25. The furnace power switch, the chart switches and the template switch were turned on simultaneously to begin the analysis.

When the microswitch was positioned behind the hole in the 15 degrees template, the sample would heat to approximately 1050°C and the instrument would turn completely off automatically.

About two and one-half hours were allowed for the furnace to cool. The furnace was cooled below 50°C before the next analysis.

Preparation of Compounds

Source of Materials

Lanthanum oxide was obtained from the Lindsay Light and Chemical Company, Inc. and was used as such without any further purification.

Neodymium was obtained from Dr. Laurence L. Quill as the "GX-9" cut from a double magnesium nitrate fractional crystallization series. The neodymium and magnesium were separated by the following procedure. Fifty milliliters of the concentrated neodymium magnesium nitrate solution was diluted to four liters and heated almost to boiling. Dilute oxalic acid which was prepared by mixing nine parts distilled water with one part of a saturated solution of oxalic acid was added dropwise until the precipitation was complete. The precipitate was digested for several hours, cooled in an ice bath, filtered on No. 50 filter paper, and washed with distilled water. The precipitate was dissolved in hot concentrated nitric acid, diluted to four liters, and precipitated again with dilute oxalic acid. The preceding cycle was repeated and the product of the third precipitation was used in the preparation of the compounds in this study.

The yttrium oxide used was prepared by R. H. Jaquith and was reported to have an atomic weight of approximately 90.

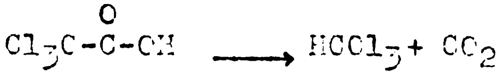
Samarium was obtained from Dr. Laurence L. Quill as a samarium perchlorate solution. The samarium was precipitated from a hot dilute solution with dilute oxalic acid. After the precipitate was digested for several hours on a hot plate and cooled in an ice bath, the precipitate was filtered from the solution on No. 50 filter paper and used in the preparation of the compounds in this study.

Praseodymium oxalate decahydrate prepared by M. L. Salutsky was used in the study of praseodymium.

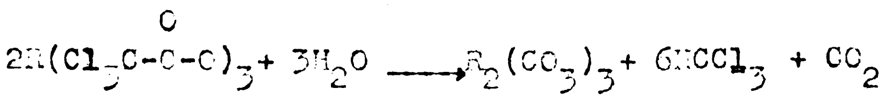
Two thorium-free cerium magnesium nitrate fractional crystallization cuts ("Ce 25" and "Ce 27") were combined. The procedure of diluting the solution, of precipitating with dilute oxalic acid, of digesting the precipitate on a hot plate several hours, of cooling in an ice bath, of filtering on No. 50 filter paper, and of dissolving the precipitate in hot concentrated nitric acid was repeated three times. The oxalate precipitate from this was used in this study.

Carbonates

The carbonates of lanthanum, neodymium, yttrium, samarium, and praseodymium were prepared by homogeneous precipitation resulting from the decomposition of the trichloroacetate ion. About fifteen grams of each oxide were dissolved in a slight excess of 25% trichloroacetic acid solution. Any solids which would not dissolve in four hours were filtered from solution. The solution was transferred to a two liter beaker, diluted to 500 ml., and heated on a hot plate for six or eight hours to decompose the excess acid and the trichloroacetate ion into chloroform, carbon dioxide and rare earth carbonate.



$$\mathrm{Cl_3C\text{-}\overset{O}{C}\text{-}CH \longrightarrow HCCl_3 + CO_2}$$



$$\mathrm{2R(Cl_3C\text{-}\overset{O}{C}\text{-}O)_3 + 3H_2O \longrightarrow R_2(CO_3)_3 + 6HCCl_3 + CO_2}$$

The carbonate was filtered on No. 50 filter paper, washed with distilled water, and dried for approximately fifteen minutes by drawing air through it with an aspirator. The compound was scraped from the filter paper into a bottle and covered until used.

The filtrates were always treated with oxalic acid to recover the rare earth content.

A satisfactory sample of cerium carbonate could not be prepared for study. The usual procedure of dissolving the oxide in a slight excess of a 25% solution of trichloroacetic acid was not applicable because ceric oxide is extremely insoluble. A ten gram sample of cerous oxalate was dissolved in hot concentrated nitric acid. Ammonium hydroxide was added slowly to neutralize the excess nitric acid and to precipitate a gelatinous material. This material was partly dissolved in a 25% solution of trichloroacetic acid. Upon the decomposition of the trichloroacetate ion in the clear solution by heat, only about one tenth gram of product was obtained. From X-ray diffraction patterns (see Appendix), this product compared closely with the patterns of lanthanum carbonate and praseodymium carbonate; therefore it was postulated to be cerous carbonate, $Ce_2(CO_3)_3$. The yield was too low for further study.

Attempts to make cerous carbonate by adding dilute sodium carbonate to a cerous solution prepared by reducing a ceric solution with hydrogen peroxide in acid solution resulted in the liberation of carbon dioxide and finally in hydrous oxides or peroxycarbonates. Ceric oxide, which could be dissolved with difficulty in hot concentrated nitric acid to which 3% hydrogen peroxide solution was added slowly, produced a cerous solution. When dilute sodium carbonate was added, an extremely insoluble precipitate resulted which was apparently a hydrous oxide. This precipitate would liberate some carbon dioxide when treated with an acid but would not completely dissolve, indicating the presence of considerable oxide.

Oxalates

The oxalates of lanthanum, neodymium, samarium, praseodymium, cerium and yttrium were prepared by dissolving the oxide or the oxalate in hot concentrated nitric acid, evaporating the solution on a hot plate until dense brown fumes of nitrogen dioxide were liberated to decompose the excess acid, diluting the solution to two or four liters, and precipitating the oxalate with dilute oxalic acid. The precipitate was digested on a hot plate for three or four hours, cooled in an ice bath, filtered on No. 50 filter paper, washed with distilled water several times, transferred to a Petrie dish to air dry for twenty-four hours, and then stored in capped bottles.

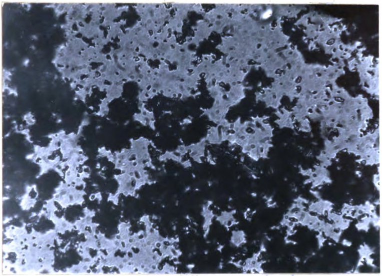


PHOTO. 5

LANTHANUM
CARBONATE

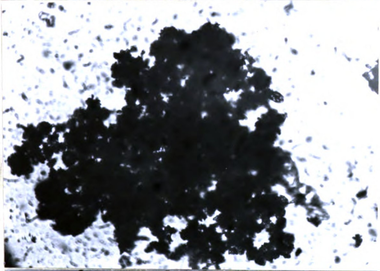


PHOTO. 6

NEODYMIUM
CARBONATE

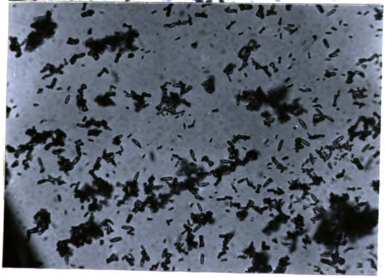


PHOTO. 7

SAMARIUM
CARBONATE

Photographs of the oxalates of lanthanum, cerium, praseodymium, neodymium, and samarium are shown on pages 48 and 49.

Analytical Techniques

Since anhydrous and hydrated carbonates and oxalates of the rare earths were utilized in this study, analytical methods were employed to give essential information about these materials. Ignition of samples to the oxide gave total weight loss. Analyses for carbonate were made by determining the amount of carbon dioxide liberated. Oxalate content was done by permanganate titration. Purity of rare earth samples excluding cerium and praseodymium was measured by equivalent weight determinations. Water content was determined by difference in weight after carbonate and oxalate measurements.

Ignition

Rare earth oxalates and carbonates are converted to the oxide when ignited to 1000°C for several hours. This procedure was used to analyze samples for total carbonate or oxalate and water of hydration. For example, if a sample was known to be a normal but hydrated oxalate, ignition to the oxide would drive off carbon monoxide, carbon dioxide, and the water of hydration. Calculations from the weight of oxide would give the amount of anhydrous oxalate and the difference

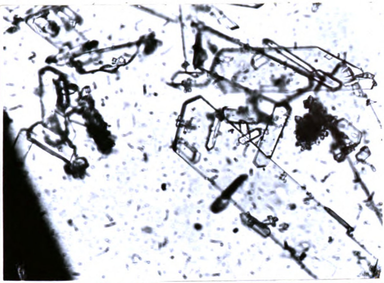


PHOTO. 8

LANTHANUM
OXALATE
DECAHYDRATE

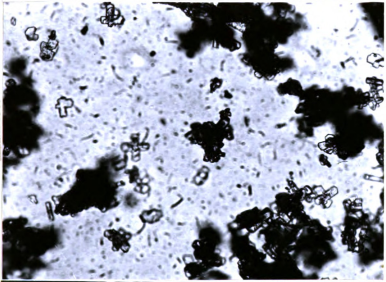


PHOTO. 9

LANTHANUM
OXALATE
HEXAHYDRATE

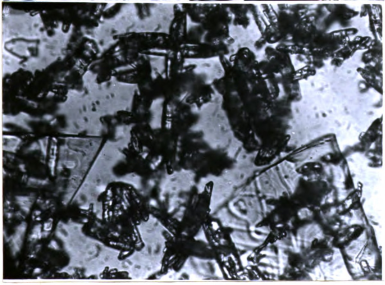


PHOTO. 10

CERIUM
OXALATE
DECAHYDRATE

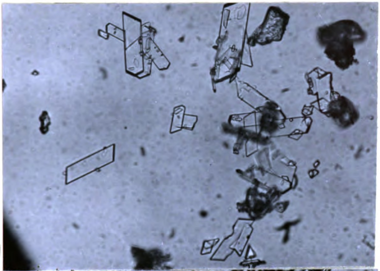


PHOTO. 11

PRASEODYMIUM
OXALATE
DECAHYDRATE

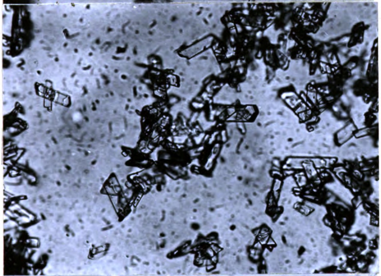


PHOTO 12

NEODYMIUM
OXALATE
DECAHYDRATE

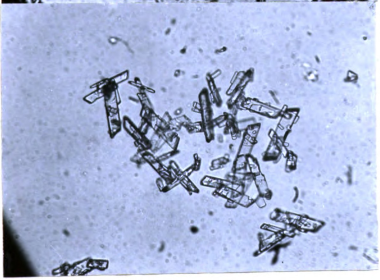


PHOTO 13

SAMARIUM
OXALATE
DECAHYDRATE

in weight of anhydrous oxalate and the original sample would be water of hydration.

One or two grams of a compound were weighed into a platinum crucible and heated in an electric muffle furnace to 1000°C. After about two hours the residue was removed, cooled in a desiccator, and weighed again. The weight of the oxide was determined and from this weight, the weight of the original compound could be calaulated. For hydrated compounds, the weight of the anhydrous compound was calculated and the difference in the weight of the original sample and the weight of the anhydrous compound was the weight of the water of hydration.

Ignition was used to aid in the identification of unknown compounds. A substance which could have been one of several possible compounds, depending upon the extant to which it had been reacted, was ignited to the oxide and from the weight lost in ignition, the choice of the correct formula of the substance could be deduced. Other tests were made to complete the identification.

Oxalate Titrations

To determine the oxalate content of a sample, either to decide the composition of the compounds or to permit calculation of rare earth equivalent weights, permanganate titrations were employed to determine the amount of the reducing group present.

An approximately 0.1 N solution of potassium permanganate was prepared by dissolving about 6.3 grams of potassium permanganate in two liters of distilled water. The solution was boiled gently for fifteen minutes and allowed to cool in a dark place over night. The solution was filtered through an asbestos fiber mat in a Gooch crucible to remove any solids and was stored in a brown bottle.

The potassium permanganate solution was standardized against weighed samples (0.2-0.3 grams) of primary standard grade sodium oxalate. The sodium oxalate was dissolved in 10 ml. of 10 N sulfuric acid and diluted to 100 ml. in a 250 ml. Erlenmeyer flask. The bulk of the titration was carried out at room temperature but was heated to 65°C before the last few milliliters were added to reach the end point. The end point was reached when a very faint pink color in the solution persisted for at least sixty seconds.

