DENSITY AND STRUCTURE STUDIES OF LANTHANUM-PRASEODYMIUM OXIDES

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DENSITY AND STRUCTURE STUDIES OF LANTHANUM-PRASEODYMIUM OXIDES

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INTRODUCTION

The question of solid solution formation versus compound formation between higher oxides of electropositive elements and oxides of the elements showing only the positive one, two, or three oxidation state has been debated for many years. The two possibilities have been of interest in rare earth oxide studies. Mixed oxide systems may be of two types: (1) synthetic mixtures prepared by combining the pure oxides or (2) naturally occurring mixtures. Many such systems have been shown to follow the additivity rules. However, some systems such as the air-ignited mixed oxide systems of lanthanum and praseodymium or neodymium and praseodymium do not completely follow the additivity rules. Since the lanthanum and praseodymium oxide system does occur naturally and has proven to be difficult to analyze because it does not follow the additivity rules, it is of interest to know more completely the behavior of this system as the composition is varied.

The virtual insolubility of cerium dioxide, when pure, in mineral acids has been explained by assuming compound formation. Prandtl(49) stated that Pr_6O_{11} and PrO_2 are solid solutions of Pr_2O_3 and Pr_2O_5. Zintl and Croatto(71) and Carlson(14) studied mixtures of lanthanum oxide and cerium dioxide and the variations of the properties of the system were believed to be evidence of solid solution formation. Zintl and Morawietz(72) prepared Na_2CeO_3, Na_2PrO_3, and $NaPrO_2$. From X-ray studies they found that each of the oxides has a sodium chloride structure. Hoffman(29,30) prepared $BaCeO_3$, $SrCeO_3$, and $BaPrO_3$. From X-ray studies he found that $BaCeO_3$ has the perovskite structure and that $BaPrO_3$ and $SrCeO_3$ are cubic. The air-ignited lanthanum oxide-praseodymium oxide system has been studied by Salutsky(58) and Prandtl and Huttner(50) and they found that at high concentrations of praseodymium oxide, oxygenation of the praseodymium becomes easier than for the pure oxide whereas in praseodymium-poor mixtures oxygenation of the praseodymium becomes very difficult.

The present study has as its object the study of the air-ignited lanthanum oxide-praseodymium oxide system and the accompanying variations of crystal structure, densities, and amounts of oxygenation with changes of composition to learn whether or not the question of solid solution versus compound formation for the system may be resolved.

SECTION I

Structure and Preparation of Lanthanon Oxides

Each of the rare earths forms a basic oxide in which the metal is trivalent. These oxides are by definition the original rare earths. Except for the oxides of cerium, praseodymium, and terbium these sesquioxides are stable toward oxidation at higher temperatures or under vigorous oxidizing conditions. A review of some of the properties of the sesquioxides will be followed by a brief discussion of those rare earth oxides in which these elements exhibit a higher oxidation state.

All of the rare earth sesquioxides except those of cerium, praseodymium, and terbium can be formed by direct combination of the free metals with oxygen and by ignition of the hydroxides, nitrates, carbonates, oxalates, sulfates, or other salts formed with anions of volatile or easily decomposed oxy-acids. Praseodymium and terbium sesquioxides may be prepared by the reduction of the higher oxides in a stream of hydrogen at about 900° C. or by ignition of the higher oxides in vacuum at above 600° C. However, the reduction of ceric oxide to the sesquioxide in a stream of hydrogen is difficult and is not rapid until the temperature is about 2000° C. and the hydrogen pressure is around 150 atmospheres. Ceric oxide is not reduced upon ignition in vacuum.

The rare earth sesquioxides are readily soluble in most acids. Those of lanthanum, praseodymium, and neodymium readily hydrate and carbonate in air and form normal salts with most of the weaker acids except hydrocyanic and hydrosulfuric acids which are too weak. This type of behavior of the sesquioxides contrasts with that of ceric oxide which is difficultly soluble even in strong acids.

In making structural studies Goldschmidt, Ulrich, and Barth(25) found that the lanthanide sesquioxides crystallize in three structural types: A, hexagonal; B, pseudotrigonal; and C, body-centered cubic. The A or hexagonal form is common from lanthanum through samarium and is obtained by high temperature ignition of appropriate compounds. Goldschmidt originally reported that only the sesquioxides of the elements samarium through lutecium assumed the C or body-centered cubic structure. However, Lohberg(38), Iandelli(34), and Bommer(7) have prepared cubic sesquioxides of the remaining rare earths. The C structure is formed at lower temperatures than the A form. The less common B or pseudotrigonal structure has been reported for the sesquioxides of praseodymium(?), neodymium, samarium, gadolinium, and dysprosium(?) and is formed at intermediate temperatures.

Since this study deals with lanthanum and praseodymium oxides, the A, C, and fluorite structures will be reviewed. Wells(65) in his review of the structures of the

rare earth oxides states that the hexagonal structure contains one lanthanum oxide molecule per unit cell. The metal ion has a coordination number of seven with the odd oxide ion being located above one face of an octahedron which is distorted by separating the oxide ions at the corners of that face. The four nearer oxygen neighbors to the lanthanum ion are at 2.42 A. and the remaining three are at 2.69 A. Values for the distances between the praseodymium and oxide ions are not given but the structures of the two sesquioxides are isotypic and the radii of the two ions are 1.04 A. for lanthanum oxide and 1.00 A. for praseodymium sesquioxide.

The C or body-centered cubic structure, having 16 molecules of sesquioxide per unit cell, is closely related to the fluorite structure from which it may be derived by removing one-quarter of the anions and rearranging the ions slightly so that all the metal ions are six coordinated.

Unlike the other lanthanons, cerium, praseodymium, and terbium, upon ignition of the free metals or salts of volatile or easily decomposed oxy-acids in air or oxygen form oxides in which the oxidation number of the metals is higher than three. Cerium sesquioxide left in the open air slowly transforms to cerium dioxide. Upon air ignition, praseodymium and terbium or their appropriate compounds form Pr_6O_{11} and Tb_4O_7, respectively. Of these three higher oxides cerium dioxide has the fluorite structure whereas Pr_6O_{11} and Tb_4O_7 form "defect" fluorite structures.

There are two possible arrangements for a "defect" fluorite structure: namely, a lattice in which all the cation positions are filled and some of the anion positions are vacant or a lattice in which all the cation and anion positions are filled and the excess cations are located interstitially. McCullough(42) and Hund and Peetz(33) think that the first suggestion is the more probable one for the structure. However, Vickery(64) using data by Martin(40) and Foex and Loriers(23) believes the second possibility to be more probable. No comprehensive structural studies have been reported for Tb_4O_7. Vickery also states that the cubic lines characteristic of the C structure of the sesquioxides have been observed in the X-ray powder diagrams of Pr_6O_{11} and Tb_4O_7. This latter idea implies that lines characteristic of both body-centered and face-centered cubic structures would have to be present on the same powder diagram. However, in this investigation only cubic lines corresponding to the face-centered cubic fluorite structure were found.

SECTION II

Lanthanum Oxide

Experimental

Since lanthanum oxide is a part of the system studied in this investigation, it was thought advisable to recheck the values of the density and of the lattice constants of the hexagonal structure. Except for the earliest values there is good agreement among the reported density values. It was also felt that the reported lattice constant values were not too precise. Therefore, it was decided to redetermine the density and lattice constants for the oxide having the hexagonal structure.

Lanthanum from four different sources was used in this investigation. Two of the samples were from the lanthanum-rich ends of two different extensively fractionated double magnesium nitrate recrystallization series from this laboratory. The lanthanum material was recovered from the fractions by double precipitation as the oxalate. The absorption spectrum of an almost saturated solution of the chloride was checked visually through a layer five centimeters thick for the presence of other lanthanides exhibiting absorption in the visible range. Some "spectroscopically" pure material was obtained from Dr. L. L. Quill. The fourth sample of lanthanum material was obtained from the Lindsay Chemical Company as 99.95 per cent pure and was checked for the presence of other lanthanons in the same manner as the first two source materials. All the oxide samples after ignition were pure white.

Three oxide samples were prepared from each source material. By ignition, one sample was prepared from the nitrate, one from the carbonate, and one from the oxalate. Each sample was air ignited for at least two days in an electric muffle furnace at 900° C. to insure complete calcination and annealling of the oxide product so very sharp X-ray lines would be obtained. Each sample upon removal from the furnace was placed in a desiccator to cool. For X-ray analysis Lindemann capillaries were filled with the oxides as soon as possible after cooling.

Powder diagrams were taken on a Norelco X-ray diffraction machine using a Hull-Debye-Scherrer type camera of 57.3 millimeter radius. Copper radiation filtered through nickel foil was used. Films were measured with a steel metric scale having a sliding vernier reading to ±0.005 centimeters. The linear readings were converted to 2θ values by the method recommended by Straumanis(61). For samples having the hexagonal structures the lattice constants were calculated from the equation,

$$\sin^2\theta = F_1(h^2+hk+k^2) + F_2(l)^2 ,$$

and the relationships,

$$a = \frac{\lambda}{3\sqrt{F_1}} \quad \text{and} \quad c = \frac{\lambda}{4\sqrt{F_2}}$$

Since one film obtained was unreadable, only eleven films were measured. The 2θ values for each plane producing a reflection were averaged. The 2θ values, relative intensities, $\sin^2\theta$ values, and planes producing reflections are given in Table I. There was good agreement among all the 2θ values for all films.

TABLE I

X-ray Data for Lanthanum Oxide

Line	Plane	Relative Intensity	2θ	$\sin^2\theta$
1	$10\bar{1}0$	w	26.28	0.05168
2	0002	w	29.25	.06375
3	$10\bar{1}1$	vs	30.12	.06751
4	$10\bar{1}2$	s	39.63	.11490
5	$11\bar{2}0$	s	46.22	.15406
6	$10\bar{1}3$	s	52.28	.19410
7	$20\bar{2}0$	vvw	53.94	.20568
8	$11\bar{2}2$	s	55.55	.21716
9	$20\bar{2}1$	w	56.10	.22113
10	0004	vvw	60.52	.25394
11	$20\bar{2}2$	vw	62.41	.26843
12	$10\bar{1}4$	vvw	67.04	.30495
13	$20\bar{2}3$	w	72.22	.34732
14	$21\bar{3}0$	vvw	73.58	.35866
15	$21\bar{3}1$	s	75.46	.37447
16	$11\bar{2}4$	w	79.26	.40683
17	$21\bar{3}2$	vw	81.00	.42178
18	$10\bar{1}5$	w	83.89	.44678
19	$30\bar{3}0$	vw	85.47	.46060
20	$21\bar{3}3$	w	90.04	.50035
21	$30\bar{3}2$	vw	92.73	.52381

$$\sin^2\theta = 0.05130(h^2+hk+k^2) + 0.01577(l)^2$$

$$a = \frac{1.5418}{3\sqrt{0.05130}} = 3.930 \pm 0.001\,\text{A}.$$

$$c = \frac{1.5418}{4\sqrt{0.01577}} = 6.139 \pm 0.002\,\text{A}.$$

Lattice constants of pure lanthanum sesquioxide were calculated from these data as follows. For Cu $K\alpha$ = 1.5418 A.,

$$\sin^2\theta = 0.05130(h^2+hk+k^2) + 0.01577(l)^2$$

and

$$a = \frac{1.5418}{3\sqrt{0.05130}} \quad \text{and} \quad c = \frac{1.5418}{4\sqrt{0.01577}}$$

from which the lattice constants are a = 3.930 ± 0.001 A. and c = 6.139 ± 0.002 A. The mean square error was calculated according to the method of least squares. These values were used also to calculate the X-ray density as will be shown later.

Table II summarizes the literature data and that of this study for the lattice constants of lanthanum oxide.

TABLE II

Lattice Constants of Lanthanum Oxide

Hexagonal			
Lattice Constants		Worker	Reference
a	c		
3.93	6.12	Goldschmidt *et al.*	25
3.93	6.12	Zachariasen	68
3.945	6.151	Pauling	48
3.927	6.114	Zintl and Croatto	71
3.922	6.120	Croatto	15
3.930	6.139	This work	

Cubic		
Lattice Constants	Worker	Reference
a		
11.4	Lohberg	38
11.40	Bommer	7
11.38	Iandelli	34

The agreement among the values for the *a* axis is good except for the values reported by Pauling and by Croatto. Agreement of the values for the length of the *c* axis is not as good. For this work the value found for the *c* axis is somewhat higher than the reported values with the exception of the one given by Pauling.

Density measurements of lanthanum oxide were made at 25.00 0.02° C. One weight pycnometer has a thermometer and a small capillary side arm and the other has a ground glass stopper with a capillary hole. Both pycnometers were calibrated with redistilled water, the density of water being taken as 0.99705 g./ml. at 25.00° C. The xylene used was the middle one-third of freshly distilled C.P. isomeric xylene. At three different times newly distilled xylene was prepared. The three different samples used had densities of 0.85900, 0.85869, and 0.85828 g./ml., respectively.

