BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2379—2383 (1976)

The Thermodynamics of Nonstoichiometric $Pr_{1-y}Gd_yO_{1.5+\delta}$

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(Received February 2, 1976)

In order to contribute to the study of the thermodynamics of point defects in ionic crystals, the nonstoichiometry, δ, of $Pr_{1-y}Gd_yO_{1.5+\delta}$ ($y=0$, 0.1, 0.2, and 0.4) with a wide nonstoichiometric composition range was measured as a function of the oxygen partial pressure. Assuming that excess oxygen ions preferentially occupy Z-sites of the bixbyite structure and that the Pr^{3+} and Pr^{4+} ions are distributed on cationic sites at random, the equilibrium constant, K, was calculated for

$$2Pr^{4+} + O_z^{2-} = 2Pr^{3+} + V_z + \frac{1}{2}O_2$$

It was found that $\ln K$ changes with δ in the relation;

$$\ln K = A + B\delta + C\delta^2$$

The parabolic dependence of $\ln K$ on δ is interpreted in terms of the changes in the energy of the defect formation and in the interaction energy between defects with the volume.

As transport phenomena in solids are closely related to point defects, the elucidation of a transport mechanism necessitates detailed studies of its defects. Since the pioneering works by Wagner and Schottky,1) many studies have been made of point defects and nonstoichiomitry in ionic crystals. In early thermodynamic treatments the ideal solution approximation was employed to deal with point defects.2) Although the approximation was experimentally proved to be applicable to many cases, some difficulties arose in the interpretation of the thermodynamic and transport properties of ionic crystals, which have wide nonstoichiometric composition ranges.3) Several models, *e.g.*, the blocking model,4–7) the microdomain model,8,9) and the cluster model,10–14) have been proposed for picturing the structure of point defects in such nonstoichiometric crystals. However, scarcely no experimental verification of these models has been undertaken.

In order to elucidate the relation between the defect structure and the thermodynamic or transport properties of nonstoichiometric oxides, the present authors have carried out a series of studies of the $Pr_{1-y}Gd_yO_{1.5+\delta}$ system.

There are several phases between $PrO_{1.5}$ and $PrO_{2.0}$.15,16) At high temperatures, $PrO_{1.5}$ takes the hexagonal structure (A-type) called the θ-phase, whereas it takes the cubic structure (C-type) at low temperatures. The fluorite structure oxide, $PrO_{2+\delta}$, is called the α-phase. Between the fluorite structure oxide and the C-type one, there are several phases, such as the ι and β phases. Above 900 °C, a relatively wide nonstoichiometric phase called the σ-phase appears. The structure of the σ-phase is substantially the bixbyite one, which is regarded as a distorted fluorite structure regularly lacking one fourth of its anions. Anionic vacant sites are characteristic of the bixbyite structure and were named "Z-sites" by Anderson.17) Hyde *et al.*15) have pointed out that excess anions in the bixbyite structure oxide may occupy the Z-sites. The preferential occupancy of the Z-sites by excess oxygen ions in a bixbyite structure was experimentally verified from the relationship between the lattice parameter of Y_2O_3 doped with ZrO_2 and its density.18) It was also previously shown by the present authors19) that the X-ray peak intensity due to the superstructure of $Pr_{1-y}Gd_yO_{1.5+\delta}$ decreases with the increase in δ.

The present work aims to contribute to the thermodynamics of nonstoichiometric solids containing high-concentration-point defects, using σ-phase solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$ as samples.

Experimental

Praseodymium oxide and gadolinium oxide of a 99.99% purity, supplied by the Shin-etsu Chemical Company, were used as the starting materials. These oxides were dissolved in G. R. grade nitric acid, and the two solutions were mixed in the desired proportions. The mixed solution was then added to a solution of G. R. grade oxalic acid to obtain the coprecipitate of praseodymium gadolinium oxalate, which was then converted into an oxide solid solution, $Pr_{1-y}Gd_yO_{1.5+\delta}$, by calcination, followed by heating at 1550 °C for homogenization.

About 1.5 g of the oxide sample was weighed in a quartz basket, suspended from a Cahn RG Electrobalance with a quartz fibre and placed in a reaction tube heated by an electric furnance. The oxygen partial pressure in the tube was controlled by gas mixtures of argon and oxygen. The circulation of the gas mixtures was carried out by means of an electromagnetic piston pump. The nonstoichiometry was determined gravimetrically, assuming that the $Pr_{1-y}Gd_yO_{1.5+\delta}$ solid solutions were stoichiometric in a pure CO atmosphere.