The oxalate content of the rare earth samples was determined by using about 0.2 grams of the lanthanum, neodymium, yttrium, or samarium preparation weighed into a 250 ml. Erlenmeyer flask, dissolved in 10 ml. of 10 N sulfuric acid, diluted to 100 ml., and titrated with the standardized potassium permanganate solution. The titration procedure was the same as described for standardization of the potassium permanganate solution.

The weight of the anhydrous rare earth oxalate could be calculated by the formula :

$$\mathrm{Gm}\ [R_2(C_2O_4)_3] = \frac{\mathrm{MW}\ [R2(C2O4)3] \times \mathrm{ml.}\ [\mathrm{KMnO_4}] \times \mathrm{N}\ [\mathrm{KMnO_4}]}{6000}$$

Gm = Grams MW = Molecular Weight

The difference in the weight of the sample and the calculated weight of the anhydrous oxalate was the weight of the water of hydration present in the compound.

This technique could not be used on cerium and praseodymium because of the higher oxidation states shown by these two elements. The strong yellow color of the ceric ion covered the end point also.

Carbon Dioxide Content

The carbonate content of various specimens was measured by liberating carbon dioxide with an acid, then collecting by absorption and weighing the carbon dioxide.

The absorption train[49] passed the carbon dioxide liberated by 3 N hydrochloric acid through a condenser, a concentrated sulfuric acid bubble drier to remove most of the water vapor present, a U-tube filled with anhydrous copper sulfate on pumice stone to remove any hydrogen chloride gas, a U-tube filled two-thirds with ascarite and one-third with anhydrous magnesium perchlorate to absorb the carbon dioxide and the water liberated by the absorption reaction, and finally a tube containing magnesium perchlorate to prevent water vapor from the aspirator backing up into the carbon dioxide absorption tube.

A drying tube filled with ascarite was placed over the hydrochloric acid funnel to prevent any carbon dioxide from entering the train.

A carbonate sample (2.0-3.0 grams) was placed in a dry reaction flask and air was passed through the train at a rate of about two or three bubbles per second for fifteen minutes to clear the system of carbon dioxide. The train was closed off and the carbon dioxide absorption tube was removed and weighed against an empty U-tube as a tare. The absorption tube was replaced in the train and 10 ml. of 3 N hydrochloric acid was added quickly to the acid drop funnel when the ascarite tube was removed. With the aspirator disconnected, the hydrochloric acid was added drop-wise to the sample slowly so that the liberation of carbon dioxide would not proceed too quickly. When the reaction was complete and all the acid was added, the aspirator was used to allow carbon dioxide-free air to pass through the train and sweep the carbon dioxide present into the absorbing tube. The solution in the reaction flask was heated to a gentle boil three times to expel any dissolved carbon dioxide. After thirty minutes, the vacuum was removed and the absorption tube was weighed against the tare again. The increase in weight was the weight of the absorbed carbon dioxide.

The amount of rare earth present was determined by filtering out the carbon from the solution in the reaction flask and precipitating the rare earth with dilute oxalic acid. The oxalate precipitate was filtered on a medium sintered glass filtering funnel, washed, and dissolved with 40 ml. of 10 N sulfuric acid. The resulting oxalate solution was titrated with standardized potassium permanganate solution. The rare earth content was determined as the oxide by the formula:

$$\text{Gm } (R_2O_3) = \frac{\text{MW } (R_2O_3) \text{ X ml. } (KMnO_4) \text{ X N } (KMnO_4)}{6000}$$

The results were reported as.

$$\frac{\text{Grams Carbon Dioxide}}{\text{Grams Rare Earth Oxide}}$$

X-Ray Powder Diffraction Patterns

In addition to the many chemical analyses made for identification of samples, X-ray diffraction diagrams were also used. The powder diffraction patterns were taken with a Norelco X-ray apparatus using a Hull-Debye-Scherrer type camera of 57.3 millimeter radius. Powdered samples packed in 0.2 millimeter capillaries were exposed to copper K_α radiation filtered through nickel foil. The films were measured with a steel metric scale using a cross hair sliding vernier reading to 0.005 centimeters.

The linear distances in centimeters measured from the center of the X-ray beam hole to the diffraction lines were equal to 2θ diffraction angles. The diffraction angles were converted to "d" values (interplanar distances in angstroms) from the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacings"[50]. The "d" values of the oxides were compared with values listed in "Index to the X-ray Powder Data File"[51].

EXPERIMENTAL AND RESULTS

Lanthanum Carbonate

Many hydrates of the carbonates of the rare earth elements have been reported. Their variable compositions have depended on the conditions of preparation.

Fresh lanthanum carbonate which had been rinsed with acetone and dried on the filter by pulling air through for one hour analyzed to be 54.15% lanthanum oxide. Upon differential thermal analysis, a curve like DTA Curve No. 1 was obtained. After this material was air dried for three days, the curve was like DTA Curve No. 2 and analyzed to be 72.12% lanthanum oxide. The change from 54.15% to 72.12% lanthanum oxide due to air drying indicated that the freshly prepared material may have occluded considerable water or was an unstable hydrate containing bound molecules of water.

Constant relative humidity chambers were prepared in desiccators in an attempt to establish the presence of intermediate hydrates. Saturated solutions of potassium carbonate dihydrate (43% relative humidity), calcium nitrate tetrahydrate (51% relative humidity), magnesium acetate tetrahydrate (65% relative humidity), ammonium sulfate (81% relative humidity) and zinc sulfate heptahydrate (90% relative humidity) with excess solid[52] were prepared in the separate desiccators. Approximately five grams of fresh damp lanthanum carbonate and five grams of anhydrous lanthanum carbonate (air dried one year) were placed in each desiccator and given two to three weeks to reach equilibrium. Differential thermal analysis curves of these samples were very similar, and DTA curve No. 2 is typical. Peaks indicative of hydration were not observed. Average analyses were about 72.2% lanthanum oxide.

The anhydrous lanthanum carbonate began to decompose about 420-430°C. The peak indicating an endothermic reaction reached a maximum around 510°C (DTA Curves Nos. 1, 2, and 4). A second endothermic peak began slowly around 690°C and increased rapidly around 780°C. A maximum was reached at approximately 880°C. The decomposition to the oxide was completed by 910°C.

When lanthanum carbonate was heated to 540°C for eight hours, the resulting material gave a differential thermal analysis curve like DTA Curve No. 3 and analyzed to be 88.38% lanthanum oxide. Since lanthanum dioxycarbonate ($La_2O_3 \cdot CO_2$) contains 88.18% lanthanum oxide, the material was postulated to be the dioxycarbonate.

Lanthanum carbonate was prepared and stored in the presence of water vapor at room temperature for two years to allow any hydrate to reach a stable equilibrium. A second sample was allowed to air dry for about one year. The room relative humidity during the final month of air drying and during all the experiments was between fifteen and twenty per cent.

The differential thermal analysis curve (DTA Curve No. 4 A) for the material kept in the presence of water

vapor for two years showed a group of small peaks in the temperature range of 50° to $220^\circ C$. Analysis of this material by igniting to the oxide indicated 72.68% lanthanum oxide present. Theoretically there is 71.1% lanthanum oxide in anhydrous lanthanum carbonate. The material air dried for one year (DTA Curve No. 4 B) analyzed to be 72.75% lanthanum oxide.

Cerium Carbonate

A satisfactory cerium carbonate sample could not be prepared for study (See page 44, Preparation of Compounds).

Praseodymium Carbonate

A small sample of praseodymium carbonate air dried for twenty-four hours gave a differential thermal analysis curve like DTA Curve No. 5 which did not indicate any water of hydration.

The carbonate began to decompose at $430^\circ C$ as shown by the endothermic peak and reached a maximum at $495^\circ C$. Two small endothermic peaks followed with maxima at 630° and $700^\circ C$. The decomposition was completed to the oxide (Pr_6O_{11}) by $730^\circ C$. Between 960-$990^\circ C$, the oxide undergoes an endothermic change which is reversible. This peak is probably due to an oxide crystal inversion.

Neodymium Carbonate

The effect of air drying a sample of neodymium carbonate is shown in DTA Curve No. 6. The damp carbonate analyzed to have an apparent molecular weight of 591 (molecular weight of $Nd_2(CO_3)_3 \cdot 7H_2O = 592$). After air drying for eighteen hours, the material analyzed to be 73.13% neodymium oxide. Anhydrous neodymium carbonate contains 71.81% neodymium oxide.

Neodymium carbonate began to decompose about 420°C and reached a maximum in the endothermic peak around 500°C. A second endothermic peak began slowly around 655°C and reached a maximum at 800°C. The reaction was complete by 835°C.

When neodymium carbonate was heated to 510°C for twelve hours (DTA Curve No.7), the material analyzed to be 86.57% neodymium oxide. Neodymium dioxycarbonate ($Nd_2O_3 \cdot CO_2$) contains 88.44% neodymium oxide.

Samarium Carbonate

Samarium carbonate when spread thinly and air dried for only one and one-half hours showed no hydrate present when subjected to differential thermal analysis DTA Curve No.8). The material analyzed to be 72.91% samarium oxide. Anhydrous samarium carbonate contains 72.56% samarium oxide. Around 410°C the anhydrous carbonate began to decompose endothermally. A second endothermic peak began slowly around 610°C and increased rapidly at 680°C to reach a maximum at 770°C. The conversion to the oxide was completed by 810°C.

Yttrium Carbonate

The source of yttrium was an oxide sample prepared by Jaquith[47] in a study of the separation of yttrium from rare earth elements. It was determined that the average atomic weight of the metal ion was about 92. The atomic weight of pure yttrium is 88.92.

The average atomic weight of this sample will be used in the theoretical calculations in this study.

A damp sample of yttrium carbonate produced a differential thermal analysis curve similar to DTA Curve No.9 and indicated a possible stable hydrate. After air drying the carbonate for forty-eight hours, the material was found to contain 58.46% yttrium oxide. The dihydrate contains 57.99% yttrium oxide.

When the hydrate was heated for thirteen hours at 96°C, a material (DTA Curve No.10) contained 63.59% yttrium oxide. The anhydrous carbonate contains 63.74% yttrium oxide.

The anhydrous carbonate (DTA Curve No.10) began to decompose endothermally slowly at 100°C and reached a maximum at 200°C. At 580°C a second endothermic peak began and reached a maximum around 620°C. A third peak which reached a maximum at 670°C began before the second peak was completed. All the reactions were completed by 740°C.

A compound (DTA Curve No. 11) containing 72.85% yttrium oxide resulted when the hydrate was heated to 260-70°C for eighteen hours. Yttrium oxydicarbonate ($Y_2O_3 \cdot 2CO_2$) contains 72.51% yttrium oxide.

Lanthanum Oxalate

A. Hydrates

Lanthanum oxalate which had been precipitated from a nitrate solution with dilute oxalic acid was found to form two hydrates which were stable to air drying and gave two different X-ray powder diffraction patterns. A decahydrate (DTA Curve No. 13) (Photo 8) which gave no intermediate hydrate when decomposed was formed when the material was first precipitated. The hexahydrate (DTA Curve No. 13 B) (Photo No. 9) was formed by adding dilute oxalic acid to a nitrate solution or by hydrolyzing dimethyl oxalate in a nitrate solution and digesting the precipitate on a steam bath for six hours or more. When analyzed by differential thermal analysis, the hexahydrate indicated the formation of an intermediate hydrate. After heating a sample of the hexahydrate to 96°C for twelve hours, the residue analyzed to be a tetrahydrate (DTA Curve No. 14 A). The anhydrous oxalate could be formed by heating the hexahydrate to 200°C for seven hours (DTA Curve 14 B).

A study of the relative stabilities of the hydrate in wqter during digestion was made. Approximately 2 gm. of the decahydrate was placed in a 250 ml. wide mouth glass jar. To this was added 5-10 mg. of the hexahydrate and 100 ml. of distilled water. The jar was then covered with a ground glass plate to inhibit evaporation of water. A second jar was prepared similarly with the hexahydrate. Both hydrates were then digested for seven days at 82-85°C. X-ray powder diffraction patterns of both samples were identical and the compounds analyzed to be the hexahydrate.

Azeotropic dehydration by refluxing the hydrates with toluene for twenty-four hours did not give definite hydrates. The dried material from the decahydrate analyzed to be 57.49% lanthanum oxide (Approximately a 1.35 hydrate) while that from the hexahydrate analyzed to be 54.44% lanthanum oxide (approximately 3.15 hydrate).

Slow dehydration of the hexahydrated oxalate over anhydrous magnesium perchlorate for three months resulted in a compound which approximated a 4.5 hydrate.