For a typical density determination, a freshly ignited sample of lanthanum oxide weighing about three grams was weighed into a clean dry pycnometer, xylene was introduced over the solid, and then the unit was placed in a vacuum system to remove any occluded air bubbles. The xylene was allowed to boil for at least a half hour at room temperature, the unit was removed from the vacuum system, filled completely with xylene and then placed in a thermostated bath at 25.00 0.02° C. The time necessary for establishment of thermal equilibrium was determined by placing the pycnometer having the thermometer in the thermostated bath and finding how long it took for the temperature in the pycnometer and bath to become equal. This time (fifteen minutes) was quadrupled to guarantee thermal equilibrium. Accordingly, after one hour the pycnometer was removed from the bath, capped, cooled in a stream of cold water, wiped dry, and placed in the balance case for weighing. Each sample was weighed four times with the pycnometer being treated in the same manner described above between each weighing. Densities were calculated by the following formula,

$$d_s = \frac{w_s \cdot d_{solv.}}{d_{solv.} V_{pyc.} - w_{unit} - w_s}$$

d_s = density of the solid
$d_{solv.}$ = density of the solvent
w_s = weight of the solid sample
w_{unit} = weight of the solid plus solvent contained in the pycnometer
$V_{pyc.}$ = volume of the pycnometer

The pycnometric densities for three samples were found to be 6.58, 6.46, and 6.63 g./cc., the average being 6.56 g./cc.

The X-ray density for lanthanum oxide was calculated from the previously mentioned lattice constants according to the equation,

$$d_s = \frac{M.W._s}{N\ a^2 c \sin 60^\circ}$$

$$= \frac{325.84}{0.6026 \cdot 10^{-24} (3.930 \cdot 10^{-8})^2 6.139 \cdot 10^{-8} \cdot 0.86605}$$

where,

$M.W._s$ = moleculer weight of the solid (1942 atomic weights)
$N.$ = Avogadro's number
a and c = the lattice constants of the hexagonal structure

The density calculated according to the above method is 6.585 g./cc.

The density values given for hexagonal lanthanum oxide are tabulated in Table III.

TABLE III

Pycnometric Densities

Hexagonal Lanthanum Oxide

Density	Worker	Literature
6.48	Nilson and Petterson	46
6.41	Brauner	11
6.51	Prandtl	49
6.57	Zachariasen	68
6.55	Zintl and Croatto	71
6.52	Croatto	15
6.56	This work	

The pycnometric density determined for hexagonal lanthanum oxide in this study agrees very well with literature values except for those by Brauner and Nilson and Petterson. All densities agree within one per cent. The X-ray density, 6.585 g./cc. is slightly higher than the pycnometric density. This is expected since microscopic cracks and crystal imperfections will be formed that cause voids which are not filled with the immersing liquid.

SUMMARY

The lattice constants of hexagonal La_2O_3 have been redetermined. The length of the a axis found for the unit cell agrees well with the literature values but the c value of the axis found in this work is larger than all but one value found in the literature. The cubic lattice dimension was not redetermined but literature values are given.

The redetermination of the density of hexagonal La_2O_3 shows good correspondence with the literature values and the density calculated from X-ray data.

SECTION III

Praseodymium Oxides

Historical

The three common oxides of praseodymium are Pr_2O_3, PrO_2, and Pr_6O_{11}. The sesquioxide and dioxide must be prepared under special conditions. The sesquioxide is prepared by reduction from a higher oxide in a stream of hydrogen or by ignition in a vacuum. If the reduction is performed at higher temperatures, the hexagonal structure results; if at temperatures below 700° C., the cubic structure forms.

Foex(22), measuring the change in length of a small cylinder of the sesquioxide with change in temperature, found the oxide undergoes an irreversible transition from the cubic to the hexagonal structure at about 900° C. with a decrease in volume. Since the molecular volumes of the cubic and hexagonal structures of the sesquioxide, as calculated from the lattice constants reported by Eyring, Lohr, and Cunningham(18), are 52.07 and 46.69, respectively, a contraction of the oxide during the transition from the cubic to the hexagonal structure would be expected. The only way to convert the hexagonal back to the cubic form is to ignite the oxide to Pr_6O_{11} and again reduce to the sesquioxide below 700° C. The B structure(25) is obtainable only upon the ignition of praseodymium sulfate in a stream of hydrogen at 900° C.

Praseodymium sesquioxide readily dissolves in most acids to form bright green solutions and is converted completely to Pr_6O_{11} upon air ignition.

The most easily prepared and most common praseodymium oxide is Pr_6O_{11}. This oxide has a face-centered cubic "defect" fluorite structure and is obtained upon air ignition of the appropriate salts. The exact structure of the oxide is still unknown. As stated earlier in this writing, McCullough(42) and Hund and Peetz(33) believed the defects to be anion vacancies whereas Vickery(63) believed that the fluorite lattice was completely filled and the excess cations were accommodated interstitially. In general its chemical nature is similar to that of the dioxide.

The positive four oxidation state has been observed only on the oxides. However, Nakatsuka and Chang(46) reported that they prepared praseodymium(IV) and neodymium(IV) ions by air oxidation and anode oxidation of ammoniacal solutions of the rare earth ions in a solution of 8-quinolinol-5-sulfonic acid. Ramsey, Douglas, and Yost(54) repeated their experiments and felt that Nakatsuka and Chang only found new complexes of the two rare earth ions in the positive three state.

Marsh(39) suggested PrO as another possible oxide of praseodymium. However, it was obtained by hydrogen reduction of a solid solution of praseodymium oxides in thorium dioxide and no other evidence has been given for its existence.

Praseodymium dioxide, the other stoichiometric compound of praseodymium, has the face-centered cubic fluorite structure. Pagel and Brinton(47) prepared 99.2 per cent pure praseodymium dioxide by ignition of Pr_2O_3 in pure oxygen at about 25 atmospheres pressure and 355° C. for about five hours. McCullough(42,43) and Eyring, Lohr, and Cunningham(18) using the same principle but pressures of above fifty atmospheres produced PrO_2 for X-ray analysis. The dioxide is dark brown to black.

Several studies have been made of the praseodymium-oxygen system. Pagel and Brinton(47) studied the effects of temperature, ignition time, oxygen pressure, and rate of cooling on the amount of oxygenation of praseodymium oxide. They found that the amount of oxygenation of air-ignited praseodymium oxide varies with the conditions of ignition and cooling and that the amount of oxygenation depends on the oxygen pressure and temperature of ignition. Martin(40) made structural studies and dissociation pressures measurements on a series of nonstoichiometric oxides of praseodymium as well as conductivity measurements on Pr_6O_{11}. He reported that between $PrO_{1.50}$ and $PrO_{1.55}$ the system is hexagonal; between $PrO_{1.55}$ and $PrO_{1.75}$ the hexagonal and cubic structures coexist and above $PrO_{1.75}$ the system is cubic. He stated that below 780° C. the air-ignited oxide is an electron conductor whereas above that temperature it is a positive hole conductor.

Ferguson(19) and Ferguson, Guth, and Eyring(20) who investigated the isothermal dissociation pressures of the praseodymium-oxygen system at different temperatures and oxygen pressures, reported that there appears to be two compositions at which the oxide is particularly stable, namely: $PrO_{1.715}$ and $PrO_{1.80}$. Asprey(5) made X-ray studies of the structure of some nonstoichiometric oxides and found the following:

Oxide	Structure	Lattice Constant
$PrO_{1.66}$	body-centered cubic	5.532 A.
$PrO_{1.718}$	face-centered cubic	5.499 A.
$PrO_{1.833}$	face-centered cubic	5.467 A.
PrO_2	face-centered cubic	5.392 A.

The information from Ferguson and Asprey indicates that, under their respective experimental conditions, changes of some physical properties in the praseodymium-oxygen system are not linear with changes in the amount of oxygenation.

Foex(21) from his observations that the resistivity of Pr_6O_{11} is much lower than that of the sesquioxide believes that Pr_6O_{11} is a salt like compound or at least a phenomenon similar to that observed in Fe_3O_4 and Ti_3O_5.

Rabideau and Glockler(53) prepared oxides of praseodymium intermediate between Pr_6O_{11} and PrO_2 by oxidizing lower oxides at room temperature and atmospheric pressure with ozone.

Gruen, Koehler, and Katz(26) using atomic oxygen, prepared $PrO_{2.02}$ which has the fluorite structure with a lattice constant of 5.380 A.

Foex and Loriers(23) studied the thermal decomposition of the praseodymium-oxygen system with increasing temperature by gravimetric and dilatometric methods. Samples were prepared by ignition of nitrates to 650° C. and cooling in air at 0.5° C. per hour. The samples were slowly heated in air from 18° to 800° C. and variations of mass and size studied with temperature increase. Dilatometric data showed maxima in density at PrO_2 and Pr_6O_{11}. Gravimetric data showed plateaus corresponding to PrO_2 at 265° C. and Pr_6O_{11} at 350° C.

Praseodymium Oxides

Experimental

Praseodymium materials used in this investigation for determining the lattice constants of praseodymium oxides and the density of Pr_6O_{11} were obtained from Dr. L. L. Quill and labeled "spectroscopically" pure. The Pr_6O_{11} was prepared by igniting freshly precipitated oxalates in an electric muffle furnace at 900° C. for two or more days to insure complete calcination and to anneal the material so sharper X-ray lines could be obtained. Pr_2O_3 was prepared by reducing Pr_6O_{11} in a stream of hydrogen at 900° C. in a tube furnace. After reduction the sample was allowed to cool to about 75° C. in hydrogen before removing it from the system.

Since Pr_6O_{11} is a nonstoichiometric oxide, it was necessary to determine the amount of oxygenation of the air-ignited material. This amount of oxygen over that required for Pr_2O_3 is called "excess" oxygen. It was determined by the method recommended by Salutsky(58). Freshly ignited oxide samples weighing 0.0900 to 0.1250 grams were weighed into 250 ml. iodine flasks. To the sample in each flask are added first 10 ml. of 0.1 *M* potassium iodide solution and then 25 ml. of 6 *N* sulfuric acid. The flask is immediately stoppered and gently swirled to dissolve the oxide. The solution time varies depending on the nature of the oxide and the particle size. The liberated iodine is titrated with 0.03 $\underline{N}$ sodium thiosulfate using 3-4 ml. of 1 per cent starch solution as the indicator.

The calculation for the per cent "excess" oxygen is

$$\text{Per cent "Excess" Oxygen} = NV \cdot \frac{O}{2000} \cdot \frac{100}{S.W.}$$

N represents the normality of the sodium thiosulfate solution, V its volume, $\frac{O}{2000}$ the milliequivalent weight of oxygen, and S.W. the sample weight. The amount of "excess" oxygen in air-ignited praseodymium oxide was determined to be 3.14 weight per cent. The calculated amount is 3.13 weight per cent.

The methods of taking and measuring the X-ray films and of calculating the lattice constants of Pr_2O_3 were the same as for La_2O_3. The 2θ values, relative intensities, $\sin^2\theta$ values, and planes producing reflections are given in Table IV.

The lattice constants of hexagonal Pr_2O_3 were calculated from the equation $\sin^2\theta = 0.05335(h^2+hk+k^2) + 0.01647(l)^2$ and the relationships,

$$a = \frac{1.5418}{3\ \sqrt{0.05335}} \quad \text{and} \quad c = \frac{1.5418}{4\ \sqrt{0.01647}}.$$

The lattice constants calculated are a = 3.854 ± 0.001 and c = 6.007 ± 0.002 A. Literature values for the cubic and hexagonal structure determined in this study are given in Table V. There is good agreement between the literature

TABLE IV

X-ray Data for Hexagonal Praseodymium Sesquioxide

Line	Plane	Relative Intensity	2θ	$\sin^2\theta$
1	$10\bar{1}0$	w	26.84	0.05387
2	0002	w	29.79	.06608
3	$10\bar{1}1$	vs	30.70	.07007
4	$10\bar{1}2$	s	40.46	.11957
5	$11\bar{2}0$	s	47.22	.16041
6	$10\bar{1}3$	s	53.38	.20175
7	$20\bar{2}0$	vvvw	55.03	.21343
8	$11\bar{2}2$	s	56.78	.22607
9	$20\bar{2}1$	w	57.34	.23018
10	0004	vvvw	61.69	.26288
11	$20\bar{2}2$	vvw	63.80	.27925
12	$10\bar{1}4$	vvvw	68.50	.31675
13	$20\bar{2}3$	vw	73.91	.36142
14	$21\bar{3}0$	vvvw	75.31	.37320
15	$21\bar{3}1$	w	77.27	.38982
16	$11\bar{2}4$	vw	81.17	.42324
17	$21\bar{3}2$	vvw	83.02	.43924
18	$10\bar{1}5$	vw	85.88	.46408
19	$30\bar{3}0$	vvw	87.68	.47976
20	$21\bar{3}3$	w	92.49	.52172
21	$30\bar{3}2$	vw	95.19	.54523

$$\sin^2\theta = 0.05335(h^2+hk+k^2) + 0.01647(l)^2$$

$$a = \frac{1.5418}{3\sqrt{0.05335}} = 3.854 \pm 0.001 \text{ A.}$$

$$c = \frac{1.5418}{4\sqrt{0.01647}} = 6.007 \pm 0.002 \text{ A.}$$

TABLE V

Lattice Constants of Praseodymium Sesquioxides

Symmetry	Lattice Constants			Workers	Literature
	Hexagonal		Cubic		
	a	c	a		
Cubic			11.116	Bommer	7
Cubic			11.136	Iandelli	34
Cubic			11.14	McCullough	42
Cubic			11.136	Gruen, Koehler, and Katz	26
Cubic			11.14	Eyring, Lohr, and Cunningham	18
Hexagonal	3.85	6.00		Goldschmidt, *et al.*	25
Hexagonal	3.85	6.00		Zachariasen	68
Hexagonal	3.851	5.996		Pauling	48
Hexagonal	3.85	6.00		Barbezat and Loriers	6
Hexagonal	3.859	6.008		Eyring, Lohr, and Cunningham	18
Hexagonal	3.854	6.007		This work	

values of the lattice constants of the hexagonal structure and those of this study. The lattice constant for the cubic structure was not determined but the literature values are included so they may be used in a later discussion.