Results and Discussion

Figures 1 to 4 give the nonstoichiometry δ of σ-phase oxide, $Pr_{1-y}Gd_yO_{1.5+\delta}$, as a function of the oxygen partial pressure and the temperature. As may be seen in these figures, the stability region of the σ-phase extends upon the formation of solid solutions between praseodymium oxide and gadolinium oxide. If point defects in the nonstoichiometric σ-phase oxide tend to form a local or long-range ordering, the stability region of the σ-phase will be narrowed by the addition of gadolinium oxide to praseodymium oxide, because the ordering is

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** Present address, Electrotechnical Laboratory, Tanashi, Tokyo 188 prevented by the formation of a solid solution. The results of the present work, therefore, suggest that point defects in the σ-phase oxide are distributed at random. The dependence of the electronic conductivity on δ was well interpreted in terms of the random distribution of Pr^{3+} and Pr^{4+} in the $Pr_{1-y}Gd_yO_{1.5+\delta}$ solid solution.[20]

Accordingly, the equilibrium between σ-phase oxide and oxygen can be expressed by;

$$2Pr^{4+} + O_z^{2-} = 2Pr^{3+} + V_z + \frac{1}{2}O_2 \qquad (1)$$

where O_z^{2-} denotes oxygen ions occupying the Z-site and where V_z represents the vacant Z-site. The mass action law for (1) is;

$$K = \frac{[Pr^{3+}]^2[V_z]P_{O_2}^{1/2}}{[Pr^{4+}]^2[O_z^{2-}]} = \frac{(0.5-\delta)(1-y-2\delta)^2P_{O_2}^{1/2}}{4\delta^3}. \qquad (2)$$

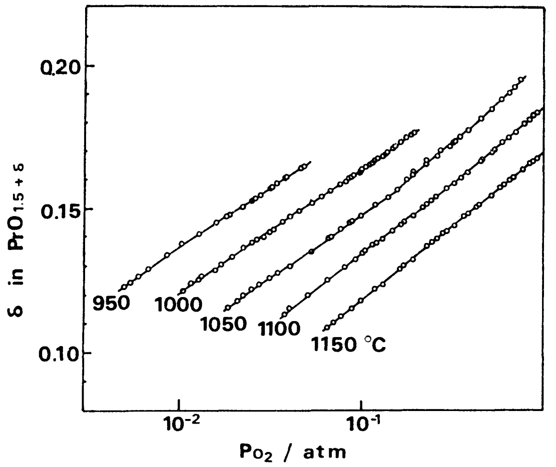

Fig. 1. The dependence of δ on P_{O_2} for $PrO_{1.5+\delta}$.

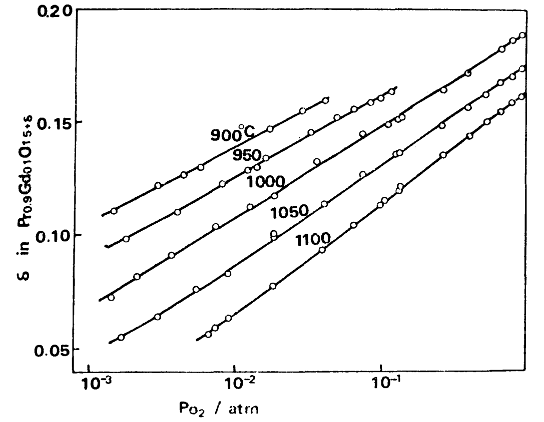

Fig. 2. The dependence of δ on P_{O_2} for $Pr_{0.9}Gd_{0.1}O_{1.5+\delta}$.

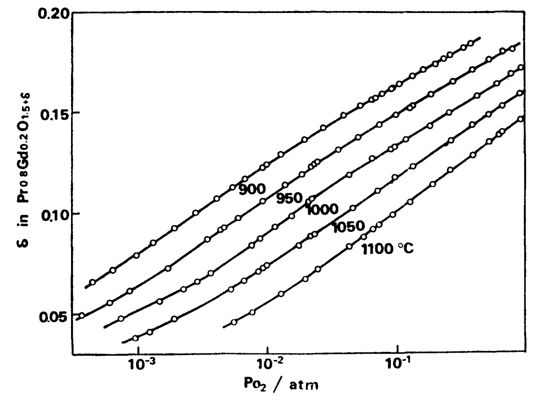

Fig. 3. The dependence of δ on P_{O_2} for $Pr_{0.8}Gd_{0.2}O_{1.5+\delta}$.