B. Oxalate Decomposition

The decomposition of the oxalate (DTA Curve No. 14 B) began at 375-85°C. The two sharp peaks at approximately 395°C and 405°C indicated exothermic reactions. During the heating process, the white oxalate changed to a pale yellow brown color. At about 500°C a less intense exothermic reaction began and continued for about the next 125 degrees. The material became shiny black from carbon formed during the reaction. A final peak beginning at 700°C and reaching a maximum at 790-800°C was noted to be endothermic. The reaction was complete to lanthanum oxide by 835°C.

X-ray powder diffraction patterns were made of the anhydrous oxalate, the pale yellow brown material, the shiny black material, and the white oxide which had been removed from the differential thermal analysis furnace, but only the oxide gave a diffraction pattern. All the other materials appeared to be amorphous.

Attempts were made to reproduce these compounds outside of the differential thermal analysis furnace by heating lanthanum oxalate at a lower temperature than indicated by the analysis curves, for a long period of time. After the hexahydrate of the oxalate had been heated to 335°C for ten hours (DTA Curve No. 15) or 300°C for fifty-three hours (DTA Curve No. 16), the resulting pale yellow brown compounds analyzed to be 78.66% and 78.53% lanthanum oxide, respectively. Lanthanum oxydicarbonate ($La_2O_3 \cdot 2CO_2$) contains 78.78% lanthanum oxide. The compound dissolved in 3 N hydrochloric acid with the evolution of carbon dioxide. A solution of the compound in 10 N sulfuric acid did not decolor permanganate solution.

The shiny black material, which could be formed when the oxalate was heated to 405°C for five hours, evolved carbon dioxide when dissolved in 3 N hydrochloric acid and left insoluble carbon. The carbon dioxide content of the material was determined by collecting the evolved carbon dioxide with ascarite (the gain in weight represented the amount of carbon dioxide). The lanthanum was determined by precipitation with oxalic acid and titrating the precipitated oxalate with a standardized permanganate solution (See page 50). The ratio of $\frac{\text{grams of carbon dioxide}}{\text{grams of lanthanum oxide}} \times 100$ was found to be 13.83. This ratio for lanthanum dioxycarbonate ($La_2O_3 \cdot CO_2$) is 13.51.

Cerium Oxalate

Cerium oxalate (Photo 10) was precipitated by oxalic acid from a nitrate solution and after air drying analyzed to be 47.67% ceric oxide. The decahydrate contains 47.53% ceric oxide. Differential thermal analysis of this material gave a curve similar to DTA Curve No. 17 and indicated no intermediate hydrates. Dehydration was slow. After three months over anhydrous magnesium perchlorate, the oxalate analyzed to be cerium oxalate 4.14 hydrate. After heating the hydrate at 96°C for fourteen hours, the material was not completely dehydrated (DTA Curve No. 18). The material contained 61.33% ceric oxide which corresponded to a 0.93 hydrate.

The anhydrous oxalate began to decompose exothermally at 320°C. When the decomposition was almost complete, a very sharp exothermic peak at about 355°C occurred, indicating the oxidation of the cerous to ceric oxide. The reaction was complete by 390°C.

Praseodymium Oxalate

The sample studied was a decahydrate (Photo 11) which had been prepared and analyzed by Salutsky[43]. The differential thermal analysis curve indicated that no intermediate hydrates were formed (DTA Curve No. 19). The anhydrous oxalate was prepared by heating the hydrate to 105°C for twenty-four hours (DTA Curve No. 20). The oxalate began decomposing about 375°C and gave two exothermic peaks around 380° and 390°C. A second strong exothermic peak began about 410°C and reached a maximum around 450°C. A final endothermic peak beginning at 500°C and reaching a maximum aroung 600°C indicated the conversion of the material to a steel black oxide. At about 970°C, a reversible conversion of the oxide was noted. This change is probably due to an oxide crystal inversion.

Neodymium Oxalate

A. Hydrates

Only the decahydrate (Photo 12) was found when neodymium oxalate was precipitated from a nitrate solution with dilute oxalic acid or dimethyl oxalate. When this hydrate was studied by differential thermal analysis, two endothermic peaks were formed as the water of hydration was driven off (DTA Curve No. 21). The first peak began about 120°C and reached a maximum around 190°C. The second peak had a maximum at about 255°C. When the decahydrate was heated at 96°C for thirty-six hours (DTA Curve No. 22), the compound analyzed to be 56.23% neodymium oxide. The dihydrate is 57.1% neodymium oxide. In the thermogravimetric curve of neodymium oxalate determined by Wendlandt[28], a break in the curve corresponded approximately to the dihydrate.

The complete dehydration of the oxalate was difficult. After heating the decahydrate to 170°C for fourteen hours or 200°C for ten and one-half hours, the materials analyzed to be 59.78% and 60.33% neodymium oxide respectively. Anhydrous neodymium oxalate contains 60.75% neodymium oxide.

When the decahydrate was kept over anhydrous magnesium perchlorate for two weeks, it was only dehydrated to a compound corresponding to neodymium oxalate nine hydrate.

B. Anhydrous Oxalate

Neodymium oxalate began to decompose at approximately 385°C and produced two exothermic peaks at about 390°C and 410°C. The pale blue oxalate changed to a brownish blue with a tinge of yellow in this region. At about 510°C a large exothermic peak starts and shows double maxima about 10-15 degrees apart in the region of 585°C. The material turned black in this temperature range. Finally an endothermic peak beginning between 625-640°C indicated the conversion of the material to the pale blue neodymium oxide by 750°C.

To prepare these intermediate materials the hydrated oxalate was heated to 345°C for four hours or 335°C for six hours to produce the brownish blue yellow product. By weight loss this material appeared to be neodymium oxydicarbonate ($Nd_2O_3 \cdot 2CO_2$); it gave a differential thermal analysis curve similar to DTA Curve No. 24. When the hydrate was heated to 300°C for fifty-three hours (DTA Curve No. 25), the product analyzed to be 80.61% neodymium oxide. Neodymium oxydicarbonate contains 79.27% neodymium oxide.

Since one of the possible structures for the partially decomposed oxalate includes a peroxide linkage and was reported by Günther and Rehaag[36], a test for the peroxide group was made. To approximately a tenth gram of this material dissolved in two ml. of 1 M sulfuric acid was added two ml. of a dilute titanium

(IV) sulfate solution. An intense yellow color due to a titanium peroxysulfate complex is indicative of the presence of the peroxide group. In the testing no color was noted; hence it can be concluded that the material did not have a peroxide linkage.

Samarium Oxalate:

Samarium oxalate (Photo 13) precipitated from a perchlorate solution by dilute oxalic acid and digested over night on a hot plate analyzed to be 46.91% samarium oxide when air dried (DTA Curve No. 27). The decahydrate contains 46.83% samarium oxide. When the decahydrate was studied by differential thermal analysis, the curve indicated the formation of two intermediate hydrates. The dehydration began at 65°C and the first endothermic peak reached a maximum at 140°C. The second and third endothermic peaks were at 180°C and 260-70°C.

When the hydrate was heated to 47°C for ten hours, all of the water of the first stable hydrate had not been removed (DTA Curve No. 28). The material analyzed to contain 50.85% samarium. The hexahydrate contains 51.3% samarium oxide.

The product, after heating the hydrate at 96°C for twenty-four hours, analyzed to be 54.33% samarium oxide. The tetrahydrate contains 54.70% samarium oxide.

No attempt was made to prepare the anhydrous oxalate, but it probably could have been prepared by heating the hydrate to 150-160°C for twenty-four hours.

At about 330°C, the anhydrous oxalate began to decompose exothermally and produced two sharp peaks at 390° and 400°C. A second exothermic peak began slowly around 520-30°C and reached two maxima about ten to fifteen degrees apart around 590°C.

The usual final endothermic peak was almost completely absent in this decomposition. When the oxalate was heated to 320°C for fifteen hours, the resulting material (DTA Curve No. 30) analyzed to be 79.93% samarium oxide. Samarium oxydicarbonate ($Sm_2O_3 \cdot 2CO_2$) contains 79.86% samarium oxide.

Yttrium Oxalate

The average atomic weight of 92 for yttrium which was determined for this sample of yttrium was used for the theoretical calculations in this study.

Yttrium oxalate precipitated from a nitrate solution by dilute oxalic acid was air dried for 18 hours and analyzed to be 37.09% yttrium oxide. The decahydrate of yttrium oxalate contains 36.95% yttrium oxide. When this hydrate was studied by differential thermal analysis, the curve (DTA Curve No. 31) gave evidence of an intermediate hydrate. When the hydrate was heated to 96°C for eighteen hours, the material obtained was analyzed to be 46.48% yttrium oxide and produced a curve similar to DTA Curve No. 32. A yttrium oxalate trihydrate would contain 46.22% yttrium oxide.

The anhydrous oxalate was prepared by heating the hydrate to 260-70° for twenty hours (DTA Curve No. 33). The anhydrous oxalate began to decompose around 395°C and produced two exothermic peaks at 410°C and 425°C. A second exothermic peak began around 530°C and reached a maximum around 630-50°C. The reaction was completed to the oxide between 660-80°C.

CONCLUSIONS

Differential thermal analysis proved to be a useful tool in understanding the decomposition of the carbonates and oxalates of the rare earths. The presence of intermediate hydrates and compounds along with crystal inversions were readily detected. Differential thermal analysis probably gives the best indication of changes which take place in a bulk of material during decomposition. This type information would be most useful for large scale decompositions as used in commercial productions.

The most serious drawback of the technique is the difficulty of analyzing the intermediate products which formed during the decomposition. The rather small sample required in the analysis does not yield a quantity of product large enough for direct analysis for the rare earth elements.

The hydrates which have been reported for the carbonates of the rare earth elements appear to have been only varying amounts of water absorbed in the carbonate materials and did not constitute any definite hydrates. Even under conditions of high relative humidity no stable hydrate could be found. Yttrium carbonate may have formed a stable dihydrate although the impurity of the yttrium sample may have resulted in the calculated 1.84 hydrate.

All the carbonates studied began to decompose around 420-30°C except yttrium carbonate. Ambrozhii and Nikolaevskaya[53] also found that the temperatures of the first stage of decomposition of lanthanum, cerium, praseodymium and neodymium carbonates were close but they reported a range of 460-513°C for the first step.

The carbonates of lanthanum, neodymium, and samarium decomposed to the dioxycarbonate compounds ($R_2O_3 \cdot CO_2$) and then to the oxide. Final decomposition of these compounds to the oxide occurred at increasingly lower temperatures as the oxides became more acidic.

Praseodymium and yttrium carbonates behaved differently. Praseodymium carbonate began to decompose at 430°C, perhaps to the oxydicarbonate which in turn decomposed in two steps to the oxide. The tendency of praseodymium to form higher oxides may be responsible for the final decomposition occurring at a lower temperature than would be expected when compared with the behavior of lanthanum or neodymium carbonates. A reversible reaction occurring at 960°C was probably due to a crystalline inversion of the oxide (Pr_6O_{11}). This inversion has not been reported in the literature.

Yttrium carbonate began to decompose at 100°C and converted to yttrium oxydicarbonate. This low temperature of decomposition may be a result of instability in the crystal lattice due to the small size of the yttrium ion. No reason can be given for the appearance and stability of the oxydicarbonate for yttrium.

Decahydrates for lanthanum, cerium, praseodymium, neodymium, samarium, and yttrium oxalates were found.

A hexahydrate was also found for lanthanum oxalate which would decompose to a tetrahydrate. The decahydrate of lanthanum and praseodymium had no intermediate hydrates. Neodymium oxalate decahydrate formed a dihydrate as an intermediate. The decahydrate of samarium oxalate decomposed to a hexahydrate and then to a tetrahydrate. A trihydrate was the intermediate hydrate formed when yttrium oxalate decahydrate was dehydrated.

When the oxalates began to decompose, two exothermic peaks about ten degrees apart were formed in the differential thermal analysis curve. Gilpin and McCrone[54] studied the crystal structure of lanthanum oxalate decahydrate and found that as the water of hydration was removed from the crystal, the physical appearance remained unchanged but the material became amorphous to X-ray diffraction. This open skeleton expanded lattice which accommodated the water of hydration becomes unstable around 385°C; collapse of the lattice could liberate energy which would result in the first exothermic peak. When the crystal bonds which stabilized the oxalate ion were broken, the oxalate ion decomposed into carbon dioxide and carbon monoxide and left the compound, $M_2O_3 \cdot 2CO_2$.

Upon further heating, the oxydicarbonate compound decomposed exothermally to the dioxycarbonate and then finally endothermally to the oxide. The oxide of praseodymium again showed the reversible reaction at 960-70°C.

Carbon which was formed during the decomposition resulted from the disproportionation of carbon monoxide into carbon dioxide and carbon. The oxidation of this carbon in the sample tended to reduce the size of the last endothermic peak associated with the liberation of the last molecule of carbon dioxide.

