An X-Ray Study of Non-stoichiometric $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$

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(Received August 27, 1975)

Non-stoichiometric $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ ($\delta=0.000$, 0.075, 0.120, and 0.157), with a bixbyite structure, was investigated by X-ray diffraction. The intensities of the superlattice lines were found to decrease with an increase in δ. The structure analysis has revealed that metal ions gradually move to the ideal positions of the fluorite structure with an increase in δ and that excess oxygen ions preferentially occupy the Z-sites.

The bixbyite structure common in rare-earth sesquioxides is closely related to the fluorite structure. For example, the X-ray powder pattern of the bixbyite structure can be interpreted as the superposition of the superlattice lines on the pattern of the fluorite structure. The unit cell of the bixbyite structure[1] (space group Ia3) is composed of eight unit cells with the fluorite structure, in which one-fourth of the oxygen-ion sites are vacant. These vacant sites, named Z-sites by Anderson,[2] can be regarded as interstitial positions for the bixbyite structure. Oxygen ions, O(1), occupy the general positions (48e) of Ia3. One-fourth of the metal ions, M(1), occupy the (8b) special positions, with the remaining three-fourths, M(2), occupy the (24d) special positions. As is shown in Fig. 1, the coordination polyhedron around M(2) is a cube consisting of six oxygen ions and two Z-sites. The Z-sites occupy the face diagonal corners, and the position of the M(2) ion is displaced from the centre of this cube.

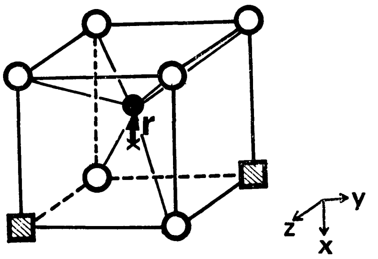

Fig. 1. Schematic drawing of the coordination polyhedron surrounding M (2) ion.
○: oxygen ion, ▨: Z-site, ●: M (2) ion, ×: the centre of the cube, ***r***: the displacement vector.

Rare-earth sesquioxides, such as $CeO_{1.5+\delta}$, $PrO_{1.5+\delta}$, and $TbO_{1.5+\delta}$, change their non-stoichiometry, δ, with the change in the oxygen partial pressure and the temperature. On the basis of the ordered intermediate phases of Pr_nO_{2n-2} ($n=7$, 9, 10, 11, 12), Hyde and his co-investigators[3] suggested that the excess oxygen ions in the non-stoichiometric σ-phase of $PrO_{1.5+\delta}$ occupy the Z-sites. Bratton[4] measured the density and lattice constants of yttria doped with zirconia and concluded that the predominant point defects are not cation vacancies but interstitial anions. Subbarao and his co-workers[5] obtained a similar result on yttria doped with thoria and inferred that such interstitial positions were Z-sites.

The present authors have carried out an X-ray diffraction study of non-stoichiometric $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ and have found that the intensities of the superlattice lines decrease with the increase in δ. The purpose of the present study is to elucidate the relationship between the intensities of the superlattice lines and the non-stoichiometry of $Pr_{0.6}Gd_{0.4}O_{1.6+\delta}$, which has a wide non-stoichiometric range.

Experimental

Praseodymium oxide and gadolinium oxide supplied by the Shin-etsu Chemical Co. were used as the starting materials. The purity of the oxides was 99.99%. Each oxide was dissolved in G. R. -grade nitric acid, and the two solutions were mixed in such a ratio that a composition of Pr: Gd= 3: 2 was obtained. Then an excess amount of a G. R. -grade oxalic acid solution was added, and the resulting oxalate precipitate was separated by filtration, oven-dried, and decomposed into oxide in air at 900 °C. Then the oxide sample was ground in an agate mortar, cold-pressed at 7 ton/cm², and sintered at 1550 °C for 20 h to homogenize the solid solution. The samples thus treated were placed in a quartz basket, suspended from a beam of a Cahn RG electrobalance,[6] and equilibrated with gas mixtures of argon and oxygen at 900 °C so that δ-values of 0.000, 0.075, 0.120, and 0.157 could be obtained. Then the samples were quenched to room temperature as soon as possible. The X-ray diffraction study was carried out using Rigaku Rotaflex PV 100 with Ni-filtered Cu*Kα* radiation. The intensity calculation was done by means of a HITAC-8700/8800 computer. The atomic scattering factors were taken from the International Table for X-ray Crystallography.[7] The program used for the computation was the full matrix least-squares program for X-ray powder diffraction.[8] In the least-squares calculations, the quantity of $\sum(I_o-I_c)^2$ was minimized. The reliability factor, R, was defined as $\sum|I_o-I_c|/\sum I_o$. Twenty-nine reflection lines observed in each sample were used in the calculation.