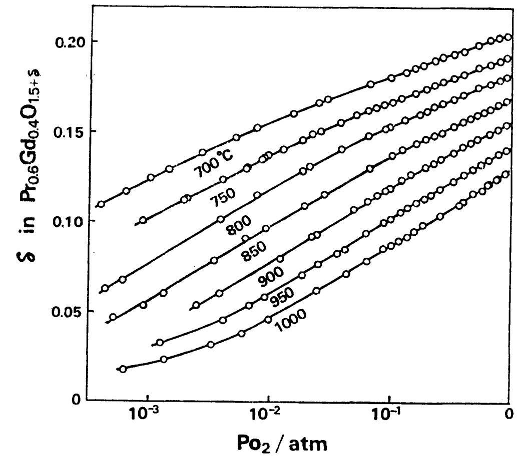

Fig. 4. The dependence of δ on P_{O_2} for $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$.

If the interaction between defects is extremely weak, the value of K should be constant, as is shown by Eq. 2. It may be seen, however, that $\ln K$ is not constant, but parabolically changes with the increase in δ.

In order to examine whether or not the relation between $\ln K$ and δ is well expressed by;

$$\ln K = A + B\delta + C\delta^2 \qquad (3)$$

the values of A, B, and C were determined by the least-squares method. The solid lines in Fig. 5 represent the least-squares curves, which are in good coincidence with the open circles.

The dependence of $\ln K$ on δ indicates that the energy required for the formation of point defects is a function of the concentration of oxygen ions occupying Z-sites.

The dependence of $\ln K$ on δ might be interpreted by other models, *e.g.*, a model wherein $V_O^{\cdot}$, $V_O^{\cdot\cdot}$, V_{Pr}'', and V_{Pr}''' vacancies are taken into consideration; the blocking model, wherein defects of the same kind do not occupy two neighboring sites, or the Bragg-Williams approximation, wherein the bixbyite structure is regarded as an ordered phase consisting of an O_I sublattice and an O_z sublattice. However, the results of calculation did not agree with the observed ones.

A similar dependence of $\ln K$ on δ, given in Fig. 5 and Eq. 3, has been reported for a few hydride systems.[21,22] As to the other oxide systems, preliminary experiments by the present authors have shown that the $TbO_{1.5+\delta}$ of the bixbyite structure and the $CeO_{2-\delta}$ of the fluorite structure have wide nonstoichiometric composition ranges and that $\ln K$ changes parabolically with δ.

Harashima *et al*[21] have interpreted the dependence of the composition of hydrides on the hydrogen pressure, assuming that the energy of the formation of defects and the interaction energy between defects depends on the molar volume of the crystal. Below, Harashima's treatment will be extended to the present system in

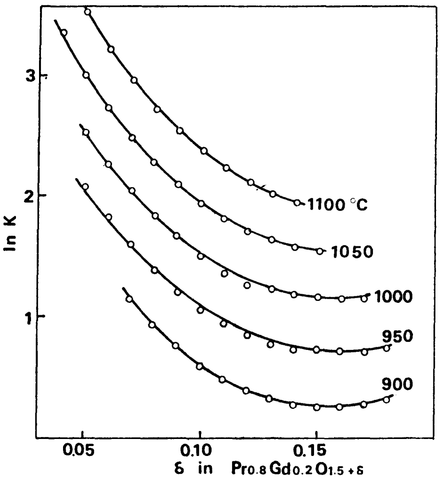

Fig. 5. The dependence of ln K on δ for $Pr_{0.8}Gd_{0.2}O_{1.5+\delta}$.

order to interpret the relation between ln$K$ and δ.