Materials for determining the lattice constant of Pr_6O_{11} were the same as used for X-ray determinations of the hexagonal sesquioxide. Freshly precipitated praseodymium oxalate was ignited for two days in an electric muffle furnace at 900° C. to insure complete calcination and to anneal the sample for obtaining sharper lines on the powder diagrams. The freshly ignited material was removed from the muffle furnace, allowed to cool for about a minute and placed in a desiccator to cool. As soon as possible a

Lindemann capillary tube was filled for X-ray analysis. Two films were prepared and measured in the same manner as described for La_2O_3. A lattice constant was calculated from the equation,

$$a^2 = \frac{{}^2\ (h^2+k^2+l^2)}{\sin^2\theta}$$

for each reflection line. The lattice constants were averaged arithmetically to obtain an average lattice constant for the film. The relative intensities, 2θ and $\sin^2\theta$ values, and planes producing reflections are given in Table VI. Values from the first two lines were not averaged because they varied too greatly from the rest of the values. The lattice constants determined were a = 5.460 ± 0.003 A. and a = 5.464 ± 0.004 A., the average being 5.462 ± 0.004 A.

TABLE VI

X-ray Data for Pr_6O_{11}

Line	Plane	Relative Intensity	Film 472		Film 525	
			2θ	$\sin^2\theta$	2θ	$\sin^2\theta$
1	111	s	28.40	0.06018	28.41	0.06022
2	200	w	32.86	.08000	32.91	.08024
3	220	s	47.07	.15945	47.12	.15977
4	311	s	55.86	.21939	55.87	.21946
5	222	vw	58.57	.23927	58.57	.23927
6	400	vw	68.66	.31805	68.83	.31943
7	331	w	75.94	.37853	75.93	.37844
8	420	w	78.20	.39775	78.28	.39844
9	422	w	87.39	.47723	87.38	.47715
10	333 511	w	94.16	.53627	94.34	.53784
$a = \frac{2.377(h^2+k^2+l^2)}{\sin^2\theta}$			5.464±0.004		5.460±0.003	

Literature values for the lattice constants of PrO_x oxides having a cubic structure and x greater than 1.50 are given in Table VII. The value determined in this work for the lattice constant of Pr_6O_{11} agrees very well with those reported in the literature. A lattice constant of PrO_2 was not determined in this investigation but literature values are given for purposes of later comparison.

TABLE VII

Lattice Constants of Higher Oxides of Praseodymium

Formula	Lattice Constant	Worker	Literature
$PrO_{1.66}$	5.532	Asprey	5
$PrO_{1.718}$	5.400	Asprey	5
Pr_6O_{11}	10.98	Goldschmidt *et al.*	25
Pr_6O_{11}	5.467	Asprey	5
Pr_6O_{11}	5.468	McCullough	42
Pr_6O_{11}	5.462	This work	
PrO_2	5.39	Scherrer and Palacios	60
PrO_2	5.392	Asprey	5
PrO_2	5.394	McCullough	42
PrO_2	5.40	Barbezat and Loriers	6
PrO_2	5.395	Eyring, Lohr, and Cunningham	18
$PrO_{2.02}$	5.380	Gruen, Koehler, and Katz	26

As the amount of oxygen in the cubic praseodymium oxide structure increases, the lattice contracts. The change of the lattice constant with change in amount of oxygen in the oxide is discontinuous.

The pycnometric density of Pr_6O_{11} was determined in the same manner as for La_2O_3 and was found to be 6.83 g./cc. The X-ray density is calculated to be 6.83 g./cc.,

$$d_s = \frac{2/3\ Pr_6O_{11}}{a^3\ N} = \frac{2/3\ 1021.62}{(5.462 \cdot 10^{-8})^3\ 0.6026 \cdot 10^{24}} = 6.83\ g./cc.$$

Densities reported by other workers are given in Table VIII. It is noted that the density found in this study is greater than previously reported values but agrees closely with the X-ray density value.

TABLE VIII

Reported Densities of Air-Ignited Praseodymium Oxide

Value	Worker	Literature
6.704	Brauner	11
6.71	Prandtl	49
6.61	Prandtl and Huttner	50
6.83	This work	

SUMMARY

The lattice constants of hexagonal Pr_2O_3 have been redetermined and found to be in good agreement with the literature values. The redeterminations of the lattice constant and density of Pr_6O_{11} show good correspondence of the lattice constant with the literature values but that the density value is higher.

The amount of excess oxygen calculated for Pr_6O_{11} is 3.13 per cent by weight. The amount of excess oxygen determined for two samples of air-ignited praseodymium was 3.14 per cent by weight.

SECTION IV

Mixed Oxides

Historical

Since the system being studied involves a dioxide having the fluorite structure and rare earth sesquioxides, this type of system will be reviewed.

A number of workers(8, 9, 14, 15, 31, 32, 39, 41, 42, 43, 44, 49, 50, 58, 71) have reported observations on systems of dioxides having the fluorite structure with lanthanon sesquioxides. Hund and Durrwachter(31) working with the lanthanum(III) - thorium(IV) oxide system and Zintl and Croatto(71) and Carlson(14) with the lanthanum(III) - cerium(IV) oxide system reported that the fluorite structure remained as the sesquioxide was added to the dioxide to form solid solutions. They further stated that anion vacancies were created to accommodate the deficiency of oxide ions rather than the fluorite structure remaining completely filled and the excess cations being situated interstitially. X-ray investigations by these workers also showed that the change in lattice constant of the fluorite structure is linear with change in concentration of La_2O_3 and that the fluorite structure became saturated at about fifty mole per cent sesquioxide. This concentration of sesquioxide in the fluorite structure corresponds very closely to that found by Martin(40).

McCullough(42,43) stated that for binary systems of lanthanum, praseodymium, or neodymium sesquioxides with cerium, praseodymium, or thorium dioxides the fluorite structure becomes saturated at some concentration depending on the oxide pair and undergoes no further change except to decrease in amount as the concentration of sesquioxide is further increased. Brauer and Gradinger(8) found that the yttrium(III) - cerium(IV) oxide system tends to undergo a continuous transition from the face-centered cubic fluorite structure of the dioxide to the body-centered cubic C structure of the yttrium oxide. McCullough and Britton(44) studying the same system as well as the yttrium(III) - praseodymium(IV) oxide system came to the same conclusion.

Investigations by Salutsky(58) and Prandtl and Huttner(50) of the air-ignited lanthanum oxide-praseodymium oxide system showed that as the amount of lanthanum oxide increased, the "excess" oxygen first increases over that predicted for all the praseodymium existing as Pr_6O_{11} to a peak and then rapidly decreases as the amount of La_2O_3 increases further.

Marsh(39) states that at least two factors influence the amount of oxygenation of praseodymium in mixtures of one mole of Pr_2O_3 to two moles of some other rare earth showing only the positive three oxidation state; namely, the relative stabilities of the hexagonal and cubic structures and the ionic radius of the metal ion of the sesquioxide used for dilution. As the ionic radius of the lanthanon ion in the diluting sesquioxide decreases and as the hexagonal structure becomes more stable, the amount of oxygenation of the praseodymium in the mixture decreases. Accordingly, as the atomic number of the lanthanon ion of the diluting sesquioxide increases, the amount of oxygenation of praseodymium in mixtures will reach a peak at some intermediate lanthanon and decrease with further increase in atomic number.

Brauer and Haag(9) and Carlson(14) determining the rate of solubility of the La_2O_3 - CeO_2 system in mineral acids found that at high concentrations of CeO_2 the rate of solubility was very slow but began to increase when the concentration had decreased to about 70-80 mole per cent.

Although binary oxide systems of La_2O_3, Nd_2O_3, Sm_2O_3, Yb_2O_3, or Sc_2O_3 with U_3O_8 do not involve a pure dioxide having the fluorite structure, it is felt that information concerning these systems reported by Hund and Peetz(32) is pertinent. They report solid solutions form which have the fluorite structure in the composition range of about 25-70 mole per cent of the sesquioxide. The fluorite structure forms with anion vacancies until all the fluorite structure is completely filled and any excess oxygen is distributed statistically among the octahedral vacancies.

When two compounds are mixed, the question of whether there is solid solution formation or compound formation arises. Prandtl(49) reported that Pr_6O_{11} and PrO_2 are types of praseodymates. Though the praseodymium - oxygen system has been studied by several methods, the question of solid solution formation versus compound formation is still unresolved.

Mixed Oxides

Experimental

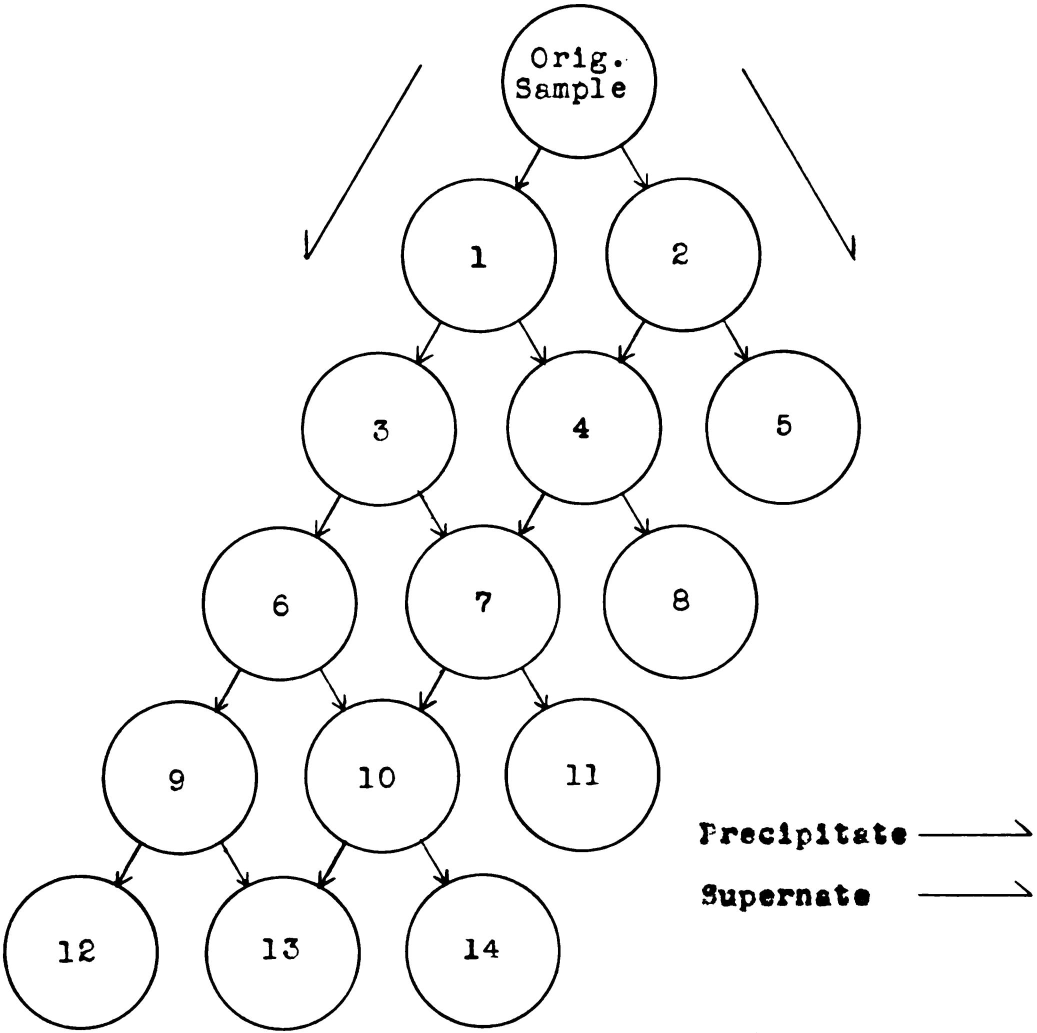
Praseodymium-poor samples for this study were obtained by separation using homogeneous precipitation of the carbonate of material from the lanthanum-rich end of a double magnesium-rare earth nitrate recrystallization series.

For this procedure a method developed by Salutsky(58) was used. Freshly ignited oxide is dissolved in a minimum amount of 25 per cent trichloroacetic acid, the solution diluted to give a concentration of about ten to twelve grams of rare earth oxide per liter of solution. The solution is heated to 90° C. to decompose the trichloroacetate ion to chloroform and carbonic acid. The rare earth ions were precipitated as carbonates. In order to calculate the time required to precipitate 80 per cent of the rare earth ions from solution, rate constants for the decomposition of the trichloroacetate ion were obtained from the work by Verhoek(62). For 90° C. the time required was 86 minutes.