Results and Discussion

Table 1 shows the relative intensities of typical superlattice lines of $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ as a function of the non-stoichiometry, δ. The strongest line, (222), is

TABLE 1. OBSERVED INTENSITIES OF SUPERLATTICE LINES AS A FUNCTION OF NON-STOICHIOMETRY OF $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$

hkl	$(Ihkl)\times10^2/I(222)$			
	$\delta=0.000$	$\delta=0.075$	$\delta=0.120$	$\delta=0.157$
112	8.5	7.2	4.7	1.7
114	5.0	4.3	2.4	1.4
233	4.2	3.6	2.6	1.3
143	7.2	6.1	3.5	2.2
253	4.7	4.0	2.6	1.3
154	4.6	3.9	2.6	1.3
163	6.8	5.9	3.9	2.0

TABLE 2. ATOMIC AND LATTICE PARAMETERS WITH THEIR STANDARD DEVIATIONS[a)]

δ	O(1)				Z-sites		M(2)	R	a_0
	A_1	x	y	z	A_z	x	u		
0.000	1.27	0.392	0.133	0.405	0.23	0.447	−0.0307	0.046	11.006 Å
	(0.08)	(0.008)	(0.010)	(0.006)	(0.08)	(0.012)	(0.0017)		(0.006)
0.075	1.67	0.392	0.161	0.364	−0.09	0.157	−0.0275	0.047	10.957
	(0.10)	(0.010)	(0.007)	(0.008)	(0.10)	(0.049)	(0.0019)		(0.007)
0.120	1.32	0.384	0.145	0.384	0.30	0.219	−0.0233	0.027	10.927
	(0.06)	(0.008)	(0.007)	(0.007)	(0.06)	(0.011)	(0.0015)		(0.006)
0.157	1.39	0.387	0.147	0.373	0.27	0.054	−0.0166	0.037	10.897
	(0.08)	(0.009)	(0.011)	(0.009)	(0.08)	(0.009)	(0.0017)		(0.005)

a) M(1) atoms are at (1/4 1/4 1/4) and its equivalents, and M(2) at (u 0 1/4) and the equivalents. O(1) atoms are at (x y z) and the equivalents, and Z-sites are (x x x) and the equivalents.

taken as the standard for the calculation of the relative intensities. As may be seen in the table, the intensities of the superlattice lines decrease with increase in δ. In the structure analysis, it was assumed that gadolinium and praseodymium ions are randomly distributed between M(1) and M(2) cation sites and that the atomic scattering factors for the ions equal those for neutral atoms. Two distribution parameters, A_1 and A_z, were introduced for the analysis. A_1 and A_z are the average numbers of oxygen ions on O(1) sites and on Z-sites respectively per metal ion. The numbers of total oxygen ions (*i.e.*, A_1+A_z), O(1) sites, and Z-sites per metal ion are $1.5+\delta$, 1.5, and 0.5 respectively. The intensities were calculated by the least-squares method by changing the A_1, A_z, and positional parameters. In a preliminary calculation, minimum R-value was obtained for the over-all temperature factor, B, of 1 Å^2. Therefore, the least-squares calculations were carried out on the assumption of $B=1$ Å^2. The smallest values of the reliability factor, R, were obtained when the distribution and positional parameters had the values given in Table 2. The standard deviations and lattice parameters are also given in the same table. The R-values ranging from 2.7 to 4.7% are satisfactorily small from the point of view of X-ray powder diffraction analysis. The atomic parameters of the oxygen ions have much larger standard deviations than those for the M(2) ions.