It could not be determined definitely in this study whether the formation of the oxydicarbonate and the dioxycarbonate were a result of partial decomposition of the oxalate ions to the carbonate or were the products of a reaction between an oxide and carbon dioxide formed in the decomposition. The materials were amorphous in X-ray diffraction studies.

As the acidity of the rare earth oxide increased, there was a marked decrease in the size of the last endothermic peak which indicated the decomposition of the dioxycarbonate compound.

In the study by Wendlandt[28] in which the oxalate was decomposed as a very thin layer which allowed very little interreaction of the decomposition products, the dioxycarbonate was reported for only lanthanum, the most basic of the rare earths.

Also, since this peak was present in the carbonate compounds, one might conclude that in the decomposition of the oxalate, the dioxycarbonate compound was formed by the reaction of the oxide and carbon dioxide.

X-ray diffraction patterns for all of the carbonates studied (see Appendix) show very close resemblances for the crystal structures of the carbonates. This behavior would be expected because of the similarity of the size and charge on the metal ion of the elements studied. A satisfactory diffraction pattern for yttrium carbonate was not obtained.

Two definite patterns for the prepared deca- and hexahydrates of lanthanum oxalate were found. The "d" values for the decahydrate compared closely with the values of Gilpin and McCrone[54]. The decahydrates of lanthanum, cerium, praseodymium, neodymium, and samarium are again very similar. The lines of the X-ray diffraction pattern of the decahydrate of yttrium oxalate were spread slightly further apart and are more intense. Samarium also formed two stable hydrates as shown by the X-ray patterns.

Vickery[55] discussed work by Goldschmidt who stated the rare earth oxides usually form hexagonal, cubic and in some cases pseudotrigonal crystals. The X-ray diffraction patterns of the lanthanum and neodymium oxides are identified as hexagonal. The patterns of praseodymium oxide (Pr_6O_{11}) below 960°C and of cerium oxide are cubic. Yttrium oxide gave a pattern identified as a body centered cube[51]. The pattern for samarium oxide was not identified but may be the pseudotrigonal structure proposed by Goldschmidt. The "d" values for the oxides of lanthanum, neodymium, praseodymium and yttrium compared well with the values of Reed[56] and the "Index to X-ray Powder Data File"[51].

SUMMARY

1. An apparatus for observing the thermal changes during thermal decomposition of rare earth carbonates and oxalates was designed and constructed.

2. The decomposition process for rare earth carbonates consisted only of endothermic reactions and generally formed only a dioxycarbonate compound as an intermediate.

3. The decomposition processes for the rare earth oxalates were both endothermic and exothermic reactions and usually formed both an oxydicarbonate and a dioxycarbonate intermediate.

4. The decomposition process for the cerium compounds differs somewhat from that for other rare earth element compounds due to the fact that the cerium (III) ion is easily oxidized to cerium (IV). In general, the cerium compounds were all converted to ceric oxide (CeO_2) by 400°C.

5. In general, the temperatures for the final stage of decomposition for the carbonates and oxalates decreased with decreasing basicity of the elements.

6. The dehydration of hydrated compounds could be followed, in most cases, by means of differential thermal analysis.

7. A reversible change in the crystal structure of praseodymium oxide (Pr_6O_{11}) occurs at 960°C. This change has not previously been reported and must be studied further.

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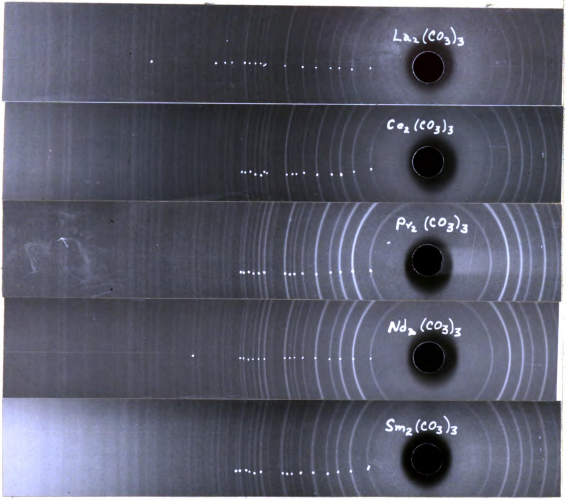
APPENDIX

X-Ray Diffraction Patterns. -- In the contact prints of the diffraction patterns, dots were placed on the lines which were measured and tabulated in the following tables.

RI	Relative Intensity
s	Strong
m	Medium
w	weak
vw	very weak
vvw	very very weak

Differential Thermal Analysis Curves. -- All peaks above the base line are endothermic and all peaks below the base line are exothermic. A peak deflection of one inch indicates about a 0.2 millivolt differential between the sample and the inert standard.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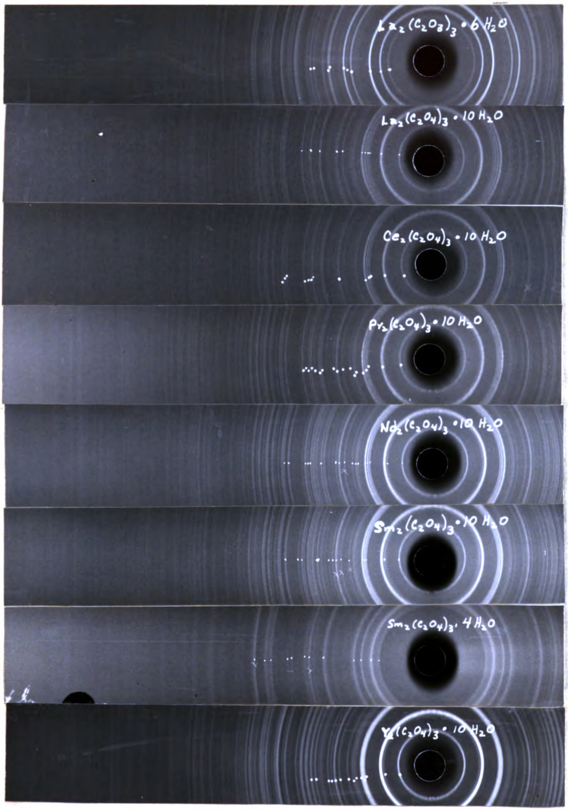
$Ce_2(CO_3)_3$
$Pr_2(CO_3)_3$
$Nd_2(CO_3)_3$
$Sm_2(CO_3)_3$

$La_2(CO_3)_3$			$Nd_2(CO_3)_3$		
R.I.	2 θ	d	R.I.	2 θ	d
m	1.610	5.5003	m	1.614	5.4868
m	2.100	4.2267	s	2.079	4.2689
m	2.425	3.6671	s	2.419	3.6760
m	2.665	3.3420	w	2.679	3.3249
m	3.030	2.9472	s	2.060	2.9190
m	3.390	2.6430	w	2.399	2.6353
			w	3.624	2.4766
m	3.845	2.3392	vw	3.739	2.4031
vvw	4.365	2.0719	m	3.879	2.3195
vvw	4.425	2.0451	w	4.409	2.0524
vvw	4.500	2.0128	w	4.564	1.9860
w	4.655	1.9493	w	4.714	1.9262
vw	4.790	1.8974	vvw	4.829	1.8830
w	4.920	1.8503	vw	4.969	1.8331
vvw	5.275	1.7338	vvw	5.059	1.8027
vw	5.440	1.6851			
vw	5.690	1.6168			
vvw	5.810	1.5863	vvw	6.289	1.4765

$Pr_2(CO_3)_3$			$Sm_2(CO_3)_3$			$Ce_2(CO_3)_3$		
R.I.	2 θ	d	R.I.	2 θ	D	R.I.	2 θ	d
m	1.597	5.5443	w	1.623	5.4566	w	1.605	5.5174
s	2.062	4.3037	s	2.100	4.2267	m	2.070	4.2872
s	2.404	3.6986	s	2.447	3.6346	m	2.420	3.6745
m	2.668	3.3383	w	2.722	3.2733	m	2.665	3.3420
s	3.033	2.9444	m	3.103	2.8795	m	3.039	2.9387
m	3.378	2.6511	w	3.422	2.6180	w	3.389	2.6427
m	3.603	2.4906	vvw	3.670	2.4466	vw	3.589	2.5000
w	3.712	2.4199	vvw	3.782	2.3767	vw	3.710	2.4212
s	3.863	2.3287	m	3.902	2.3063	m	3.854	2.3339
m	4.383	2.0637	w	4.462	2.0290	w	4.365	2.0718
						vw	4.433	2.0416
m	4.536	1.9976	w	4.623	1.9600	w	4.525	2.0022
w	4.678	1.9402	vw	4.772	1.9042	w	4.664	1.9457
vw	4.813	1.8889	vvw	4.867	1.8692	vw	4.805	1.8918
w	4.927		w	5.022	1.8151	w	4.935	1.8450
vw	5.028	1.8131	vvw	5.117	1.7836	vvw	4.995	1.8242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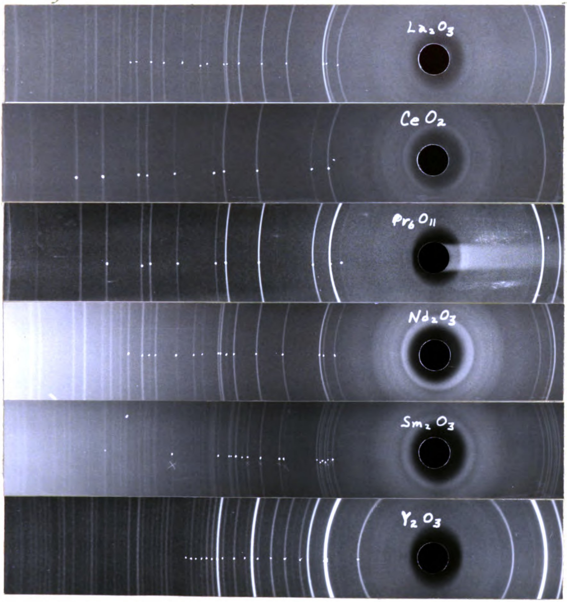
$La_2(C_2O_4)_3 \cdot 10H_2O$
$Ce_2(C_2O_4)_3 \cdot 10H_2O$
$Pr_2(C_2O_4)_3 \cdot 10H_2O$
$Nd_2(C_2O_4)_3 \cdot 10H_2O$
$Sm_2(C_2O_4)_3 \cdot 10H_2O$
$Sm_2(C_2O_4)_3 \cdot 4H_2O$
$Y_2(C_2O_4)_3 \cdot 10H_2O$

$La_2(C_2O_4)_3\cdot10H_2O$			$Ce_2(C_2O_4)_3\cdot10H_2O$			$Pr_2(C_2O_4)_3\cdot10H_2O$		
R.I.	2 Θ	d	R.I.	2 Θ	d	R.I.	2 Θ	d
m	8.50	10.394	m	8.58	10.297	m	8.57	10.307
s	13.30	6.6513	s	13.43	6.5873	s	13.42	6.5927
vvw	16.30	5.4333	w	17.16	5.1629	w	17.42	5.0864
vw	17.00	5.1211	w	17.73	4.9976	w	17.92	4.9456
w	17.60	5.0348	m	18.48	4.7970	m	18.67	4.7484
m	18.30	4.8437				vvw	20.53	4.3224
						vvw	21.00	4.2267
						vvw	21.91	4.0532
vvw	23.50	3.7824				vvw	23.97	3.7092
vvw	25.15	3.5384	mw	25.28	3.5199	mw	25.42	3.5009
						vvw	26.22	3.3958
mw	29.45	3.0303				vw	29.51	3.0243
						vw	30.12	2.9644
						vvw	31.42	2.8447
vw	31.80	2.8115	w	32.03	2.7919	vw	31.67	2.8228
			vvw	32.58	2.7460	vw	32.87	2.7224
			vvw	33.44	2.6773	ww	33.68	2.6588
vw	34.20	2.6195	w	34.43	2.6023	mw	34.50	2.5974
			vvw	38.88	2.3143			
			vvw	39.63	2.2723			
			vvw	40.23	2.2397			