The pyramidal method of fractional precipitation given in Illustration I was used. To designate fraction steps the precipitate from the first precipitation was numbered one and the supernatant liquid was numbered two. Decomposition of the trichloroacetate ion in fraction two

ILLUSTRATION I

Pyramidal Fractional Precipitation Method



was allowed to continue to give precipitate fraction four and supernatant liquid fraction five. Fraction five was not separated further. Fraction one was redissolved in a minimum of trichloroacetic acid and decomposed as previously described to give precipitate fraction three and supernatant liquid fraction four. Supernatant liquid fraction four and precipitate fraction four were mixed to give fraction four. Two individual materials were fractionated in the manner described above to give fractions having the composition listed in Table IX.

TABLE IX

Composition of Fractions Retained in Fractionation by Homogeneous Precipitation of the Carbonates

Series L		Series M	
Sample Designation	Composition Weight per cent Pr_2O_3	Sample Designation	Composition Weight per cent Pr_2O_3
Original Material	9.0	M-5	1.3
L-5	3.5	M-8	1.4
L-8	5.0	M-11	0.6
L-11	7.1	M-14	3.1
L-10	13.6	M-13	4.0
L-9	19.6	M-12	14.4

From these data it is observed that (a) praseodymium concentrates in the precipitate fraction and (b) the rate of concentration is fairly rapid in praseodymium-poor samples.

One fractionation using dimethyl oxalate as suggested by Salutsky(58) was performed. The praseodymium concentrations in the precipitate and in the supernatant liquid were 13.0 and 5.0 weight per cent of Pr_2O_3, respectively.

Samples of various compositions were made by mixing some of the praseodymium-poor materials, prepared as described previously, with material labeled 98 per cent pure praseodymium oxide obtained from the Lindsay Chemical Company. The spectrum analysis report of this praseodymium-rich material showed less than 0.5 per cent of neodymium oxide and only a trace of gadolinium oxide present in the sample. As a further check the absorption at 794.5 mμ of a chloride solution of a concentration of about 20 g./100 ml. of oxide mixture was checked with a Beckman DU spectrophotolometer calibrated with a standard solution of pure neodymium chloride having a concentration of 0.630 g./100 ml. of Nd_2O_3 which showed approximately the same amount of absorption as the sample. The amount of Nd_2O_3 in the sample, uncorrected for absorption by praseodymium, corresponded very well with that obtained from emission spectra measurements.

For the various studies fresh oxide samples were prepared by precipitating the rare earth ions from slightly acid nitrate solutions as the oxalates and igniting at 900° C. in an electric muffle furnace. For X-ray studies, samples were ignited for a minimum of two days in order to insure complete calcination and to anneal the crystalline material so sharp X-ray lines would result. For other than X-ray determinations samples were ignited for a minimum of twelve hours.

Material labeled "spectroscopically pure" praseodymium oxide obtained from Dr. L. L. Quill was used to calibrate a Beckman DU spectrophotolometer for the determination of the amount of praseodymium present in the oxide mixtures used. The oxide was ignited in a stream of hydrogen at 900° C. for several hours to insure complete reduction to the sesquioxide. The commercial hydrogen was dried by passing it through anhydrous magnesium perchlorate. The reduced oxide was cooled in hydrogen to prevent reoxidation. After cooling, the oxide was removed from the furnace. Samples for the preparation of different standard solutions were quickly weighed to minimize absorption of water and carbon dioxide. These samples were dissolved with hydrochloric acid, evaporated to dryness, and redissolved in water and a minimum amount of 3 <u>M</u> HCl. The samples were then transferred quantitatively to 25 ml. volumetric flasks and diluted to the mark.

For the measurement of variation of the absorption of the praseodymium(III) ion with concentration a Beckman DU spectrophotolometer was set to transmit the spectral band at 444.5 mμ where an intense absorption band characteristic of praseodymium occurs. A slit width of 0.025 mm. was used. The optical densities of these samples of different concentrations were determined. These measurements also indicate that absorption of the praseodymium(III) ion in a chloride medium for the concentrations used follows Beer's law. Calibration data are given in Table X.

TABLE X

Calibration of the Beckman Spectrophotolometer for Determination of Praseodymium(III) in a Chloride Medium

g. Pr_2O_3/25 ml.	0.0918	0.1343	0.1507	0.2026
log transmission	0.224	0.330	0.366	0.488
g. Pr_2O_3/25 ml.	0.2270	0.2859	0.2957	0.3122
log transmission	0.642	0.694	0.702	0.741
slit width = 0.025 mm.			= 444.5 mμ.	

For a series of mixtures X-ray diagrams were made and densities were determined as described for pure La_2O_3, Pr_2O_3, and Pr_6O_{11}. These data are compiled in Table XI, as well as the data for total weight per cent of praseodymium expressed as Pr_2O_3, and weight per cent "excess" oxygen.

Since the weight per cent and mole per cent composition are directly related and since some properties of oxide mixtures can be compared more easily on the basis of mole per cent, the weight per cent composition was converted to mole per cent. The mole per cent composition of the oxide mixtures was calculated on the basis that the mixture was composed of La_2O_3, Pr_2O_3, and PrO_2. The weight per cent of total praseodymium in the sample was determined spectrophotometrically as described before and expressed as Pr_2O_3. The weight per cent "excess" oxygen in the air-ignited sample was determined also. The weight per cent

TABLE XI

Data for Air-Ignited Mixed Oxides

Sample	Weight Per cent Pr_2O_3	Mole Per cent La_2O_3	Per cent "Excess" Oxygen	Density	Lattice Constants		
					Hexagonal		Cubic
					a	c	a
1	0.0	100.0		6.56	3.930	6.139	
2	2.4	97.6			3.924	6.134	
3	5.0	95.0			3.924	6.125	
4	7.1	93.0		6.59	3.922	6.116	
5	9.6	90.5			3.923	6.115	
6	13.0	87.1			3.923	6.111	
7	13.6	86.5		6.62	3.924	6.111	
8	15.7	84.5			3.920	6.104	
9	19.5	80.7		6.63	3.910	6.096	
10	24.7	75.4			3.912	6.094	
11	31.8	68.5		6.62	3.917	6.089	5.603
12	38.9	54.9	0.58	6.53	3.901	6.082	5.590
13	42.1	48.2	1.00		3.900	6.076	5.583
14	47.9	39.1	1.62	6.34			5.562
15	48.6	37.7	1.75				5.558
16	59.8	26.0	2.49				5.526
17	60.2	25.6		6.53			
18	72.2	16.5	2.83				5.506
19	77.6	13.0	2.84	6.77			5.498
20	84.0	8.6	2.92	6.80			5.488
21	90.6	4.1	3.00	6.82			
22	96.9	0.0	3.14	6.83			5.462
10 reduced in hydrogen	24.7	75.4			3.911	6.105	
15 reduced in hydrogen	49.5	50.8			3.892	6.075	
Pr_2O_3	100.0	0.0			3.854	6.007	

"excess" oxygen was converted to weight per cent PrO_2 by the following equation,

$$\text{Wt. per cent } PrO_2 = (\text{Wt. per cent "excess" oxygen}) \frac{PrO_2}{O/2}$$

$$= (\text{Wt. per cent "excess oxygen}) \frac{355.84}{8}.$$

The weight per cent Pr_2O_3 in the sample was calculated from the equation,

$$\text{Wt. per cent } Pr_2O_3 = \text{Wt. per cent "excess" oxygen} + \text{Wt. per cent total Pr as } Pr_2O_3 - \text{Wt. per cent } PrO_2.$$

The weight per cent La_2O_3 was calculated from the equation,

$$\text{Wt.per cent } La_2O_3 = 100\text{-Wt.per cent } Pr_2O_3\text{-Wt.per cent } PrO_2.$$

The lattice constants of the cubic and hexagonal structures observed in the various mixed oxides versus the mole per cent of La_2O_3 are plotted in Figures I and II, respectively. Several interesting observations can be made. Curve B represents the changes in the lattice constants of pure face-centered cubic Pr_6O_{11} and the body-centered cubic lanthanum oxide in a mixture, if the changes were additive. Curve A represents the change in the lattice constant of the *a* axis of the hexagonal structure of Pr_2O_3 and La_2O_3 in a mixture, if the changes were additive. Curve C is the change in the *c* axis of the hexagonal structure for Pr_2O_3 and La_2O_3 in a mixture, if the changes were additive. With an increasing amount of La_2O_3 the lattice constant of the cubic structure increases. Also, only the cubic structure is present until the La_2O_3 concentration reaches about 48

FIG I

VARIATION OF THE CUBIC STRUCTURE WITH COMPOSITION

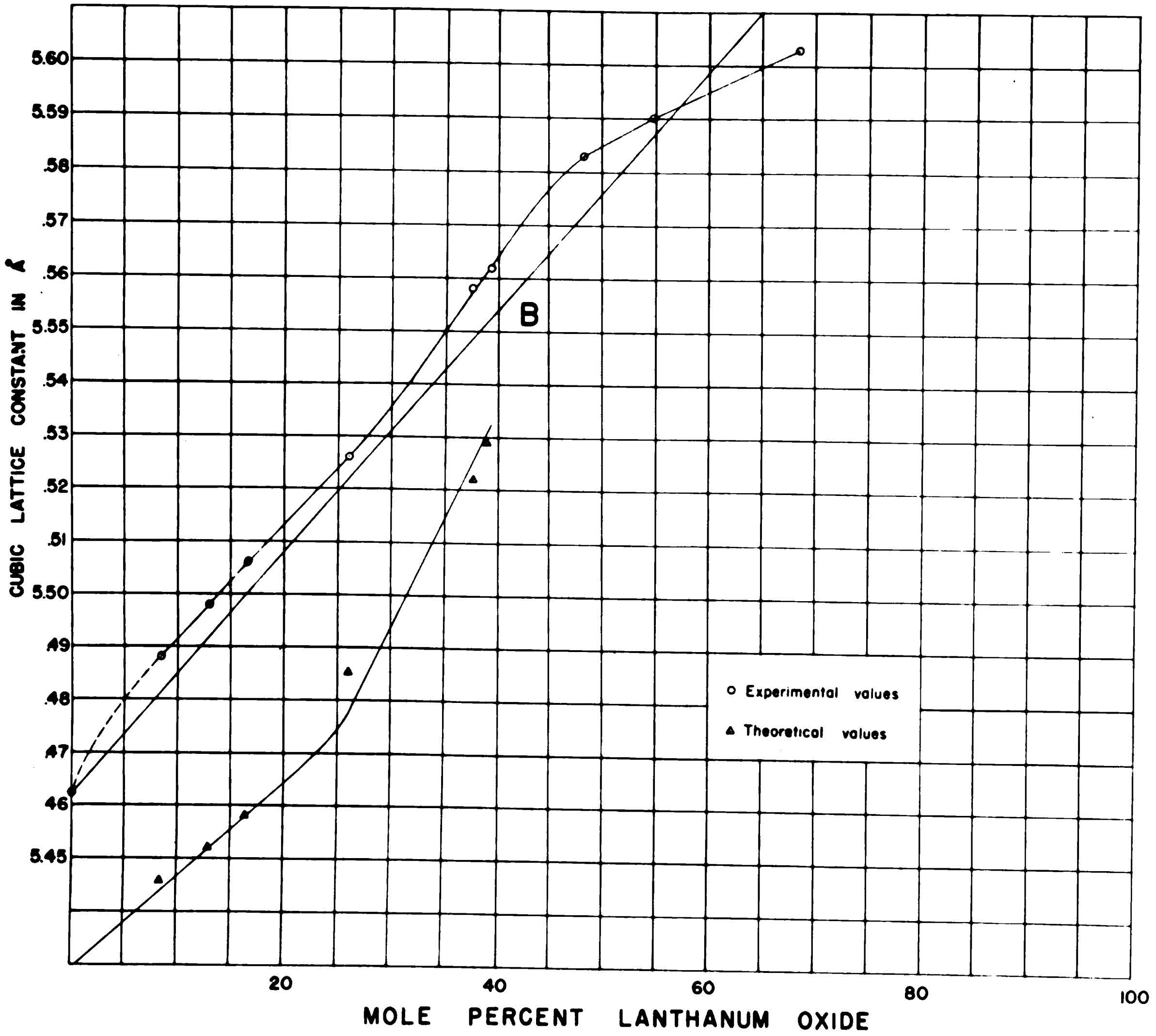
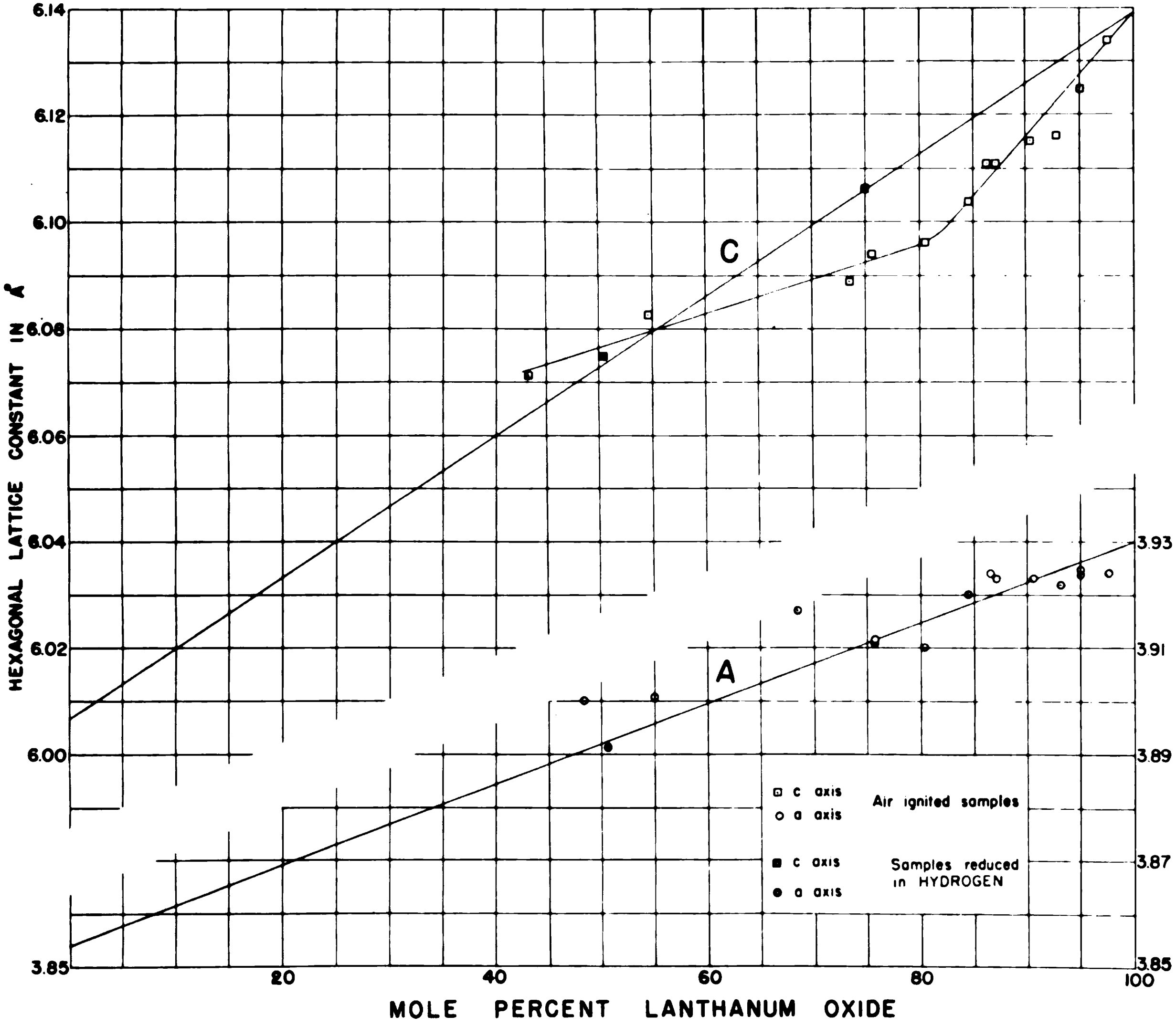