In order to examine the dependence of the observed u-values (the positional parameters of the M(2) ions) upon the atomic parameters of the oxygen ions, a calculation was made on the assumption that excess oxygen ions occupy the ideal positions of the Z-sites. The results are shown in Table 3, where the standard deviations are also given in parentheses. The values of u and R are similar to those in Table 2. This means that the u-values estimated by the least-squares method are reliable and are nearly independent of the atomic parameters of the oxygen ions.

TABLE 3. ATOMIC PARAMETERS OBTAINED ON THE ASSUMPTION THAT EXCESS OXYGEN IONS OCCUPY THE IDEAL POSITION OF THE Z-SITES

δ	O(1)			M(2)	R
	x	y	z	u	
0.000	0.400	0.128	0.413	−0.0296	0.057
	(0.006)	(0.007)	(0.005)	(0.0017)	
0.075	0.389	0.164	0.367	−0.0273	0.045
	(0.010)	(0.005)	(0.008)	(0.0017)	
0.120	0.404	0.133	0.405	−0.0232	0.031
	(0.004)	(0.005)	(0.004)	(0.0013)	
0.157	0.399	0.153	0.364	−0.0167	0.044
	(0.013)	(0.007)	(0.011)	(0.0019)	

As has been mentioned above, the Pr and Gd ions are assumed to be randomly distributed between M(1) and M(2) sites. In order to verify the validity of this assumption in the present discussion, the intensities of the superlattice lines were calculated in such extreme cases that M (1) sites were occupied by only Pr or Gd ions. The intensities were found to agree with those shown in Table 1, within the range of experimental error. This result indicates that the intensities of the superlattice lines are nearly independent of the distribution of Pr and Gd ions. This is probably caused by the small difference in scattering factors between the two kinds of cations.

The relationship between u and δ is plotted in Fig. 2. The u-value expresses the degree of displacement of M(2) ions from the centre of the coordination polyhedron. The displacement vector, $\boldsymbol{r}$, in Fig. 1 has a component of $(-u, 0, 0)$. Clearly, the displacement

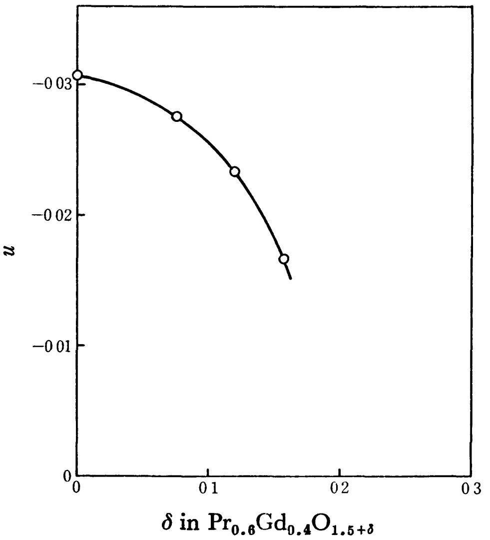

Fig. 2. Dependence of u on δ.

of the M(2) ions from the ideal positions in the fluorite structure decreases as δ increases. The negative value of u indicates that the M(2) ions shift from the ideal positions in the fluorite to the opposite direction against the plane including Z-sites. Such a tendency is generally observed in α-Mn_2O_3[9,10], In_2O_3[11], and rare-earth sesquioxides,[9–12] such as Y_2O_3, Dy_2O_3, and Tm_2O_3. Mertens and Zemann[13] have calculated the Madelung constant of yttria as a function of u and found that the Madelung energy increases with the increase in u and reaches a maximum at the observed u-value. Probably the displacement of yttrium ions is caused by the anisotropic arrangement of the oxygen ions surrounding the yttrium ions. Accordingly, the u-value can be regarded as a measure of the Coulombic anisotropy around the M(2) ions. Excess oxygen ions occupying the Z-sites would decrease the anisotropy; consequently, the M(2) ions would return to the ideal positions in the fluorite structure when the non-stoichiometry becomes large.

At $\delta=0.157$, more than 30% of the Z-sites are occupied by excess oxygen ions, while the u-value is about 50% of that at $\delta=0.000$. This means that a considerable degree of anisotropy still remains even at $\delta=0.157$. From the above discussion, it may be concluded that excess oxygen ions preferentially occpy the Z-sites.

The authors wish to express their gratitude to professor Goro Yamaguchi, the University of Tokyo, for his valuable discussions and also for allowing them to use his computer program.

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