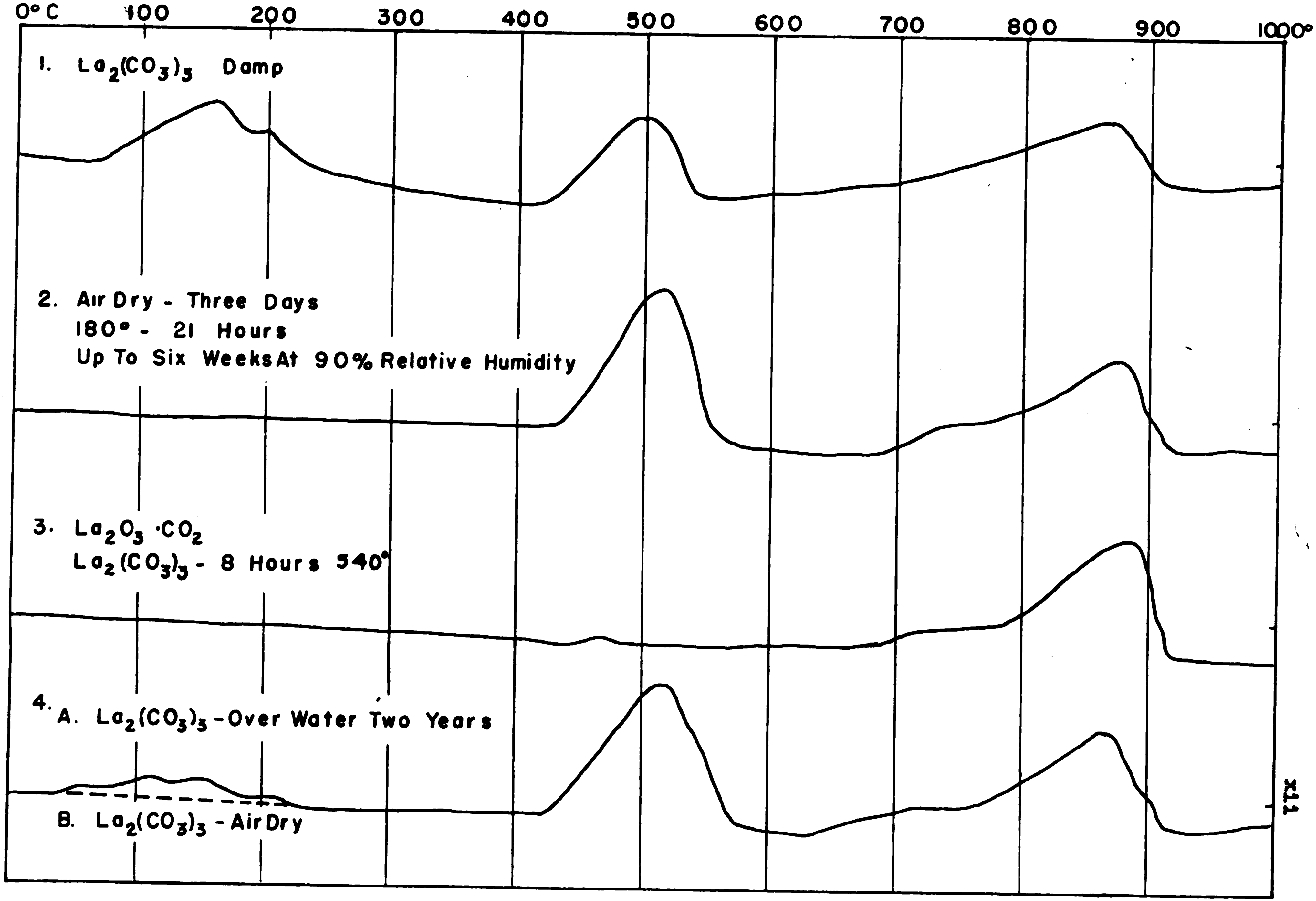
$Nd_2(C_2O_4)_3\cdot 10H_2O$			$Sm_2(C_2O_4)_3\cdot 10H_2O$			$Y_2(C_2O_4)_3\cdot 10H_2O$		
R.I.	2θ	d	R.I.	2θ	d	R.I.	2θ	d
m	8.61	10.261	m	9.32	9.4808	s	8.77	10.075
vvw	12.66	6.9861	vw	12.62	7.0081	vw	12.70	6.9642
s	13.26	6.6673	s	13.42	6.5921	s	13.57	6.5189
m	17.31	5.1175	m	17.37	5.1060	vvw	17.77	4.9870
m	17.86	4.9621	m	17.82	4.9731	w	18.26	4.8543
s	18.36	4.8280	m	18.47	4.7995	w	18.90	4.6913
vvw	20.36	4.3581	vvw	21.92	4.0513	vvw	20.52	4.3244
vvw	20.86	4.2547	vvw	24.22	3.6715	vvw	21.07	4.2128
vvw	21.76	4.0807				w	22.42	3.9621
vvw	23.96	3.7108				w	24.62	3.6128
w	24.46	3.6361						
vvw	25.31	3.5160	m	25.47	3.4939	m	25.82	3.4475
vvw	29.26	3.0496	vvw	26.37	3.3769			
vvw	32.86	2.7232	vvw	27.22	3.2733			
vvw	33.71	2.6565	vvw	30.37	2.9405			
vvw	34.68	2.6077	vw	34.42	3.6033			
vw	38.66	2.3270	vvw	35.52	2.5252			
vw	39.76	2.2651	vw	38.72	2.3235			

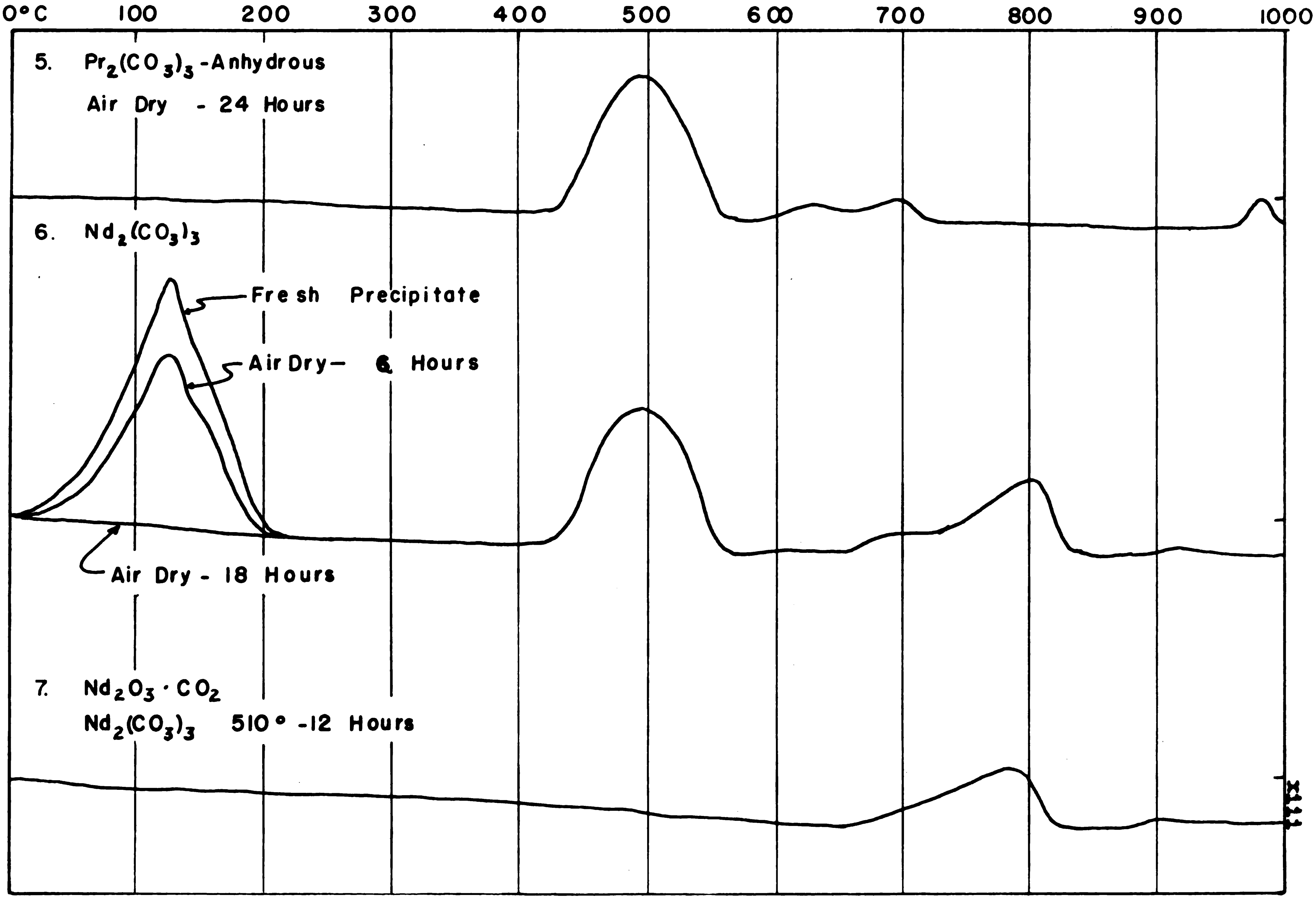
$La_2(C_2O_4)_3 \cdot 6H_2O$			$Sm_2(C_2O_4)_3 \cdot 4H_2O$		
R.I.	2θ	d	R.I.	2θ	d
m	11.38	7.7688	w	14.20	6.2317
s	13.64	6.4863	m	16.25	5.4549
s	16.51	5.3656	m	18.90	4.6913
m	21.48	4.1333	w	20.84	4.2588
vvw	22.58	3.9344	vvw	29.75	3.004
m	23.38	3.8015	w	32.60	2.7444
w	27.08	3.2899	vvw	33.90	2.6420
w	27.58	3.2314	vvw	37.20	2.4149
vw	31.43	2.8438	vvw	38.20	2.3539
vw	32.18	2.7792	vvw	42.60	2.1204
			vvw	44.15	2.0496
			m	46.95	1.9336