FIG II

VARIATION OF THE HEXAGONAL STRUCTURE WITH COMPOSITION



mole per cent. From about 48 to about 72 mole per cent La_2O_3 the cubic and hexagonal forms coexist. It is observed, too, that the lattice constant for the cubic system does not increase linearly. For example, for the initial increases in the lattice constants, the curve has a less steep slope than does the additivity Curve B for the solid solutions of cubic Pr_6O_{11} and cubic La_2O_3. From about 28 to 44 mole per cent La_2O_3 the rate of increase of the lattice constant becomes slightly greater. Above 44 mole per cent La_2O_3 the rate of increase of the lattice constant of the cubic structure decreases to less than that of Curve B. The curve of the observed cubic lattice constant crosses Curve B at about 57 mole per cent La_2O_3 and the lattice constant of mixed lanthanum and praseodymium oxide is less than that predicted from Curve B. The lattice constants of the cubic structures for compositions of less than about 56 mole per cent La_2O_3 are slightly greater than those predicted from Curve B.

In contrast to the change of the cubic lattice constant found in this study of the air-ignited lanthanum-praseodymium oxide system, Carlson(14) and Zintl and Croatto(71) investigating the La_2O_3-CeO_2 system found that the cubic lattice constants of the single phase system changed linearly with changes of composition. To learn if the observed and calculated values agree for the lattice constants of air-ignited oxide mixtures having compositions corresponding to pure Pr_6O_{11} and to samples 16, 17, 18, 19, 20, and 21, lattice constants were calculated according to the additivity rule from the lattice constants of PrO_2 and cubic Pr_2O_3 reported by Eyring, Lohr, and Cunningham(18) and the lattice constant reported by Iandelli(34) for cubic La_2O_3 by the following equation,

$$LC_m = \text{mole per cent } La_2O_3 \times LC_{La} + \text{mole per cent } Pr_2O_3 \times LC_{Pr} + \text{mole per cent } PrO_2 \times LC_{PrO_2}$$

Where LC_m = the predicted lattice constant of the mixture,

LC_{La} = the lattice constant of cubic La_2O_3

LC_{Pr} = the lattice constant of cubic Pr_2O_3

and LC_{PrO_2} = the lattice constant of PrO_2.

The calculated lattice constants are given in Table XII and are plotted in Figure I. Trends for the changes of lattice constants with changes of composition are the same for both the experimental and the theoretical lattice constants. The theoretical values are much lower than the experimental values but this might be caused by the presence of the larger lanthanum(III) and praseodymium(III) ions.

When the hexagonal and cubic structures begin to coexist at from 40 to 48 mole per cent lanthanum oxide, it is also noted that the lattice constant of the cubic structure does not change as rapidly. This is indicated by a definite change in slope of the curve above 48 mole per cent

TABLE XII

Calculated and Observed Lattice Constants of Single Phase Cubic Solid Solutions of Air-Ignited Lanthanum and Praseodymium Oxides

Sample	Mole per cent La_2O_3	Lattice Constants	
		Calculated	Observed
22	0.0	5.429	5.464
20	8.6	5.446	5.488
19	13.0	5.452	5.498
18	16.5	5.458	5.506
16	26.0	5.485	5.526
15	37.7	5.522	5.558
14	39.1	5.529	5.562

lanthanum oxide. Above approximately 72 mole per cent La_2O_3 the cubic structure disappears.

Also, as the La_2O_3 concentration increases in the composition range when the two structures coexist, the rate of change of the c axis is slow. From the curve one observes that the rate of change of the c axis compared to that of the a axis is more rapid with increase of La_2O_3. The irregularity of the rates of change of the a and c axes of the hexagonal structure is probably caused by a distortion of the lattice due to the presence of the smaller praseodymium(IV) ions in solid solution within the hexagonal structure.

Above approximately 57 mole per cent lanthanum oxide the c axis of the hexagonal structure is shorter than predicted from Curve C. Below this concentration the c axis is longer than predicted.

Since it is of interest to determine what occurs when a homogeneous mixture of La_2O_3 and Pr_2O_3 is prepared, two freshly air-ignited oxide mixtures of lanthanum and praseodymium oxides were reduced in hydrogen to give samples having 50.8 and 75.4 mole per cent La_2O_3, respectively. The X-ray powder diagram of the sample containing 50.8 mole per cent La_2O_3 had lines which corresponded to the lanthanon oxide A-type structure. The lattice constants predicted according to the additivity rule using the lattice constants of lanthanum and praseodymium sesquioxide as determined in this study were a = 3.893 A. and c = 6.074 A. The observed lattice constants were a = 3.892 A. and c = 6.075 A.

The X-ray powder diagram of the other sample (75.4 mole per cent La_2O_3) had lines corresponding to the lanthanon oxide A-type structure and several other unidentified lines. Part of the second sample was gray-white instead of pale green. Upon treatment of the sample with dilute HCl a gas was evolved that smelled like rotten eggs and turned lead acetate-saturated paper black which indicates that the gas was H_2S. A rubber stopper was used in part of the system and got very hot. Rubber stoppers have a large amount of sulfur in them which can distill from the stopper to the oxide sample. Black particles were observed after dissolution of the gray material. Two sets of diffraction lines were observed in the X-ray powder diagram of this sample. One set could not be explained except that they were not caused by hexagonal crystal lattice. The other set corresponded to the lanthanon oxide A-type structure. Its composition was 75.4 mole per cent La_2O_3. The predicted lattice constants are $a = 3.911$ A., and $c = 6.106$ A. The observed lattice constants are $a = 3.911$ A. and $c = 6.105$A. The relative intensities, 2θ values, planes producing reflections, $\sin^2\theta$ values, and the factors F_1 and F_2 for each film are given in Table XIII.

To better understand the trends in the lattice constant changes, the curves of Figures I, II, and III can be compared. In Figure III the number of atomic weights of "excess" oxygen per mole of Pr_2O_3, with all the praseodymium expressed as the sesquioxide regardless of the degree of oxygenation, is plotted against the mole per cent La_2O_3. The line drawn parallel to the abcissa at 0.667 corresponds to the value that should be observed if all the praseodymium in the mixtures exists as Pr_6O_{11}. As the La_2O_3 concentration is increased in the air-ignited mixture, starting at pure praseodymium oxide, the ratio goes above that corresponding to the assumption that all the praseodymium in the mixtures exists as Pr_6O_{11}. This means that the presence of a small amount of La_2O_3 in the mixture favors an increase in the oxygenation of the praseodymium. As the amount of La_2O_3 is further increased the degree of

TABLE XIII

X-ray Data for Solid Solutions of Lanthanum and Praseodymium Sesquioxides Obtained by Reduction of Air-Ignited Mixed Oxides with Hydrogen

Line	Plane	Relative Intensity	Sample 10 2θ	Sample 10 $\sin^2\theta$	Sample 15 2θ	Sample 15 $\sin^2\theta$
1	$10\bar{1}0$	w	26.33	0.05188	26.46	0.05237
2	0002	w	29.34	.06414	29.47	.06568
3	$10\bar{1}1$	vs	30.14	.06759	30.27	.06816
4	$10\bar{1}2$	s	39.77	.11568	40.03	.11715
5	$11\bar{2}0$	s	46.39	.15513	46.74	.15734
6	$10\bar{1}3$	s	52.56	.19604	52.80	.19770
7	$20\bar{2}0$	vvw	54.17	.20731	54.46	.20937
8	$11\bar{2}2$	s	55.82	.21910	56.16	.22157
9	$20\bar{2}1$	w	56.32	.22273	56.71	.22556
10	0004	vvw			61.12	.25851
11	$20\bar{2}2$	vw	62.69	.27060	63.07	.27355
12	$10\bar{1}4$	vvw	67.26	.30673	67.68	.31011
13	$20\bar{2}3$	w	72.67	.35106	73.04	.35415
14	$21\bar{3}1$	s	75.88	.37718	76.29	.38150
15	$11\bar{2}4$	w	79.75	.41103	80.25	.41533
16	$21\bar{3}2$	vw	81.40	.42523	82.00	.43041
17	$10\bar{1}5$	w	84.46	.45173	84.90	.45555
18	$30\bar{3}0$	vw	85.92	.46442	86.41	.46869
19	$21\bar{3}3$	w	90.73	.50637	91.22	.51065
20	$30\bar{3}2$	vw	93.34	.52913	93.97	.53462