Let us denote the number of cationic sites in $Pr_{1-y}Gd_yO_{1.5+\delta}$ of the bixbyite structure by $2N$, the number of total praseodymium ions by $2N(1-y)$, and the number of Z-sites by N. Assuming the random distribution of O_z^{2-} ions on Z-sites and that of Pr^{3+} and Pr^{4+} ions on cationic sites, we obtain the following expression for the Gibbs free energy of a crystal;

$$G(N_z) = G_0(T) + H(N_z) - kT\ln\left\{\frac{N!}{N_z!(N-N_z)!} \times \frac{[2N(1-y)]!}{(2N_z)![2N(1-y)-2N_z]!}\right\} \tag{4}$$

where N_z is the number of O_z^{2-} ions, $G_0(T)$ is the Gibbs free energy at a constant T for the stoichiometric oxide ($\delta=0$, $N_z=0$), and $H(N_z)$ is the difference in enthalpy between the nonstoichiometric oxide (δ, N_z) and the stoichiometric oxide.

N_z is independent of the content of Gd^{3+} ions, y; therefore, the contribution of Gd^{3+} ions to the Gibbs free energy is included in $G_0(T)$. By differentiating Eq. 4 with N_z and replacing $N_z/2N$ by δ, one obtains;

$$\ln[\lambda_{O_2}]^{1/2} = \ln\left[\frac{4\delta^3}{(0.5-\delta)(1-y-2\delta)^2}\right] + \frac{\partial H(\delta)/\partial\delta}{2NkT} \tag{5}$$

where λ_{O_2} is the absolute activity of the oxygen molecule. The relation between the absolute activity and the oxygen partial pressure is;

$$\ln[\lambda_{O_2}] = \ln P_{O_2} - \frac{\chi_{O_2}}{kT} + \frac{\Psi}{N_0kT} \tag{6}$$

where χ_{O_2} is the dissociation energy of the molecular oxygen, Ψ is the free energy function $(G_T^\circ - H_0^\circ)/T$, and N_0 is Avogadro's number. From Eqs. 2, 5, and 6, we obtain:

$$\ln K = \frac{1}{kT}\left[\frac{1}{2N}\cdot\frac{\partial H(\delta)}{\partial\delta} + \frac{\chi_{O_2}}{2}\right] - \frac{\Psi}{2N_0k} \tag{7}$$

In Eq. 7, χ_{O_2} is constant and Ψ is independent of δ. If ε is the energy required for introducing an atomic oxygen into the bixbyite lattice to form an O_z^{2-} ion and two Pr^{4+} ions converted from Pr^{3+} ions, ω is the interaction energy between two adjacent O_z^{2-} ions, and z is the number of neighboring sites of an O_z^{2-} ion, the enthalpy changes, $H(N_z)$ and $H(\delta)$, are expressed by;

$$H(N_z) = -N_z\varepsilon - \frac{z}{2}N_z\left(\frac{N_z}{2N}\right)\omega \tag{8}$$

$$H(\delta) = -2N(\varepsilon\delta + z\omega\delta^2) \tag{9}$$

When ε and ω are constant, these equations give the enthalpy changes for the regular solution.

According to Harashima, ε and ω change with the volume of the crystal, V;

$$\varepsilon = \varepsilon_0 + \left(\frac{\partial\varepsilon}{\partial V}\right)(V-V_0) \tag{10}$$

$$\omega = \omega_0 + \left(\frac{\partial\omega}{\partial V}\right)(V-V_0) \tag{11}$$

where ε_0, ω_0, and V_0 represent ε, ω, and V respectively at $\delta=0$. The insertion of Eqs. 10 and 11 into Eq. 9 yields;

$$H(\delta) = -2N\left\{\delta\left[\varepsilon_0 + \left(\frac{\partial\varepsilon}{\partial V}\right)(V-V_0)\right] + z\delta^2\left[\omega_0 + \left(\frac{\partial\omega}{\partial V}\right)(V-V_0)\right]\right\} \tag{12}$$

Since the volume of a crystal can be determined by the condition $(\partial G/\partial V)_T=0$, it follows from Eqs. 4 and 9 that;

$$\left(\frac{\partial G}{\partial V}\right)_{T,\delta} = \left(\frac{\partial G_0}{\partial V}\right)_T - 2N\delta\left(\frac{\partial\varepsilon}{\partial V}\right)_{T,\delta} - 2Nz\delta^2\left(\frac{\partial\omega}{\partial V}\right)_{T,\delta} = 0 \tag{13}$$

