Effect of the Substances Related to H₂O Present in Praseodymium Oxides on the Phase Transition: $\sigma\text{-PrO}_x$ or $\text{C-Pr}_2\text{O}_3 \rightarrow \text{A-Pr}_2\text{O}_3$

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The effect of the substances related to H₂O on the starting temperature T_{de} of the phase transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was investigated using a closed-system oxygen analyzer with potentiostatic operation. Commercial Pr_6O_{11} powders containing various amount of Pr(OH)_3 and pure Pr(OH)_3 powders were the starting samples. Phase transitions among the resulting oxides were repeatedly induced by heating and cooling under a constant oxygen partial pressure. The T_{de} value obtained on the first heating run for pure Pr(OH)_3 became lower than the minimum value for commercial Pr_6O_{11} . When the Pr(OH)_3 was decomposed and annealed at 773 K in a vacuum, T_{de} reached the lowest value. The CaF_2 -related $\text{Pr}_n\text{O}_{2n-2}$ phases such as $\sigma\text{-PrO}_x$ possess domain structures, and the interface energy has a large effect on the thermal stability of the bulk. Thus, it may be concluded that the H and OH dissolving near the interface of domains decreased the relative thermal stability of $\sigma\text{-PrO}_x$ to $\text{A-Pr}_2\text{O}_3$. For commercial Pr_6O_{11} powders involving a superlattice structure, containing more Pr(OH)_3 , the $\text{A-Pr}_2\text{O}_3$ obtained involved a trace of $\text{C-Pr}_2\text{O}_3$. H and OH functioned with the structure and suppressed kinetically the phase transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$. We may infer that the superlattice structure itself is closely related to H and OH; when aging at a lower temperature, the structure may appear near the surface of the particles on an early stage of the precipitation as Pr(OH)_3 or PrOOH . When the heating runs of Pr(OH)_3 were continued without the vacuum treatment, two stage transitions for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ were observed. This result implies that the interactions of H, OH and H₂O with the superlattice structure occurred inhomogeneously near the surface of the particulate form. The relative thermal stability of $\text{C-Pr}_2\text{O}_3$ to $\text{A-Pr}_2\text{O}_3$ was similar to that of $\sigma\text{-PrO}_x$ to $\text{A-Pr}_2\text{O}_3$. The transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was accompanied by the evolution of H₂O vapor.

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I. Introduction

In the Pr–O system, there are several oxide phases, expressed as $\text{Pr}_n\text{O}_{2n-2}$ ($n=4, \sim 5, 7, 9, 10, 12, \infty$)⁽¹⁾. When commercial Pr_6O_{11} ($n=12$) powders were repeatedly reduced and oxidized by heating and cooling under a constant oxygen partial pressure, the starting temperature T_{de} of the phase transition: $\sigma\text{-PrO}_x$, ($n \approx 5$) $\rightarrow \text{A-Pr}_2\text{O}_3$, ($n=4$) was dependent on the number of heating runs⁽²⁾⁽³⁾. The existence of at least two factors affecting the T_{de} value has been implied. Powder X-ray diffraction (XRD) analysis of the CaF_2 -related phases before the transition to $\text{A-Pr}_2\text{O}_3$ revealed additional peaks. These were interpreted as diffraction due to a superlattice structure involved in the bulk powders⁽³⁾. The structure disappeared once the phases changed to a hexagonal $\text{A-Pr}_2\text{O}_3$, and was

not seen again even in CaF_2 -related phases. Since the temperature T_{de} was the highest on the first heating run, a factor increasing T_{de} was attributable to the superlattice structure.

The T_{de} value for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ reached a minimum at the second heating run, then gradually increased with the number of heating runs. Thus, another factor may act to decrease the T_{de} value, which gradually disappears with repeating the heating. It has been reported that $\text{Pr}_n\text{O}_{2n-2}$ phases react slowly with water vapor and form Pr(OH)_3 ⁽⁴⁾. Thus, substances related to H₂O, e.g., H and OH contained in $\text{Pr}_n\text{O}_{2n-2}$ could be the factors that decreased the T_{de} value. We tested this notion by performing five experiments in the present study. The effects of substances related to H₂O on the phase transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ are discussed on the basis of the results.

(Experiment 1) The effect of H₂O on the phase transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was investigated using commercial Pr_6O_{11} powders containing various amounts of Pr(OH)_3 .

(Experiment 2) The decomposition of Pr(OH)_3 to Pr_2O_3 , H₂ and O₂ was investigated.

(Experiment 3) The effect of H₂O on the phase transi-

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tion: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was investigated using $\text{Pr}(\text{OH})_3$ prepared from $\text{A-Pr}_2\text{O}_3$. The $\sigma\text{-PrO}_x$ phase does not involve a superlattice structure unlike that prepared from commercial Pr_6O_{11} powders.