Sample 10 $\sin^2\theta = 0.05176(h^2+hk+k^2) + 0.01594(1)^2$

$$a = \frac{1.5418}{3\sqrt{0.05176}} = 3.912\text{ A.}$$

$$c = \frac{1.5418}{4\sqrt{0.01594}} = 6.106\text{ A.}$$

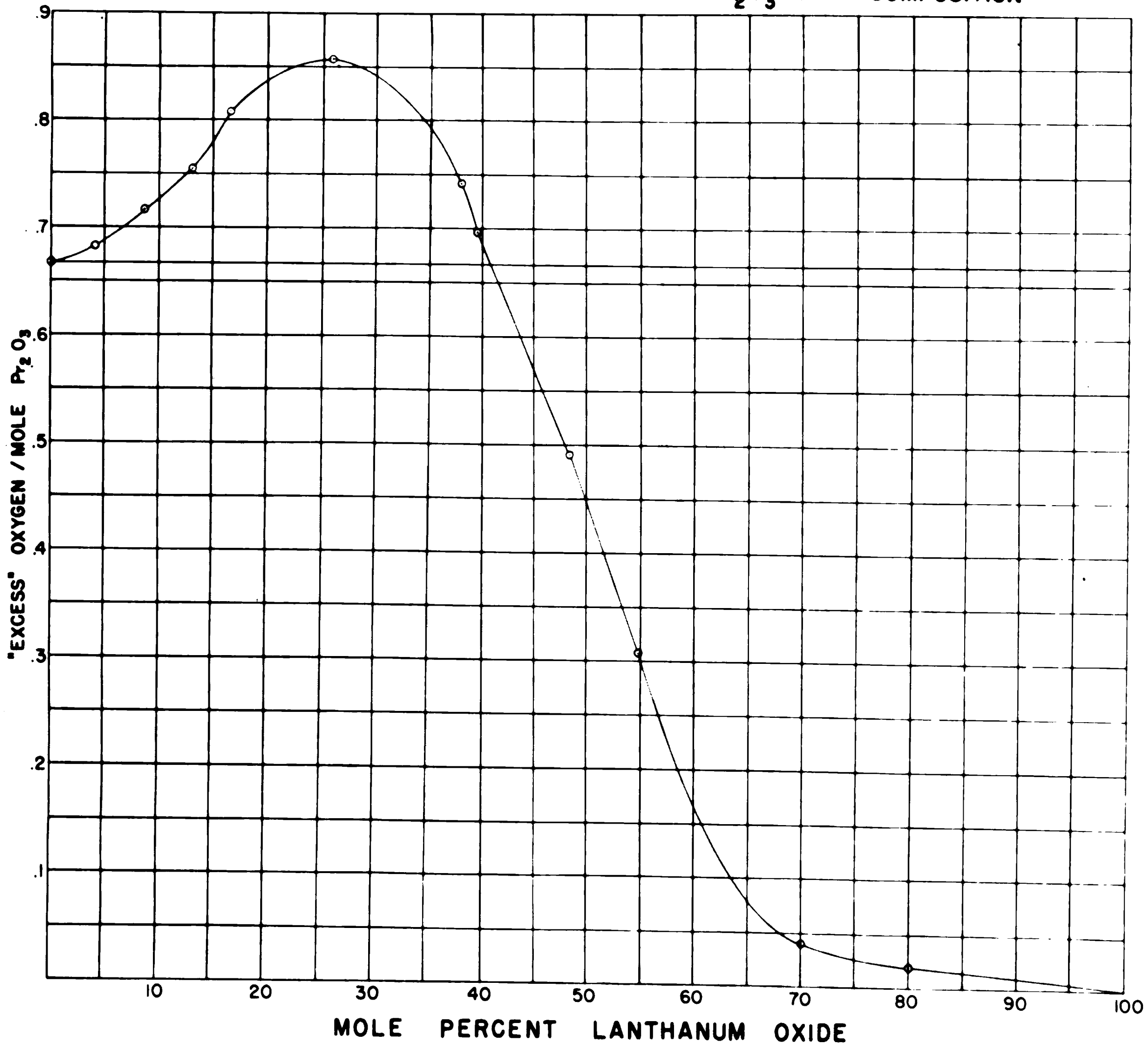
Sample 15 $\sin^2\theta = 0.05230(h^2+hk+k^2) + 0.01610(1)^2$

$$a = \frac{1.5418}{3\sqrt{0.05230}} = 3.892\text{ A.}$$

$$c = \frac{1.5418}{4\sqrt{0.01610}} = 6.075\text{ A.}$$

FIG III

VARIATION OF "EXCESS" OXYGEN / MOLE Pr_2O_3 WITH COMPOSITION



oxygenation reaches a peak of about 0.86 at approximately 28 mole per cent La_2O_3 and then drops sharply to about 0.04 at 70 mole per cent La_2O_3 then proceeds at a very slow rate of change to zero at 100 mole per cent La_2O_3. The resultant curve compares well with the one prepared by Salutsky(58).

It has been demonstrated by Hund and Durrwachter (31), Zintl and Croatto(71), and Carlson(14) that as a rare earth sesquioxide is added to a dioxide having the fluorite structure, a solid solution results by creating an anion-deficient structure and that as the amount of the sesquioxide is increased, the lattice constant of the cubic structure is increased. In air-ignited mixtures of lanthanum and praseodymium oxides the same phenomenon occurs except that the sesquioxide is derived from two sources, partly from the Pr_2O_3 present due to the fact that all the praseodymium present is not oxidized to the positive four state and partly from the La_2O_3. As the praseodymium oxide is diluted by the addition of La_2O_3 the lattice of the cubic structure is expanded and more anion deficiencies result; both of these effects favor increased oxygenation of praseodymium. As more praseodymium is oxygenated, more praseodymium(IV) ions having a smaller ionic radius are produced. The increase of the number of the smaller praseodymium(IV) ions in the mixture relative to the amount in Pr_6O_{11} will cause the lattice constant for the cubic structure to increase less rapidly than would be expected if all the praseodymium in the mixture existed as Pr_6O_{11}. This change is observed in the first part of the plot of the lattice constant of the cubic structure against the mole per cent La_2O_3 as shown in Figure I.

Prandtl and Huttner(50) investigating the air-ignited system cerium and praseodymium oxide and McCullough and Britton(44) investigating the air-ignited system yttrium and praseodymium oxide reported that when the concentration of the praseodymium was low, it was more difficult to oxygenate it. Most systems containing cerium oxide upon air ignition yield cerium dioxide which has the fluorite structure. Yttrium oxide has the rare earth oxide C structure which is closely related to the fluorite structure. It follows from the above information that high dilution favors a decreased oxygenation of the praseodymium though the fluorite structure remains in all mixtures. This can be the reason for the decrease in the amount of oxygenation after about 28 mole per cent La_2O_3 observed in this work.

Above about 28 mole per cent La_2O_3 the rate of change of the lattice constant of the cubic structure increases more rapidly than expected if all the praseodymium exists as Pr_6O_{11}. Owing to the decreased amount of oxygenation of the praseodymium the quantity of praseodymium(III) ions, relative to the amount in Pr_6O_{11}, increase and cause the increased rate of change of the lattice constant of the cubic structure. As the composition changes and the cubic structure only is present, the change of the calculated and observed lattice constants parallels the change of the amount of "excess" oxygen in the mixtures.

As the concentration of the La_2O_3 increases and the amount of the oxygenation of the praseodymium decreases, the concentration of lanthanum(III) and praseodymium(III) ions attains such a concentration that the formation of the hexagonal structure is favored. The presence of praseodymium(IV) ions in the hexagonal oxide lattice is not favored because they are too small. In this concentration range the cubic and hexagonal structures coexist. As the concentration of the La_2O_3 in the system increases, the La_2O_3 enters both structures. Since there are two structures involved as the La_2O_3 concentration increases, the rate change of the concentration of the La_2O_3 in either structure will be lower than if only one structure were present. Because of this fact the lattice constants of the two structures change more slowly as the La_2O_3 concentration increases than if only one structure were present. As the cubic structure disappears, the amount of oxygenation of the praseodymium becomes very low and its rate of change with change of La_2O_3 concentration is very slow indicating that the hexagonal structure does not accommodate readily the presence of praseodymium(IV) ions.

Since there is a relationship between the structure of a mixture and its density, it is necessary to know what changes of density occur when the composition is varied. Inspection of Figure IV reveals that in praseodymium-rich oxides the density of the mixture decreases as the La_2O_3 concentration increases and that a minimum is reached at around 45 mole per cent La_2O_3, then increases to a maximum at about 20 mole per cent La_2O_3 and finally decreases again toward the density corresponding to pure La_2O_3.

For purposes of comparison of the variation of density and structure as the composition of the mixtures are varied, the densities of the various structures of the pure oxides are given in Table XIV.

TABLE XIV

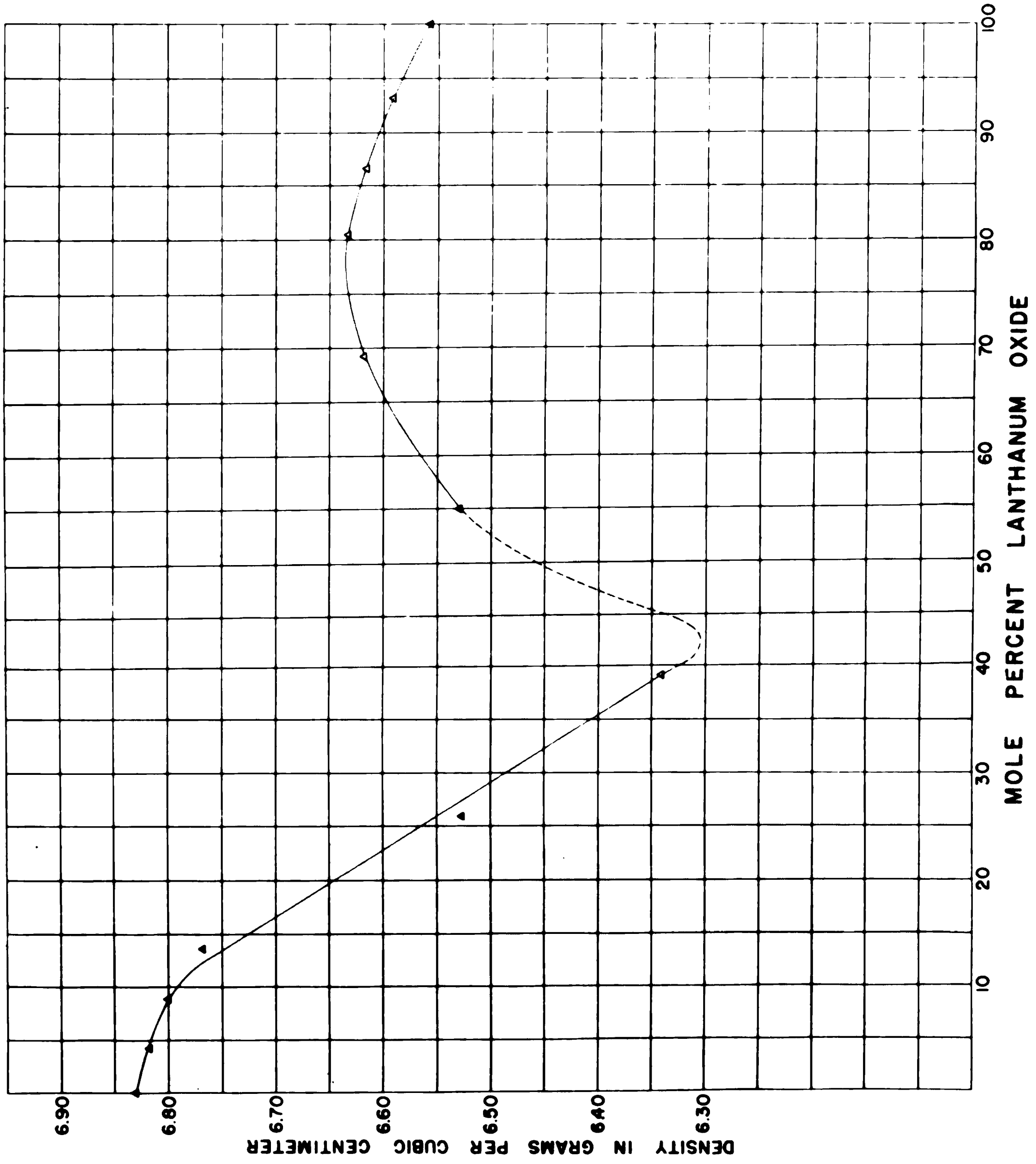
Densities of the Pure Oxides

Oxide	Structure	X-ray density	Observed density
La_2O_3	Cubic	5.93 g./cm.^{3}	
La_2O_3	Hexagonal	6.585	6.56 g./cm.^{3}
Pr_2O_3	Cubic	6.34	
Pr_2O_3	Hexagonal	7.03	
Pr_6O_{11}	Cubic	6.83	6.83

The X-ray density of cubic La_2O_3 was calculated from the lattice constant reported by Iandelli(34). The

FIG IV

VARIATION OF DENSITY WITH COMPOSITION



X-ray density of cubic Pr_2O_3 was calculated from the lattice constant of the cubic structure reported by Eyring, Lohr, and Cunningham(18). The rest of the X-ray densities were calculated from lattice constants determined in this investigation. The observed densities were determined in this work. By comparing the densities of the cubic and hexagonal forms, it can be seen that the hexagonal form is more dense. Also the hexagonal and cubic forms of Pr_2O_3 are more dense than corresponding forms of La_2O_3. Pr_6O_{11} is more dense than the cubic forms of the sesquioxides. X-ray diagrams show that only two structures occur throughout the entire composition range, both of which correspond to the structures of the pure components but with the lines displaced. When only the cubic structure is present the decrease in density of the oxide mixtures with the increasing amount of La_2O_3 can be accounted for by the expansion of the lattice structure in the mixture. When the hexagonal structure begins to appear, the density increases with the increasing amount of La_2O_3 because the proportion of the denser hexagonal structure increases. When the cubic structure disappears, the density reaches a maximum and then decreases as the La_2O_3 is less dense than hexagonal Pr_2O_3.

From the foregoing discussion it follows that the variations of the densities and structures of the oxide mixtures with variation of composition parallel one another.

Neither quantitative studies of the relative solubilities of the oxide mixtures in water nor their rates of solubility in dilute mineral acids were investigated. Qualitatively, however, the rates of solubility were observed during "excess" oxygen determinations. It was noted that above 68.5 mole per cent La_2O_3 the samples dissolved quite rapidly whereas below that concentration the rate of solubility decreased rapidly as the concentration of La_2O_3 decreased.

SUMMARY

The change of densities, structures present and their lattice dimensions, and the amount of "excess" oxygen versus composition of air-ignited lanthanum and praseodymium oxide mixtures have been investigated.

For pure praseodymium oxide and for this oxide with increasing amounts of La_2O_3 the face-centered cubic structure characteristic of Pr_6O_{11} is the only structure present to about 48 mole per cent La_2O_3. Then, the A or hexagonal structure characteristic of pure La_2O_3 coexists with the face-centered cubic structure from around 48 to approximately 72 mole per cent La_2O_3. Above about 72 mole per cent La_2O_3 the hexagonal form is the only structure present. There are breaks in the curve of the change of the cubic lattice constant with changing composition at around 27 and 47 mole per cent La_2O_3. There is a break in the curve of the change of the length of the $\underline{c}$ axis of the hexagonal form versus changing composition at about 80 mole per cent La_2O_3.