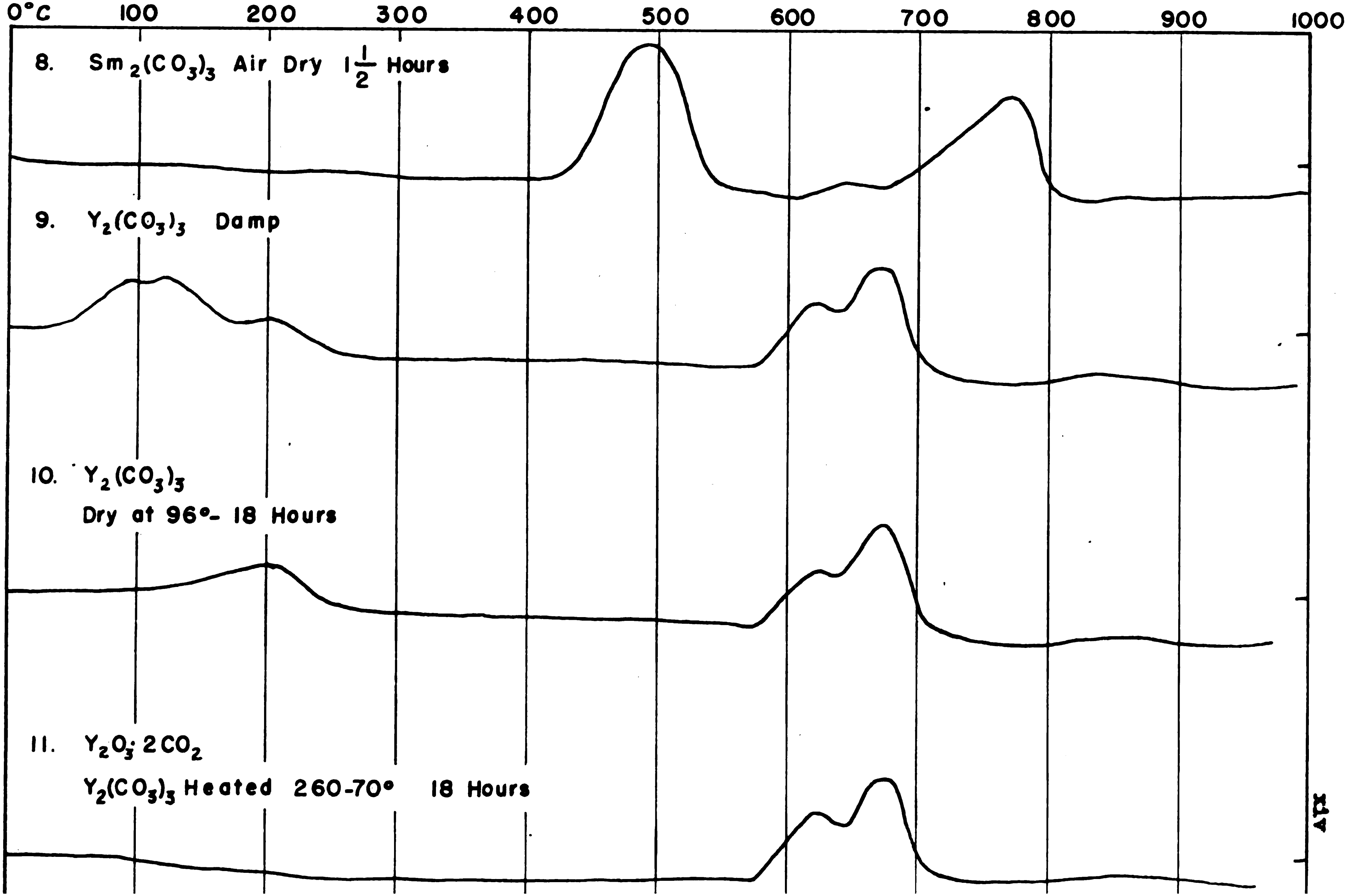

La_2O_3
CeO_2
Pr_6O_{11}
Nd_2O_3
Sm_2O_3
Y_2O_3

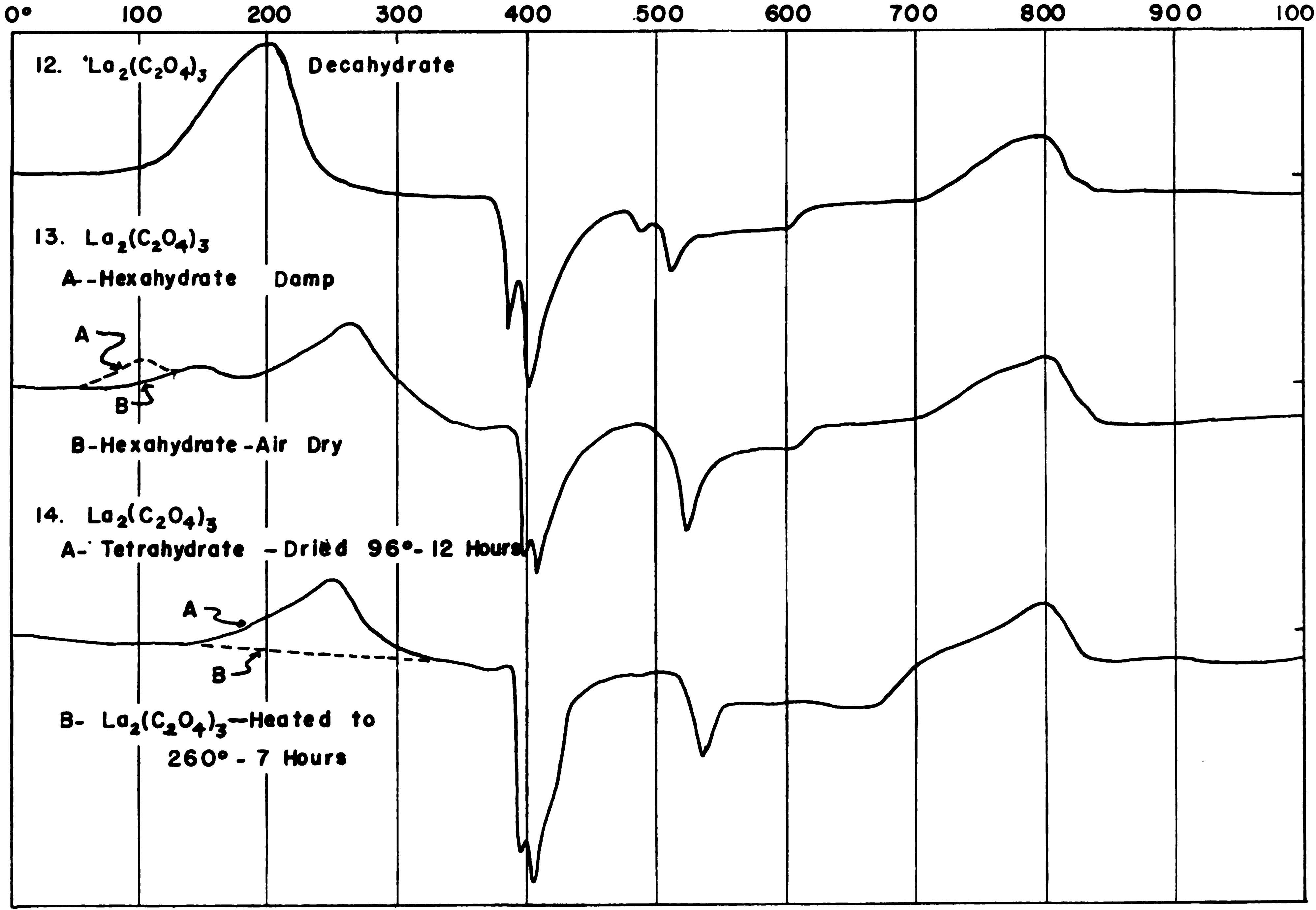
La_2O_3			CeO_2			Pr_6O_{11}		
R.I.	2 θ	d	R.I.	2 θ	d	R.I.	2 θ	d
m	26.17	3.4023				vvw	25.25	3.5244
m	29.17	3.0583	s	28.64	3.1142	s	28.10	3.1728
s	30.07	2.9692	m	33.19	2.6969	s	32.72	2.7346
m	39.57	2.2756	s	47.58	1.9095	s	47.00	1.9317
m	46.17	1.9644	s	56.48	1.6279	s	55.72	1.6485
m	52.22	1.7502	w	59.14	1.5608	m	58.37	1.5796
m	55.47	1.6551	w	69.48	1.3517	w	68.55	1.3677
mw	56.02	1.6401	m	76.69	1.2415	m	75.74	1.2547
vvw	60.47	1.5296	mw	79.14	1.2091	m	78.10	1.2226
vvw	62.32	1.4886	m	88.43	1.1045	m	87.30	1.1159
vvw	66.97	1.3961	m	95.35	1.0418			
vw	72.12	1.2931						
vw	75.37	1.2600						
w	79.17	1.2088						
vvw	80.77	1.1888						

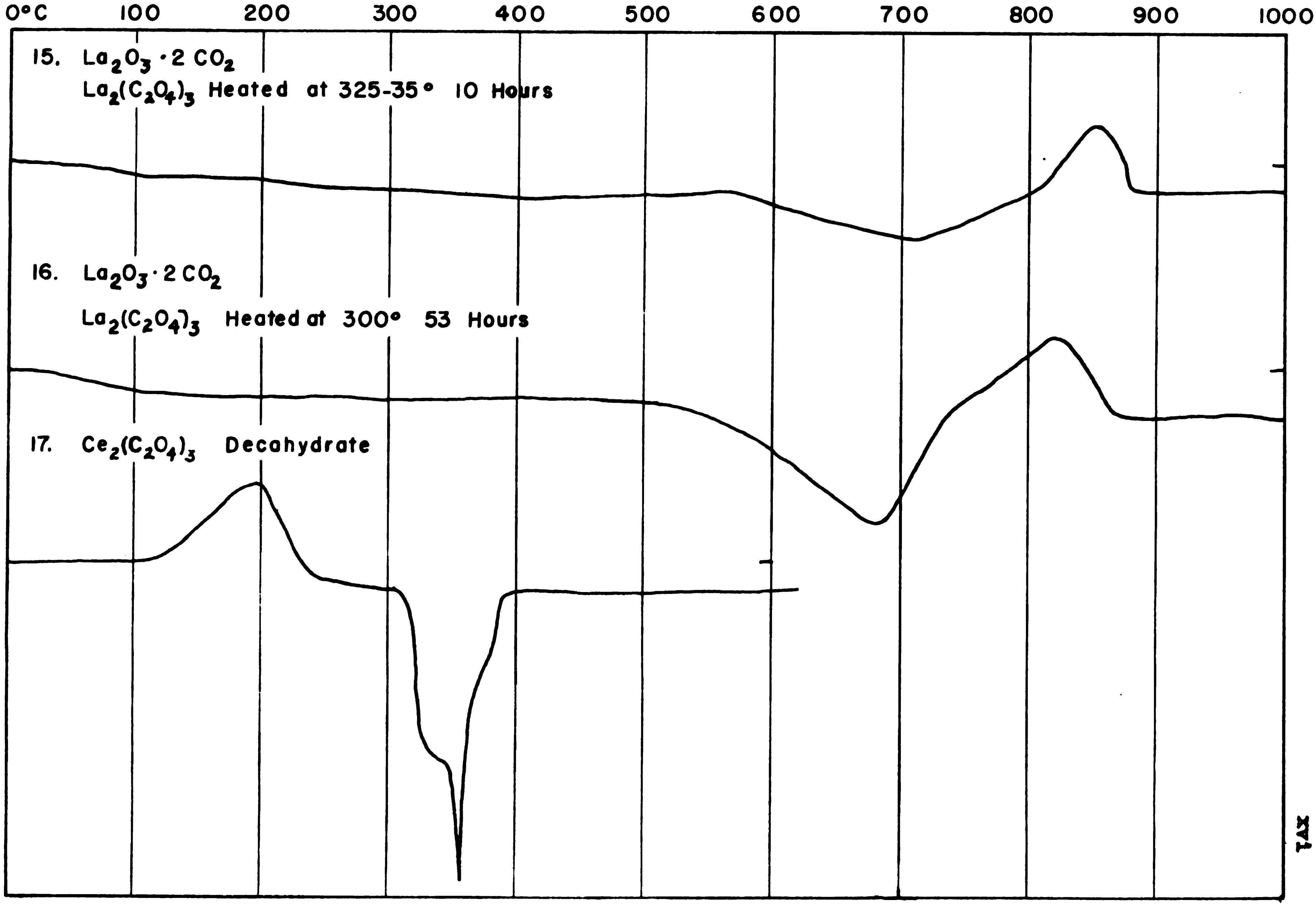
Nd_2O_3			Sm_2O_3			Y_2O_3		
R.I.	2 O	d	R.I.	2 O	d	R.I.	2 O	d
m	27.05	3.2935	s	27.98	3.1861	m	2.054	4.3203
m	29.90	2.9857	s	29.53	3.0223	vvw	2.629	3.3870
s	30.85	2.8959	s	29.98	2.9780	s	2.909	3.0670
m	40.65	2.1276	m	30.78	2.9024	s	3.374	2.6542
m	47.50	1.9125	s	31.28	2.8571	m	3.590	2.4993
m	53.55	1.7098	s	32.08	2.7876	m	3.979	2.2635
vvw	55.45	1.6556	vw	40.63	2.2186	m	4.349	2.0789
m	57.05	1.6130	s	41.88	2.1552	vw	5.989	1.5420
m	57.75	1.5950	s	46.88	1.9363	vw	5.009	1.8195
vvw	61.95	1.4966	s	50.28	1.8131	s	4.839	1.8793
w	64.15	1.4505	vvw	51.68	1.7672	vw	5.314	1.7220
vw	68.60	1.3668	m	53.38	1.7149	vw	5.614	1.6369
w	74.25	1.2761	vvw	54.68	1.6771	s	5.759	1.5990
vvw	75.85	1.2532	vw	55.18	1.6631	w	5.899	1.5645
mw	77.75	1.2273	vw	57.98	1.5893	w	6.034	1.5315
w	81.40	1.1312	vvw	70.13	1.3407	vvw	6.179	1.5002
						vvw	6.314	1.4713
						vw	6.454	1.4427
						vvw	6.584	1.4173