Taylor's expansion of $(\partial G_0/\partial V)_T$ at V_0 gives;

$$\left(\frac{\partial G_0}{\partial V}\right)_{T,\delta} \doteqdot \left(\frac{\partial G_0}{\partial V}\right)_{T,V_0} + \left(\frac{\partial^2 G_0}{\partial V^2}\right)_{T,V_0}(V-V_0)$$

$$\doteqdot -\left(\frac{\partial P}{\partial V}\right)_{V_0}(V-V_0)$$

Therefore,

$$\left(\frac{\partial G_0}{\partial V}\right)_T = \frac{V-V_0}{\kappa V_0} \tag{14}$$

where κ is the compressibility. From Eqs. 13 and 14, we obtain:

$$V - V_0 = 2N\kappa V_0\left[\delta\left(\frac{\partial\varepsilon}{\partial V}\right) + z\delta^2\left(\frac{\partial\omega}{\partial V}\right)\right] \tag{15}$$

By inserting Eq. 15 into Eq. 12 and omitting the term of δ^4, one obtains;

$$H(\delta) = -2N\left\{\varepsilon_0\delta + \left[z\omega_0 + 2N\kappa V_0\left(\frac{\partial\varepsilon}{\partial V}\right)^2\right]\delta^2 + 4N\kappa V_0 z\left(\frac{\partial\varepsilon}{\partial V}\right)\left(\frac{\partial\omega}{\partial V}\right)\delta^3\right\}$$

By putting v as the molecular volume and replacing V by $2Nv$, one obtains;

$$H(\delta) = -2N\left\{\varepsilon_0\delta + \left[z\omega_0 + \kappa v_0\left(\frac{\partial\varepsilon}{\partial v}\right)^2\right]\delta^2 + 2\kappa z v_0\left(\frac{\partial\varepsilon}{\partial v}\right)\left(\frac{\partial\omega}{\partial v}\right)\delta^3\right\} \tag{16}$$

where v_0 is the value of v at $\delta=0$. From Eqs. 7 and 16, one obtains;

$$\ln K = -\frac{1}{kT}\left\{\varepsilon_0 + 2\left[z\omega_0 + \kappa v_0\left(\frac{\partial\varepsilon}{\partial v}\right)^2\right]\delta + 6z\kappa v_0\left(\frac{\partial\varepsilon}{\partial v}\right)\left(\frac{\partial\omega}{\partial v}\right)\delta^2 - \frac{\chi_{O_2}}{2}\right\} - \frac{\Psi}{2N_0k} \tag{17}$$

By a comparison of Eq. 17 with Eq. 3, one obtains;

$$A = -\frac{1}{kT}\left(\varepsilon_0 - \frac{\chi_{O_2}}{2}\right) - \frac{\Psi}{2N_0k} \tag{18}$$

$$B = -\frac{2}{kT}\left[z\omega_0 + \kappa v_0\left(\frac{\partial\varepsilon}{\partial v}\right)^2\right] \tag{19}$$

$$C = -\frac{6z\kappa v_0}{kT}\left(\frac{\partial\varepsilon}{\partial v}\right)\left(\frac{\partial\omega}{\partial v}\right) \tag{20}$$

As may be seen in Eqs. 18, 19, and 20, A, B, and C depend on the temperature. Therefore, the values of ε_0, RTB and RTC were calculated for various temperatures and averaged, instead of the values of A, B, and C. Those values are expected to be less dependent on the temperature. The results are summarized in Table 1.

TABLE 1. ESTIMATED ENERGY PARAMETER FOR $Pr_{1-y}Gd_yO_{1.5+\delta}$[a)]

y	ε_0 / kcal mol^{-1}	RTB / kcal mol^{-1}	RTC / kcal mol^{-1}	$\partial\varepsilon/\partial v$ / kcal cm^{-3}	$\partial\omega/\partial v$ / kcal cm^{-3}	ω_0 / kcal mol^{-1}
0.0	87.2 (±0.7)	−45 (±10)	110 (±25)	−0.95	1.2	5.9
0.1	85.9 (±2)	−60 (±25)	180 (±30)	−0.95	1.9	8.4
0.2	83.1 (±0.4)	−92 (± 3)	290 (± 5)	−0.96	3.1	14
0.4	81.4 (±1.4)	−94 (± 9)	310 (±50)	−0.96	3.4	14

a) The values in parentheses are the standard deviations.

The values of χ_{O_2} and Ψ were taken from the JANAF Thermochemical Tables.[23)] Since ε_0 is the energy required for introducing one atomic oxygen into a crystal to form one O_z^{2-} ion and two Pr^{4+} ions converted from Pr^{3+} ions, it is expected to be independent of the gadolinium content. As may be seen in Table 1, ε_0 is nearly independent of the temperature and the gadolinium content as expected.