The curve of the "excess" oxygen per mole of Pr_2O_3 in the sample, expressing all praseodymium in the sample as Pr_2O_3 regardless of oxidation state, versus changing composition has been redetermined. In qualitative agreement with work by Salutsky(58) it attains a maximum at approximately 28 mole per cent La_2O_3 and

then decreases sharply with increasing concentration of La_2O_3 until about 70 mole per cent La_2O_3, then the change is very gradual toward 100 mole per cent La_2O_3.

Starting at pure Pr_6O_{11} the density of the air-ignited oxide mixtures decreases with increasing amounts of La_2O_3 until about 42 mole per cent then increases to a maximum at about 80 mole per cent La_2O_3 and finally decreases toward the density of pure La_2O_3.

In view of the above changes it is highly probable that solid solution formation is the only thing that occurs when mixtures of air-ignited lanthanum and praseodymium oxides are prepared. No new structures or structural changes were observed which usually occur with compound formation.

It has also been shown that lanthanum and praseodymium sesquioxides form solid solutions in which the hexagonal lattice dimensions follow the additivity rule.

CONCLUSIONS

1. The lattice constants of hexagonal La_2O_3 have been redetermined and found to be a = 3.930 and c = 6.139 A. The pycnometric and the X-ray density values were found to be 6.56 and 6.585 g./cc., respectively. All values were in reasonable agreement with previously determined values.

2. The lattice constant value for Pr_6O_{11} was found to be 5.462 A. The pycnometric and X-ray density values for Pr_6O_{11} were redetermined and found to be 6.83 and 6.83 g./cc., respectively. The lattice constants for hexagonal Pr_2O_3 were found to be a = 3.854 and c = 6.007 A. All values are in reasonable agreement with previously determined values.

3. The variation of the density, crystal structure, crystal lattice dimensions, and amount of "excess" oxygen has been determined for the air-ignited lanthanum-praseodymium oxide system. It has been shown that the system undergoes solid solution formation throughout with the cubic and hexagonal structures coexisting in the concentration range from about 47.5 to about 69 mole per cent La_2O_3. It has been shown that hexagonal La_2O_3 and Pr_2O_3 form solid solutions that follow the additivity rule for the lattice dimensions.

4. It has been shown that the changes in the lattice constants of the air-ignited lanthanum-praseodymium oxide system does not follow the additivity rule which fact is in qualitative agreement with the observation that the amount of oxygenation of praseodymium also does not follow the additivity rule in this system.

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APPENDIX

Pure Lanthanum Oxide
2θ Values for the Hexagonal Structure

Film		367	429	433	434	435	436	437	445	446	481	489
Line	Plane											
1	$10\bar{1}0$	26.26	26.27	26.22	26.34	26.21	26.25	26.26	26.31	26.30	26.41	26.20
2	0002	29.21	29.28	29.13	29.30	29.22	29.26	29.21	29.26	29.26	29.36	29.25
3	$10\bar{1}1$	30.06	30.13	30.04	30.25	30.12	30.06	30.08	30.12	30.11	30.22	30.10
4	$10\bar{1}2$	39.50	39.71	39.52	39.77	39.64	39.58	39.59	39.69	39.58	39.74	39.62
5	$11\bar{2}0$	46.19	46.24	46.20	46.29	46.20	46.20	46.20	46.20	46.25	46.30	46.18
6	$10\bar{1}3$	52.23	52.31	52.22	52.26	52.21	52.32	52.22	52.31	52.26	52.36	52.34
7	$20\bar{2}0$	—	—	—	—	—	—	—	53.92	53.91	54.02	53.90
8	$11\bar{2}2$	55.53	55.57	55.48	55.61	55.46	55.52	55.53	55.52	55.57	55.67	55.60
9	$20\bar{2}1$	55.93	56.12	56.03	56.22	56.16	56.13	56.08	56.12	56.07	56.17	56.10
10	0004	—	—	60.50	—	—	—	60.44	60.58	60.43	60.63	60.56
11	$20\bar{2}2$	62.27	62.39	62.35	62.43	62.53	62.44	62.34	62.44	62.38	62.49	62.41
12	$10\bar{1}4$	—	—	—	—	—	—	66.96	67.15	67.04	67.15	67.07
13	$20\bar{2}3$	72.11	72.27	72.09	72.26	72.24	72.22	72.27	72.26	72.21	72.31	72.18
14	$21\bar{3}0$	—	—	—	—	—	—	73.57	73.56	73.58	73.71	73.48
15	$21\bar{3}1$	75.36	75.44	75.40	75.52	75.50	75.48	75.45	75.47	75.41	75.57	75.49
16	$11\bar{2}4$	79.25	79.30	79.16	79.28	79.25	79.24	79.24	79.32	79.22	79.32	79.29
17	$21\bar{3}2$		81.05	80.97	81.08	81.01	81.04	80.99	81.03	80.88	81.08	80.90
18	$10\bar{1}5$	83.85	83.96	83.83	83.89	83.86	83.80	83.85	83.93	83.88	83.98	83.95
19	$30\bar{3}0$	85.45	85.52	—	85.54	85.41	85.50	85.40	85.44	85.44	85.49	85.55
20	$21\bar{3}3$	89.89	90.04	90.00	90.10	90.02	90.06	90.06	90.05	90.00	90.15	90.06
21	$30\bar{3}2$	92.64	92.74	92.66	92.76	92.68	92.72	92.92	92.70	92.65	92.80	92.72

Mixed Oxides

2θ Values for the Hexagonal Structure

Film		Sample 2			Sample 3			Sample 4		
		467	531	532	464	529	530	497	520	521
Line	Plane									
1	10$\bar{1}$0	26.35	26.34	26.28	26.42	26.30	26.28	26.29	26.42	26.36
2	0002	29.30	29.30	29.23	29.37	29.26	29.24	29.24	29.37	29.36
3	10$\bar{1}$1	30.16	30.20	30.13	30.27	30.16	30.09	30.09	30.27	30.16
4	10$\bar{1}$2	39.72	39.72	39.60	39.79	39.66	39.66	39.70	39.79	39.78
5	11$\bar{2}$0	46.24	46.28	46.21	46.41	46.24	46.33	46.35	46.40	46.33
6	10$\bar{1}$3	52.40	52.34	52.32	52.37	52.30	52.34	52.35	52.41	52.39
7	20$\bar{2}$0	———	53.94	54.03	54.02	53.90	———	53.95	54.02	54.04
8	11$\bar{2}$2	55.60	55.69	55.58	55.68	55.61	55.65	55.65	55.77	55.75
9	20$\bar{2}$1	56.11	56.25	56.13	56.23	56.21	56.25	56.20	56.22	56.25
10	0004	60.61	60.60	60.59	60.64	60.46	60.51	60.50	60.68	60.55
11	20$\bar{2}$2	62.42	62.61	62.54	62.69	62.52	62.41	62.56	62.58	62.56
12	10$\bar{1}$4	67.08	67.16	67.05	67.15	67.13	67.07	67.11	67.24	67.11
13	20$\bar{2}$3	72.29	72.47	72.31	72.36	72.34	72.33	72.41	72.50	72.37
14	21$\bar{3}$0	———	73.72	73.66	73.86	73.59	———	73.71	73.75	73.72
15	21$\bar{3}$1	75.44	75.58	75.57	75.67	75.59	75.69	75.66	75.76	75.68
16	11$\bar{2}$4	79.35	79.48	79.37	79.43	79.50	79.55	79.46	79.51	79.48
17	21$\bar{3}$2	81.00	81.19	81.13	81.18	81.15	81.15	81.26	81.37	81.18
18	10$\bar{1}$5	84.01	84.09	84.08	83.94	83.91	84.06	84.11	84.17	84.04
19	30$\bar{3}$0	85.51	85.75	85.58	85.64	85.66	———	85.71	85.77	85.64
20	21$\bar{3}$3	90.17	90.35	90.14	90.15	90.32	90.27	90.32	90.43	90.35
21	30$\bar{3}$2	92.73	92.96	92.85	92.90	92.88	93.02	93.02	93.05	93.05
F_1		0.05141	0.05148	0.05144	0.05152	0.05141	0.05149	0.05145	0.05158	0.05146
F_2		0.01574	0.01585	0.01579	0.01585	0.01585	0.01584	0.01588	0.01590	0.01589
Lattice	a	3.926	3.923	3.925	3.922	3.926	3.923	3.924	3.919	3.924
Constant	c	6.145	6.123	6.135	6.125	6.125	6.125	6.117	6.114	6.116
Average Lattice	a		3.924			3.924			3.922	
Constant	c		6.134			6.125			6.116	

Mixed Oxides
2θ Values for the Hexagonal Structure

Film		Sample 5			Sample 6			Sample 7		
		539	542	543	326	533	534	486	499	500
Line	Plane									
1	$10\bar{1}0$	26.27	26.39	26.34	26.28	26.35	26.29	26.37	26.36	26.36
2	0002	29.27	29.45	29.35	29.34	29.31	29.25	29.32	29.32	29.27
3	$10\bar{1}1$	30.12	30.25	30.20	30.19	30.21	30.10	30.18	30.18	30.18
4	$10\bar{1}2$	39.69	39.83	39.73	39.77	39.72	39.72	39.75	39.72	39.67
5	$11\bar{2}0$	46.25	46.45	46.35	46.39	46.34	46.33	46.36	46.34	46.34
6	$10\bar{1}3$	52.36	52.47	52.42	52.41	52.35	52.39	52.42	52.32	52.37
7	$20\bar{2}0$	53.92	54.13	54.03		54.05	54.09	54.08	54.03	54.03
8	$11\bar{2}2$	55.67	55.73	55.68	55.72	55.66	55.69	55.73	55.73	55.68
9	$20\bar{2}1$	56.17	56.29	56.18	56.22	56.26	56.25	56.28	56.29	56.24
10	0004	60.53	60.65	60.60	60.63	60.66	60.65	60.64	60.65	60.60
11	$20\bar{2}2$	62.48	62.71	62.51	62.54	62.62	62.61	62.65	62.61	62.51
12	$10\bar{1}4$	67.09	67.22	67.17	67.31	67.23	67.11	67.26	67.28	67.13
13	$20\bar{2}3$	72.35	72.49	72.44		72.44	72.47	72.42	72.40	72.35
14	$21\bar{3}0$		73.79	73.74	73.72	73.79	73.88	73.77	73.81	
15	$21\bar{3}1$	75.56	75.75	75.60	75.63	75.69	75.78	75.68	75.77	75.62
16	$11\bar{2}4$	79.41	79.56	79.51	79.44	79.55	79.53	79.48	79.48	79.38
17	$21\bar{3}2$	81.07	81.27	81.22	81.10	81.25	81.29	81.24	81.29	81.24
18	$10\bar{1}5$	84.07	84.23	84.18	84.06	84.11	84.09	84.14	84.15	84.00
19	$30\bar{3}0$		85.83	85.68	85.71	85.76	85.80	85.70	85.66	85.71
20	$21\bar{3}3$	90.28	90.40	90.40	90.33	90.47	90.40	90.26	90.48	90.33
21	$30\bar{3}2$	92.99	93.06	93.06	92.98	93.08	93.06	93.01	93.14	92.94
F_1		0.05145	0.05155	0.05146	0.05142	0.05151	0.05151	0.05149	0.05152	0.05141
F_2		0.01585	0.01592	0.01592	0.01591	0.01592	0.01592	0.01591	0.01592	0.01591
Lattice a		3.924	3.921	3.924	3.925	3.922	3.922	3.923	3.922	3.926
Constant c		6.125	6.110	6.110	6.112	6.110	6.110	6.112	6.110	6.112
Average Lattice a			3.923			3.923			3.924	
Constant c			6.115			6.111			6.111	