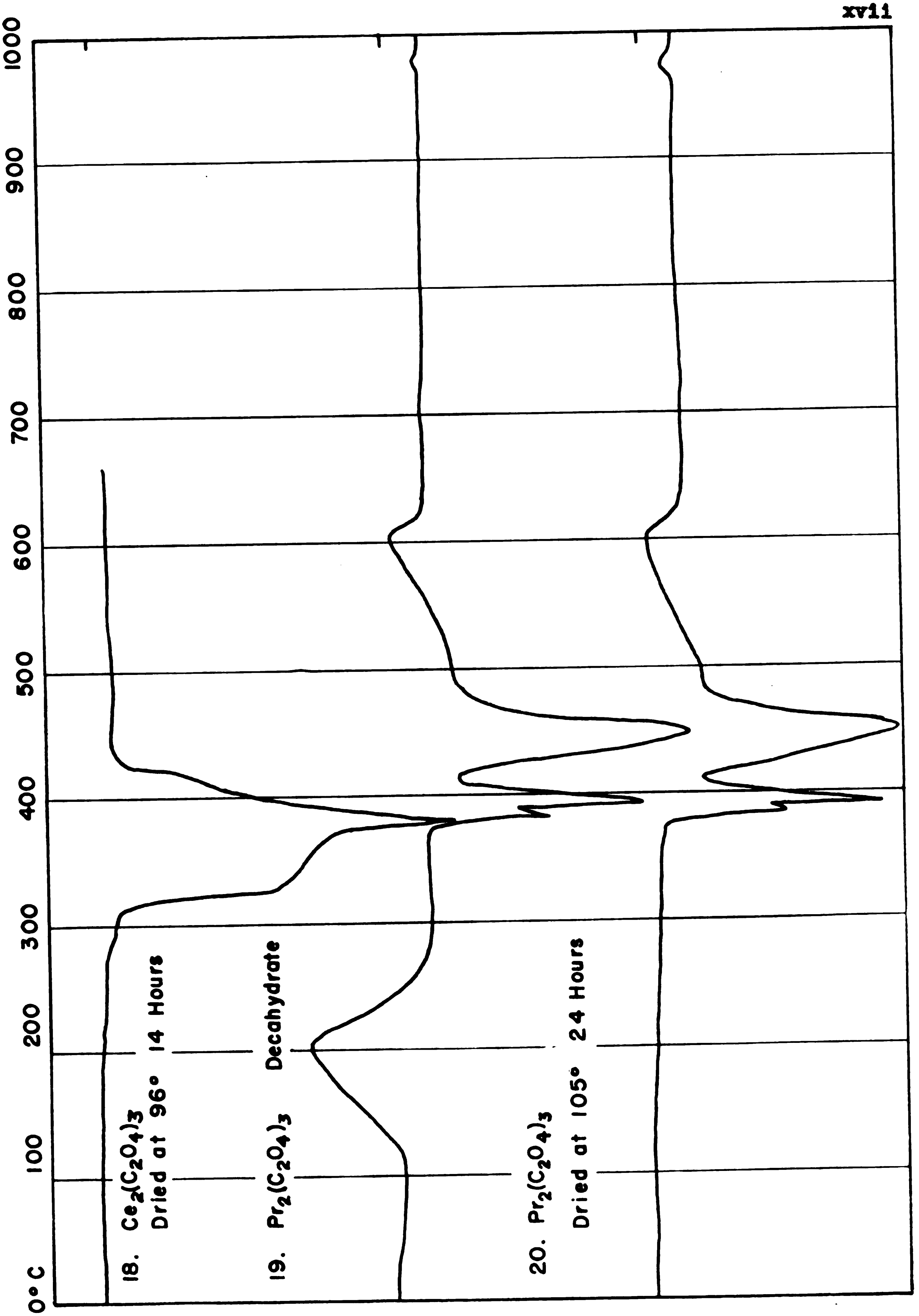

0° C
100
200
300
400
500
600
700
800
900
1000°
1. La₂(CO₃)₃ Damp
2. Air Dry - Three Days
180° - 21 Hours
Up To Six Weeks At 90% Relative Humidity
3. La₂O₃ ·CO₂
La₂(CO₃)₃ - 8 Hours 540°
4. A. La₂(CO₃)₃ - Over Water Two Years
B. La₂(CO₃)₃ - Air Dry

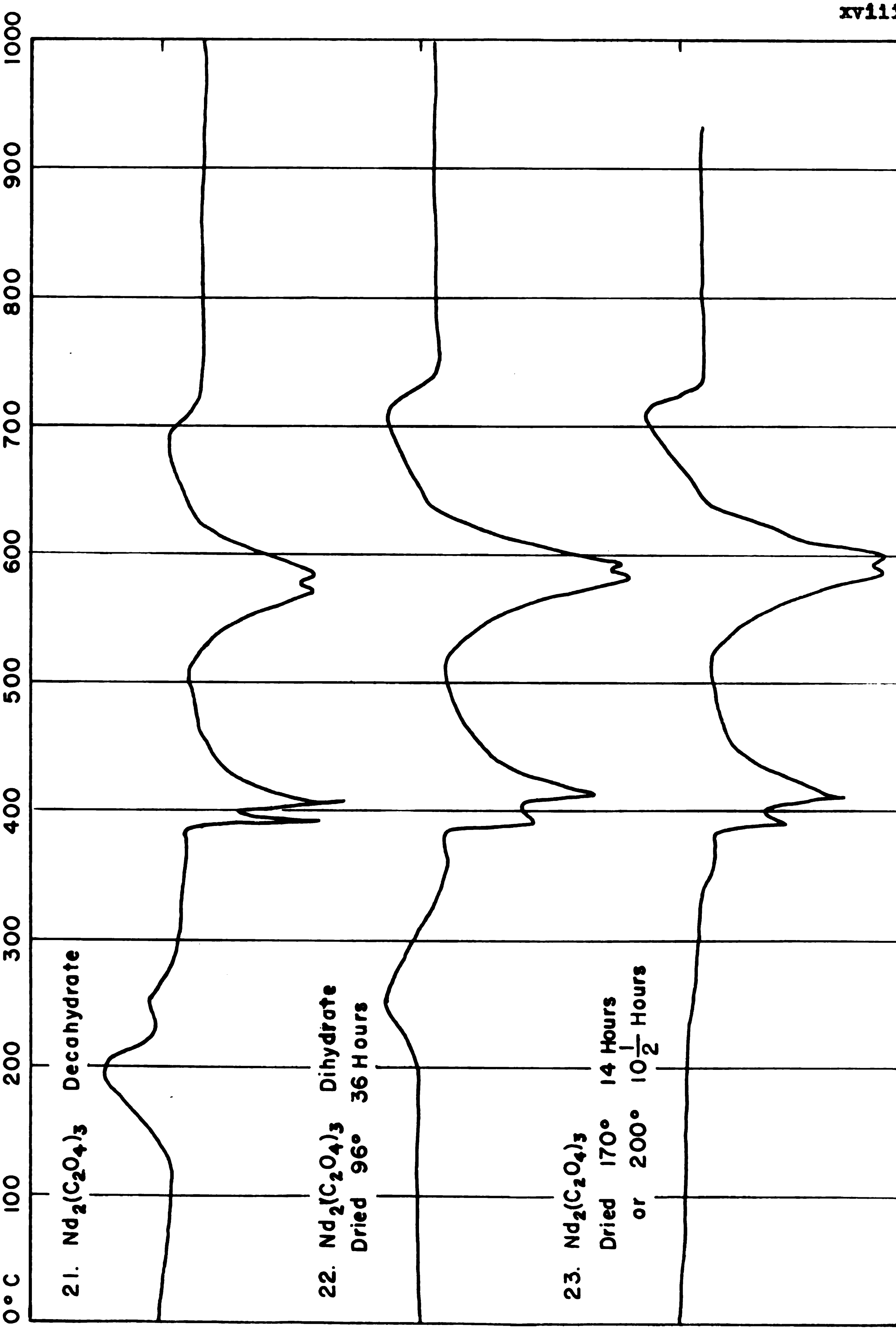

0°C
100
200
300
400
500
600
700
800
900
1000
5. $Pr_2(CO_3)_3$-Anhydrous
Air Dry - 24 Hours
6. $Nd_2(CO_3)_3$
Fresh Precipitate
Air Dry— 6 Hours
Air Dry - 18 Hours
7. $Nd_2O_3 \cdot CO_2$
$Nd_2(CO_3)_3$ 510° -12 Hours

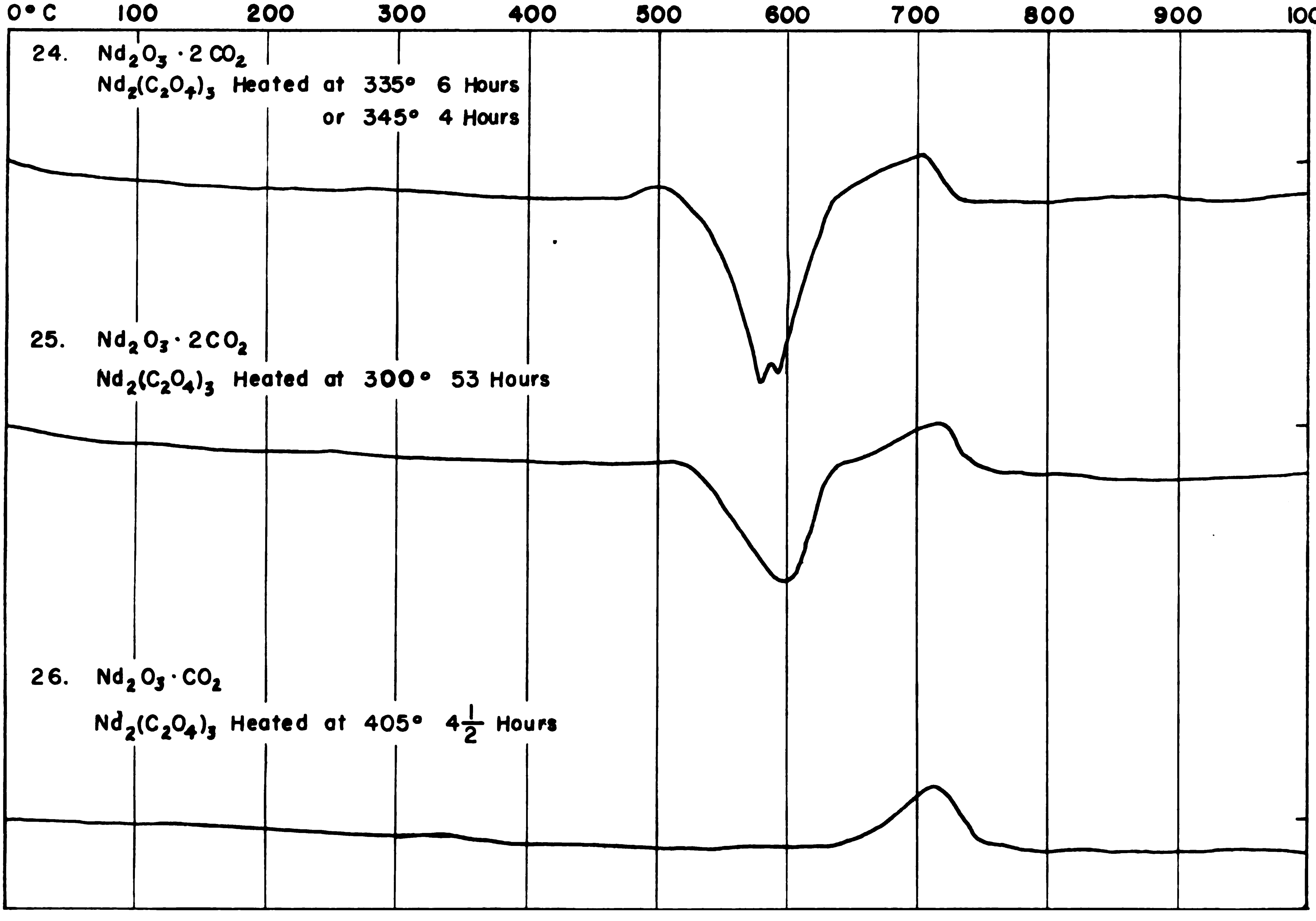

0°C
100
200
300
400
500
600
700
800
900
1000
8. $Sm_2(CO_3)_3$ Air Dry $1\frac{1}{2}$ Hours
9. $Y_2(CO_3)_3$ Damp
10. $Y_2(CO_3)_3$
Dry at 96°- 18 Hours
11. $Y_2O_3 \cdot 2CO_2$
$Y_2(CO_3)_3$ Heated 260-70° 18 Hours