The values of RTB and RTC are much scattered and depend on y and the temperature. These results may be attributed to the temperature dependence of κ, $(\partial\varepsilon/\partial v)$, and $(\partial\omega/\partial v)$. Because of the lack of compressibility data available for the calculation, it is difficult to calculate accurate values of B and C, but a rough estimation is possible.

Provided that the second term of the right hand side of Eq. 15 can be omitted, one obtains;

$$\frac{\partial\varepsilon}{\partial v} \doteqdot \frac{V - V_0}{\kappa V_0\delta} \tag{21}$$

From the compressibility data of Sm_2O_3 and Gd_2O_3,[24)] the reciprocal of the compressibility of σ-phase $PrO_{1.5+\delta}$, $(1/\kappa)$, is estimated as 2×10^{11} dyn cm^{-2}. The $(V-V_0)/V_0\delta$ ratio can be calculated from the lattice parameter of $Pr_{1-y}Gd_yO_{1.5+\delta}$.

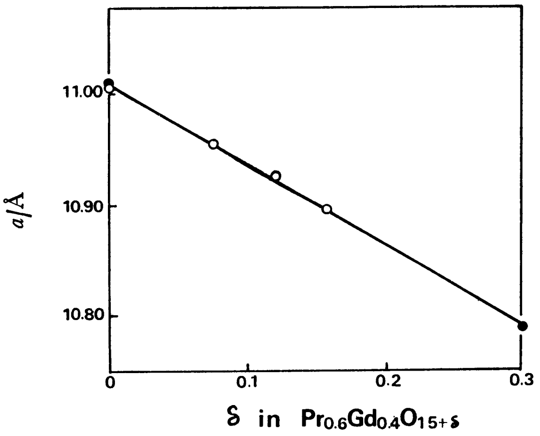

Fig. 6. The relationship between a and δ in $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$.
○: Observed, ●: calculated.

If $Pr_{1-y}Gd_yO_{1.5+\delta}$ is regarded as an solid solution consisting of $(1-y-2\delta)$ mol of $PrO_{1.5}$, 2δ mol of PrO_2, and y mol of $GdO_{1.5}$, Vegard's law holds, as is shown in Fig. 6, and the lattice parameter of $Pr_{1-y}Gd_yO_{1.5+\delta}$ is represented by;

$$a = (1-y-2\delta)a_{PrO_{1.5}} + 2\delta a_{PrO_2} + ya_{GdO_{1.5}}$$

Therefore,

$$\frac{V-V_0}{V_0\delta} = \frac{a^3 - a_0{}^3}{\delta a_0{}^3} \doteqdot \frac{(\mathrm{d}a^3/\mathrm{d}\delta)}{a_0{}^3} = \frac{6(a_{PrO_2} - a_{PrO_{1.5}})}{a_0} \tag{22}$$

The values of $(\partial\varepsilon/\partial v)$ calculated by means of Eqs. 21 and 22, and the values of ω_0 and $(\partial\omega/\partial v)$ calculated with the help of Eqs. 19 and 20 and $(\partial\varepsilon/\partial v)$ are listed in Table 1. Since the lattice parameter of $Pr_{1-y}Gd_yO_{1.5+\delta}$ decreases with an increase in y, ω_0 will be increased as y increases. Because of the lack of accuracy of κ, the values of $(\partial\varepsilon/\partial v)$ and $(\partial\omega/\partial v)$ are less accurate than those of ω_0.

Conclusion

In order to effect a thermodynamic study of bixbyite-type oxides, the nonstoichiometry δ in $Pr_{1-y}Gd_yO_{1.5+\delta}$ was determined as a function of the oxygen partial pressure. It was found that the nonstoichiometric region is extended upon the addition of gadolinium oxide and that, when $y=0.4$, δ can be increased until more than half of the praseodymium ions become tetravalent. The equilibrium between oxygen and nonstoichiometric oxide was calculated based on the random distribution of excess oxygen ions on Z-sites and of Pr^{3+} and Pr^{4+} ions on cationic sites. The parabolic dependence of $\ln K$ on δ was found.

Assuming that the energy of defect formation and the interaction energy between defects change with the molar volume of oxide, the dependence of $\ln K$ on δ was interpreted.

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