Mixed Oxides
2θ Values for the Hexagonal Structure

Film		Sample 8			Sample 9		Sample 10		
		538	540	541	490	496	549	550	551
Line	Plane								
1	$10\bar{1}0$	26.29	26.38	26.33	26.49	26.52	26.39	26.46	26.37
2	0002	29.30	29.34	29.34	29.44	29.48	29.34	29.36	29.37
3	$10\bar{1}1$	30.15	30.19	30.19	30.29	30.34	30.24	30.26	30.28
4	$10\bar{1}2$	39.72	39.77	39.78	39.90	39.94	39.81	39.88	39.85
5	$11\bar{2}0$	46.39	46.38	46.44	46.46	46.53	46.43	46.55	46.47
6	$10\bar{1}3$	52.46	52.45	52.46	52.47	52.61	52.49	52.56	52.53
7	$20\bar{2}0$	54.06	54.10	54.12	54.18	54.27	54.19	54.16	54.19
8	$11\bar{2}2$	55.71	55.75	55.82	55.83	55.93	55.85	55.82	55.89
9	$20\bar{2}1$	56.21	56.25	56.32	56.38	56.48	56.40	56.42	56.39
10	0004	60.58	60.67	60.69	60.78	60.81	60.71	60.83	60.75
11	$20\bar{2}2$	62.63	62.62	62.64	62.84	62.82	62.76	62.78	62.86
12	$10\bar{1}4$	67.29	67.18	67.21	67.39	67.45	67.32	67.34	67.37
13	$20\bar{2}3$	72.50	72.59	72.57	72.70	72.78	72.63	72.60	72.73
14	$21\bar{3}0$	73.81	73.80	73.88	74.00	74.03	74.04	74.06	73.98
15	$21\bar{3}1$	75.76	75.70	75.78	75.91	75.99	75.94	75.96	75.94
16	$11\bar{2}4$	79.57	79.61	79.60	79.71	79.76	79.75	79.72	79.75
17	$21\bar{3}2$	81.27	81.37	81.35	81.51	81.62	81.50	81.57	81.50
18	$10\bar{1}5$	84.18	84.22	84.26	84.37	84.44	84.31	84.38	84.36
19	$30\bar{3}0$	85.74	85.83	85.82	86.07	86.15	86.01	86.13	86.06
20	$21\bar{3}3$	90.45	90.49	90.53	90.63	90.67	90.62	90.79	90.73
21	$30\bar{3}2$	93.10	93.19	93.19	93.43	93.39	93.38	93.40	93.43
F_1		0.05152	0.05157	0.05160	0.05178	0.05189	0.05174	0.05181	0.05179
F_2		0.01594	0.01595	0.01596	0.01599	0.01599	0.01599	0.01600	0.01601
Lattice a		3.922	3.920	3.919	3.912	3.909	3.913	3.911	3.912
Constant c		6.106	6.104	6.102	6.096	6.096	6.096	6.094	6.092
Average									
Lattice a			3.920		3.910			3.912	
Constant c			6.104		6.096			6.094	

Mixed Oxides
2θ Values for the Hexagonal Structure

Film		Sample 11			Sample 12		Sample 13	
Line	Plane	535	536	537	491	523	512	513
1	$10\bar{1}0$	26.35	26.42	26.37	—	26.43	26.51	26.47
2	0002	29.36	29.37	29.38	29.47	29.48	29.52	29.48
3	$10\bar{1}1$	30.21	30.23	30.23	30.37	30.33	30.42	30.38
4	$10\bar{1}2$	39.78	39.75	39.80	40.00	39.95	39.98	40.00
5	$11\bar{2}0$	—	46.37	46.47	46.66	46.57	46.69	46.57
6	$10\bar{1}3$	52.50	52.58	52.54	52.68	52.73	52.80	52.69
7	$20\bar{2}0$	54.20	54.08	54.14	—	—	—	—
8	$11\bar{2}2$	55.81	55.74	55.89	55.98	55.99	56.10	56.00
9	$20\bar{2}1$	56.31	56.29	56.40	56.64	56.54	56.55	56.50
10	0004	60.72	—	60.81	—	60.95	—	—
11	$20\bar{2}2$	62.67	62.66	62.81	—	62.90	63.06	62.91
12	$10\bar{1}4$	67.28	—	67.53	—	67.56	—	—
13	$20\bar{2}3$	72.59	72.58	72.69	72.82	72.82	72.97	72.89
14	$21\bar{3}0$	74.09	—	—	—	—	—	73.99
15	$21\bar{3}1$	75.84	75.79	75.95	—	—	—	—
16	$11\bar{2}4$	79.70	79.75	79.81	79.94	79.99	80.08	80.06
17	$21\bar{3}2$	81.45	81.35	81.46	—	81.69	81.89	81.81
18	$10\bar{1}5$	84.36	84.36	84.47	—	—	84.74	84.82
19	$30\bar{3}0$	85.91	85.81	85.97	—	86.30	86.39	86.27
20	$21\bar{3}3$	90.67	90.58	90.79	—	91.06	91.15	90.99
21	$30\bar{3}2$	93.23	93.33	93.44	—	93.72	93.90	93.59
F_1		0.05161	0.05158	0.05174	0.05213	0.05203	0.05216	0.05201
F_2		0.01603	0.01601	0.01605	0.01606	0.01607	0.01611	0.01608
Lattice a		3.918	3.919	3.913	3.899	3.902	3.897	3.903
Constant c		6.089	6.093	6.085	6.083	6.081	6.074	6.079
Average Lattice a		3.917			3.901		3.900	
Constant c		6.089			6.082		6.076	

Mixed Oxides Reduced in Hydrogen
2θ Values for the Hexagonal Structure

Film		Sample 10 555	Sample 11 527
Line	Plane		
1	$10\bar{1}0$	26.33	26.46
2	0002	29.34	29.47
3	$10\bar{1}1$	30.14	30.27
4	$10\bar{1}2$	39.77	40.03
5	$11\bar{2}0$	46.39	46.74
6	$10\bar{1}3$	52.56	52.80
7	$20\bar{2}0$	54.17	54.46
8	$11\bar{2}2$	55.82	56.16
9	$20\bar{2}1$	56.32	56.71
10	0004	———	61.12
11	$20\bar{2}2$	62.69	63.07
12	$10\bar{1}4$	67.26	67.68
13	$20\bar{2}3$	72.67	73.04
14	$21\bar{3}0$	———	———
15	$21\bar{3}1$	75.88	76.29
16	$11\bar{2}4$	79.75	80.25
17	$21\bar{3}2$	81.40	82.00
18	$10\bar{1}5$	84.46	84.90
19	$30\bar{3}0$	85.92	86.41
20	$21\bar{3}3$	90.73	91.22
21	$30\bar{3}2$	93.34	93.97
F_1		0.05176	0.05230
F_2		0.01594	0.01610
Lattice a		3.912	3.892
Constant c		6.108	6.075
Mole per cent La_2O_3		75.4	50.8

Mixed Oxides
2θ Values for the Cubic Structure

Film		Sample 11			Sample 12	
		535	536	537	491	523
Line	Plane					
1	111	27.60	27.57	27.52	27.82	27.79
2	200	31.96	31.88	31.88	32.18	——
3	220	46.39	45.66	45.62	46.06	——
4	311	——	——	——	54.58	54.33
5	222	——	——	——	57.29	——
6	400	——	——	——	67.06	——
7	331	——	——	——	73.98	74.28
8	420	——	——	——	76.13	76.13
9	422	——	——	——	84.95	84.75
10	333 511	——	——	——	——	——
Lattice Constant a		5.578	5.613	5.617	5.582	5.598
Average Lattice Constant a		5.603			5.590	

Film		Sample 13			Sample 14	
		501	512	513	492	515
Line	Plane					
1	111	27.72	27.82	27.77	27.93	27.81
2	200	32.13	32.12	32.13	32.29	32.22
3	220	46.01	45.99	45.97	46.23	46.15
4	311	54.54	54.50	54.44	54.80	54.67
5	222	57.14	——	——	57.46	57.33
6	400	67.07	——	——	67.44	67.30
7	331	73.98	——	——	74.41	74.31
8	420	76.09	76.28	76.15	76.61	76.47
9	422	84.91	——	——	85.44	85.39
10	333 511	——	——	——	91.96	92.10
Lattice Constant a		5.584	5.580	5.584	5.560	5.564
Average Lattice Constant a		5.583			5.562	

Mixed Oxides
2θ Values for the Cubic Structure

Film		Sample 15			Sample 16	
		473	518	519	504	517
Line	Plane					
1	111	27.94	27.92	27.94	28.01	28.01
2	200	32.35	32.33	32.30	32.42	32.42
3	220	46.23	46.25	46.27	46.45	46.43
4	311	54.75	54.86	54.79	54.97	55.04
5	222	57.51	57.47	57.39	57.88	57.74
6	400	67.43	67.33	67.36	68.00	67.70
7	331	74.40	74.34	74.37	75.01	74.71
8	420	76.55	76.64	76.52	77.32	77.06
9	422	85.57	85.51	85.54	86.34	85.97
10	333 511	92.09	92.07	92.00	93.00	92.88
Lattice Constant a		5.553	5.559	5.561	5.519	5.534
Average Lattice Constant a		5.558			5.526	

Film		Sample 18			Sample 19		
		474	505	506	503	546	547
Line	Plane						
1	111	28.12	28.16	28.27	28.16	28.16	28.20
2	200	32.53	32.67	32.63	32.67	32.52	32.66
3	220	46.65	46.75	46.77	46.75	46.71	46.75
4	311	55.32	55.37	55.39	55.47	55.43	55.47
5	222	57.97	58.12	58.04	58.13	58.09	58.18
6	400	68.06	68.19	68.07	68.30	68.21	68.26
7	331	75.10	75.26	75.24	75.32	75.28	75.38
8	420	77.56	77.56	77.44	77.62	77.64	77.68
9	422	85.17	86.58	86.57	86.70	86.71	86.75
10	333 511	86.42	93.30	93.28	93.56	93.48	93.52
Lattice Constant a		5.508	5.503	5.507	5.497	5.500	5.496
Average Lattice Constant a		5.506			5.498		

Mixed Oxides
2θ Values for the Cubic Structure

Film		Sample 20 528	 544	 545
Line	Plane			
1	111	28.20	28.19	28.19
2	200	32.66	32.69	32.70
3	220	46.88	46.86	46.87
4	311	55.50	55.57	55.58
5	222	58.20	58.23	58.23
6	400	68.37	68.39	68.40
7	331	75.59	75.40	75.46
8	420	77.89	77.80	77.81
9	422	86.91	86.96	86.97
10	333 511	93.82	93.67	93.68
Lattice Constant a		5.487	5.489	5.489
Average Lattice Constant a			5.488	

Weight Per cent Total Pr Expressed as Pr_2O_3

	Sample I			Sample II		
Sample	Weight	Spectro-photo-meter reading	Per cent	Weight	Spectro-photo-meter reading	Per cent
2	0.7745	0.042	2.5	0.7741	0.041	2.3
3	1.0473	0.146	5.2	0.6462	0.082	4.8
4	2.0040	0.342	7.09	2.0142	0.349	7.2
5	1.3995	0.316	9.4	1.4033	0.318	9.7
6	0.4999	0.169	13.0	—	—	—
7	1.2036	0.390	13.7	2.2319	0.721	13.8
8	1.2046	0.450	15.7	1.1939	0.445	15.7
9	0.4456	0.218	20.0	0.4398	0.208	19.1
10	0.6423	0.379	24.6	0.6487	0.382	24.7
11	0.6427	0.484	31.7	0.6617	0.500	31.9
12	0.2686	0.256	39.1	0.2634	0.250	38.7
13	0.3472	0.349	42.1	0.3477	0.350	42.0
14	0.2913	0.336	48.1	0.2790	0.322	47.7
15	0.3029	0.369	48.6	0.2751	0.332	48.7
16	0.2545	0.365	59.7	0.2596	0.374	60.0
17	0.2585	0.372	60.3	0.2617	0.375	60.0
18	0.2366	0.409	72.3	0.2362	0.407	72.0
19	0.2028	0.377	77.9	0.2108	0.390	77.3
20	0.2462	0.491	84.1	0.2469	0.491	83.8
21	0.2355	0.506	90.9	0.2403	0.515	90.4

"Excess" Oxygen

		Sample I				Sample II		
Sample	Weight Sample	Volume $Na_2S_2O_3$	$N_{Na_2S_2O_3}$	Per cent	Weight Sample	Volume $Na_2S_2O_3$	$N_{Na_2S_2O_3}$	Per cent
12	0.1146	2.08	0.03693	0.54	0.1084	2.23	0.03693	0.63
13	0.1114	3.75	0.03693	1.00	0.1215	4.15	0.03693	1.01
14	0.1060	5.80	0.03693	1.62	0.1035	5.66	0.03693	1.62
15	0.1069	6.44	0.03693	1.80	0.1080	6.18	0.03693	1.70
16	0.0940	7.92	0.03693	2.49	0.0951	8.03	0.03693	2.49
18	0.0968	9.27	0.03693	2.83	0.0958	9.19	0.03693	2.83
19	0.0958	9.22	0.03693	2.84	0.0927	8.92	0.03693	2.84
20	0.0982	8.68	0.0416	2.94	0.0999	8.69	0.0416	2.90
21	0.0962	8.66	0.0416	3.00	0.0969	8.75	0.0416	3.00
Pr_6O_{11}	0.0938	9.98	0.03693	3.14	0.0901	9.59	0.03693	3.14

<u>**Density Data for Air-Ignited Oxides**</u>

Sample	Weight of Sample	Average Wt. of Sample Plus Xylene	Density of Xylene	Volume of Pycnometer	Density of Sample
La_2O_3	2.5343	24.080	0.85900	25.4733	6.46
La_2O_3	5.1145	25.926	.85900	25.0142	6.58
La_2O_3	2.5484	23.697	.85900	25.0142	6.63
4	4.0275	25.377	.85869	25.0142	6.59
7	4.5215	25.414	.85869	25.0142	6.62
9	2.4370	23.996	.85869	25.4733	6.63
11	2.8183	24.317	.85828	25.4733	6.62
12	2.5552	23.698	.85900	25.0142	6.53
14	2.7069	24.223	.85900	25.4733	6.34
17	2.9424	24.419	.85828	25.4733	6.53
19	4.3119	25.244	.85900	25.0142	6.77
20	3.8084	24.796	.85828	25.0142	6.80
21	2.8187	23.932	.85828	25.0142	6.82
Pr_6O_{11}	3.6403	25.065	.85900	25.4733	6.83