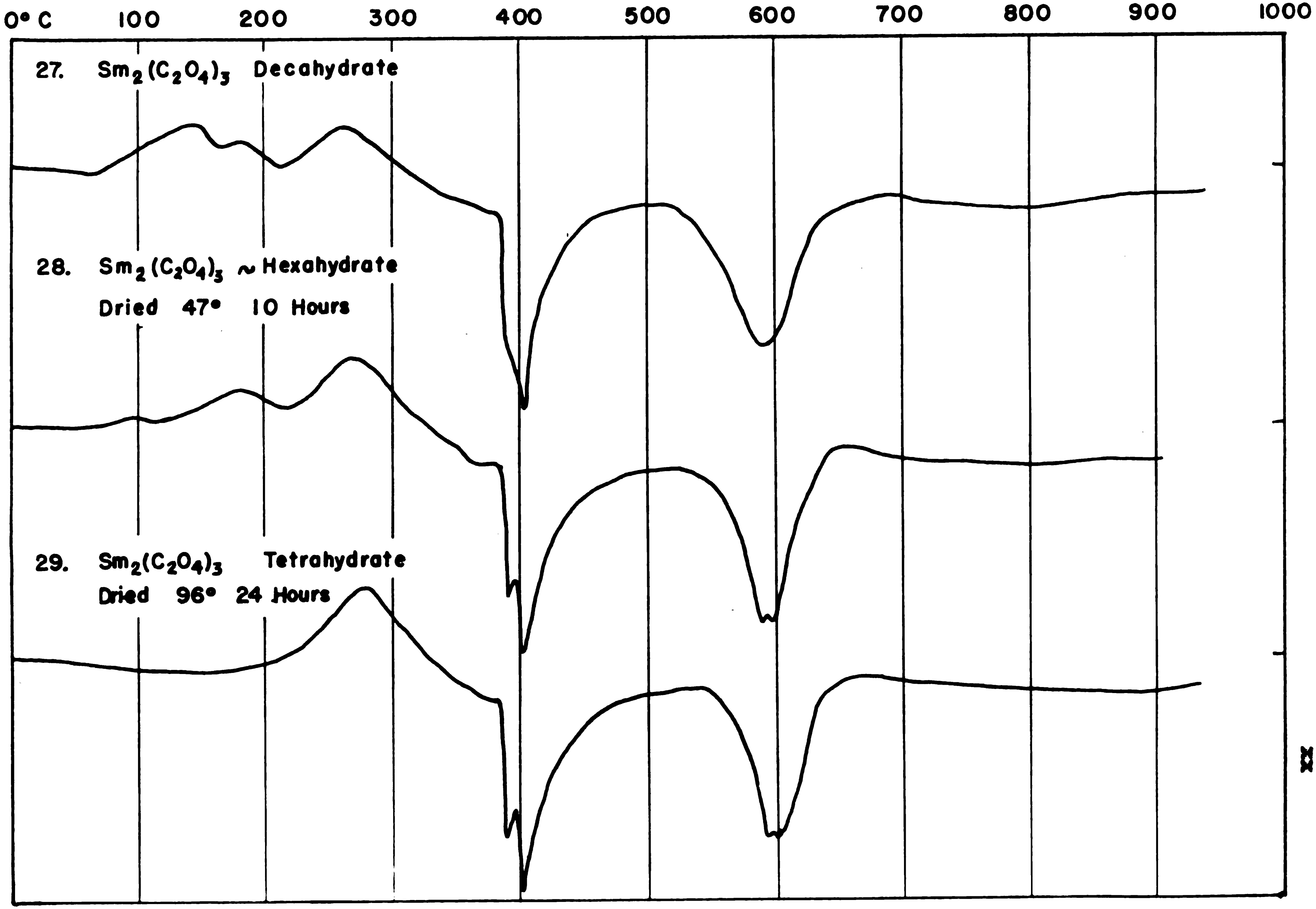

0°
100
200
300
400
500
600
700
800
900
1000
12. La₂(C₂O₄)₃ Decahydrate
13. La₂(C₂O₄)₃
A--Hexahydrate Damp
A
B
B-Hexahydrate-Air Dry
14. La₂(C₂O₄)₃
A- Tetrahydrate -Dried 96°- 12 Hours
A
B
B- La₂(C₂O₄)₃—Heated to 260° - 7 Hours

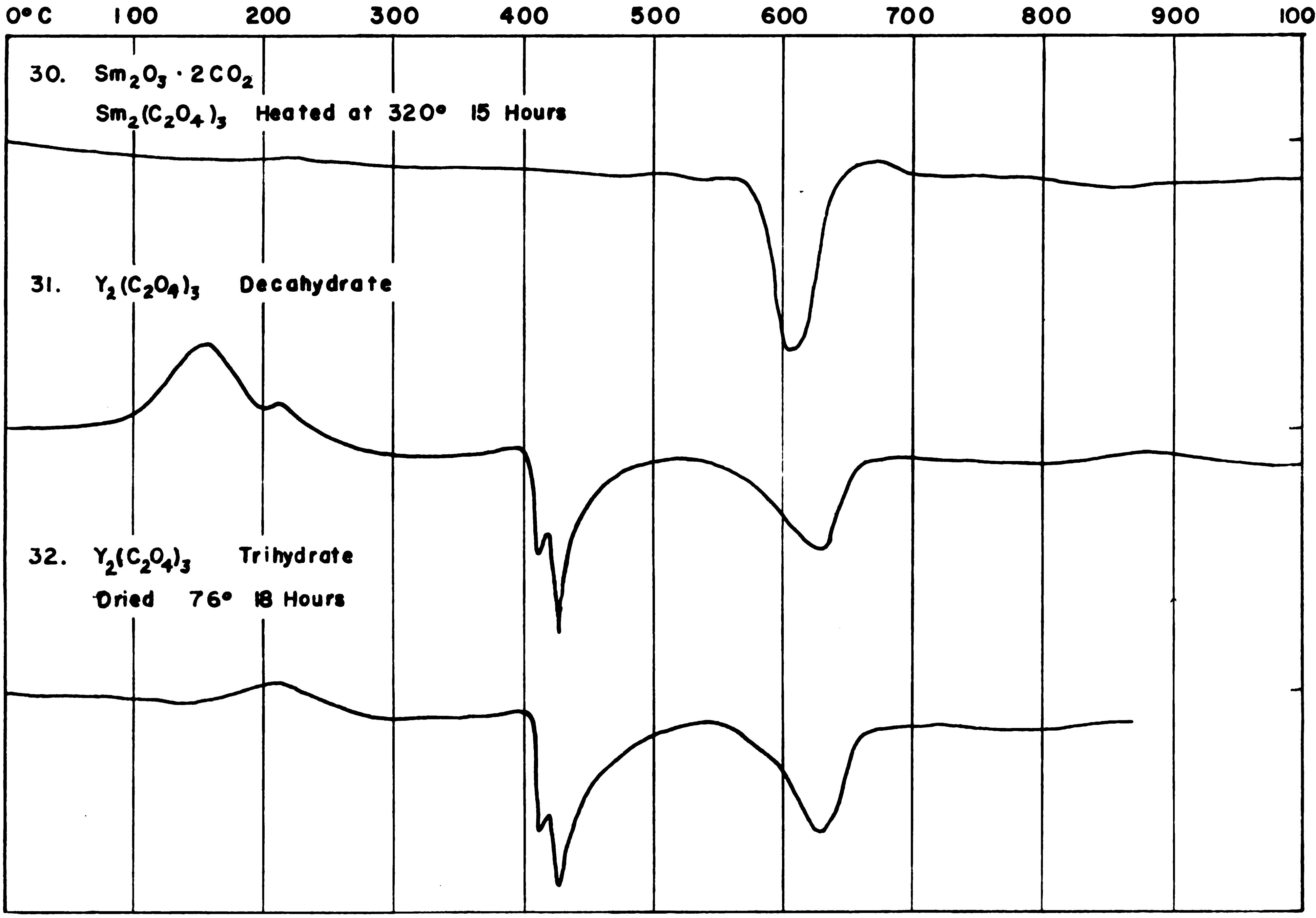

0°C
100
200
300
400
500
600
700
800
900
1000
15. $La_2O_3 \cdot 2\,CO_2$
$La_2(C_2O_4)_3$ Heated at 325-35° 10 Hours
16. $La_2O_3 \cdot 2\,CO_2$
$La_2(C_2O_4)_3$ Heated at 300° 53 Hours
17. $Ce_2(C_2O_4)_3$ Decahydrate

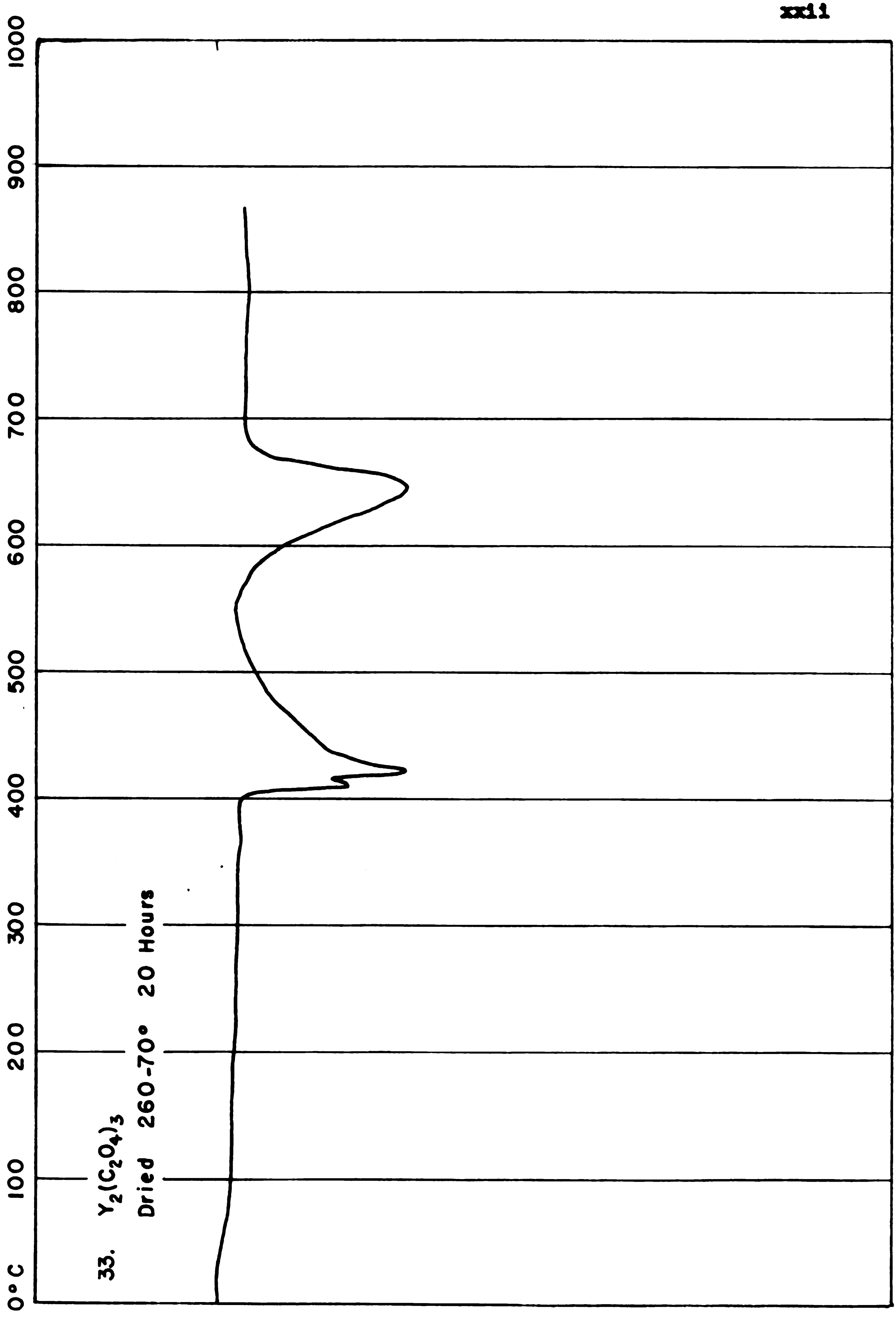

0° C
100
200
300
400
500
600
700
800
900
1000
18. $Ce_2(C_2O_4)_3$
Dried at 96° 14 Hours
19. $Pr_2(C_2O_4)_3$ Decahydrate
20. $Pr_2(C_2O_4)_3$
Dried at 105° 24 Hours


0° C
100
200
300
400
500
600
700
800
900
1000
21. $Nd_2(C_2O_4)_3$ Decahydrate
22. $Nd_2(C_2O_4)_3$ Dihydrate
Dried 96° 36 Hours
23. $Nd_2(C_2O_4)_3$
Dried 170° 14 Hours
or 200° $10\frac{1}{2}$ Hours


0° C
100
200
300
400
500
600
700
800
900
1000
24. $Nd_2O_3 \cdot 2CO_2$
$Nd_2(C_2O_4)_3$ Heated at 335° 6 Hours
or 345° 4 Hours
25. $Nd_2O_3 \cdot 2CO_2$
$Nd_2(C_2O_4)_3$ Heated at 300° 53 Hours
26. $Nd_2O_3 \cdot CO_2$
$Nd_2(C_2O_4)_3$ Heated at 405° $4\frac{1}{2}$ Hours


0° C
100
200
300
400
500
600
700
800
900
1000
27. $Sm_2(C_2O_4)_3$ Decahydrate
28. $Sm_2(C_2O_4)_3$ ~ Hexahydrate
Dried 47° 10 Hours
29. $Sm_2(C_2O_4)_3$ Tetrahydrate
Dried 96° 24 Hours


0° C
100
200
300
400
500
600
700
800
900
1000
30. $Sm_2O_3 \cdot 2CO_2$
$Sm_2(C_2O_4)_3$ Heated at 320° 15 Hours
31. $Y_2(C_2O_4)_3$ Decahydrate
32. $Y_2(C_2O_4)_3$ Trihydrate
Dried 76° 18 Hours



33. $Y_2(C_2O_4)_3$
Dried 260-70° 20 Hours