(Experiment 4) Considering that the structure of $\sigma\text{-PrO}_x$ is similar to that of $\text{C-Pr}_2\text{O}_3$, the relative thermal stability between $\text{C-Pr}_2\text{O}_3$ and $\text{A-Pr}_2\text{O}_3$ was investigated.

(Experiment 5) The phase transition: $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was induced in a highly evacuated chamber and the evolution of H_2 gas and H_2O vapor accompanying the transition was examined.

II. Experimental Apparatus and Materials

1. Closed-system oxygen analyzer

An oxygen analyzer shown in Fig. 1 is a closed-system that was constructed by connecting an electrochemical oxygen pump, a circulation pump, and a reaction chamber, in series. It was used to monitor the phase transitions among $\text{Pr}_n\text{O}_{2n-2}$ in experiments 1 and 3 and the decomposition of $\text{Pr}(\text{OH})_3$ in experiment 2. It was also used to prepare the starting phases for experiments 2, 3 and 4, and produce the final Pr_2O_3 phases for experiment 4. The theoretical basis⁽⁵⁾⁽⁶⁾ and the details of the experimental technique have been presented in earlier publications⁽³⁾⁽⁷⁾.

The electrochemical oxygen pump: Pt, air/ ZrO_2 (+CaO) electrolyte/Ar, Pt was made from a ZrO_2 (+5 mass% CaO) solid electrolyte tube (21 mm o.d., 17 mm i.d., and 500 mm long), supplied by Nippon Kagaku Kogyo Co., Ltd. Platinum paste was applied to the inside and outside surfaces of the tube over 70 mm of the

Fig. 1 A schematic drawing of the closed-system oxygen analyzer.

midsection, to serve as electrodes. The inside (10 mm wide) and outside ends of the tube were also painted with platinum paste to serve as leads. Four platinum lead wires were wound around the outside painted surfaces. A quartz glass tube (14 mm o.d. and 500 mm long) was evacuated, sealed at both ends, then placed inside the electrolyte tube to reduce the volume. The electrolyte tube was heated at 1273 K in pure O_2 gas for 3 h to remove carbon, then quickly assembled in the closed-system to avoid adsorption of CO_2 gas in air inside the tube. Swagelok at the connection parts ensured that the airtightness of the system was enhanced and the invasion of substances related to carbon was reduced as described previously⁽⁷⁾. The circulation pump was of a diaphragm-type (M&F Enterprise Co., Ltd. model DCP-10), and the reaction chamber was made of a quartz glass tube (12 mm i.d.). The experiment with four leads was performed by using a potentiostat (Hokuto-Denko #R-453).

2. Evolved gas analysis

A reaction chamber, made of an alumina tube (13 mm i.d.) closed at one end, was placed in a furnace, and connected to a vacuum chamber made of stainless steel. The chamber was evacuated by a turbo molecular pump (Balzers TSU-240). It was first confirmed that the total pressure in the chamber was below 10^{-6} Pa, then the reaction chamber at 373 K was heated to 1323 K at a rate of $R=2$ K/min. The partial pressures of the various gases generated in the vacuum chamber, the masses of which were lower than 64, were measured by a quadrupole mass spectrometer (Balzers QMG-064).

3. Chemical agents

Three Pr_6O_{11} powders, the nominal purities of which differed, were purchased as follows:

3N: from Mitsuwa Chemicals Co., Ltd., ($1\ \mu\text{m} \times 5\ \mu\text{m}$, rod shape),

4N: from Rare Metallic Co., Ltd.,

5N: from CERAC Inc., (-325 mesh).

ICP analysis revealed that the major impurities were $\text{CeO}_2 < 100$ ppm, $\text{Nd}_2\text{O}_3 \approx 100$ ppm, $\text{CaO} = 50 \sim 70$ ppm, $\text{MgO} < 100$ ppm, and a significant difference was not

Fig. 2 X-ray diffraction pattern for a commercial Pr_6O_{11} powder: 5N. $\circ$: Pr_6O_{11} , $\bullet$: Pr_2O_3 , $\triangle$: $\text{Pr}(\text{OH})_3$, $\square$: C-type $\text{Pr}_n\text{O}_{2n-2}$, *: additional peak.

recognized. In this report, the chemical agents are distinguished by the nominal purity, i.e., 3N, 4N and 5N. These powders contained Pr(OH)₃ and PrO₂, because Pr₆O₁₁ reacts very slowly with H₂O vapor and O₂ gas in air even at room temperature. The amounts of Pr(OH)₃ and PrO₂ was very low in powder 3N, the XRD pattern of which has been shown previously⁽³⁾. The XRD pattern of the powder 5N is shown in Fig. 2; it contained more PrO₂ than Pr₆O₁₁. The powder 5N contained several times more Pr(OH)₃ than powder 3N did. Powder 4N contained an intermediate amount of Pr(OH)₃. Since the data and the conclusions derived were consistent, only the results for 3N and 5N are presented here.

III. Experimental Principles and Procedures

(Experiments 1 and 3) The sample powders (about 20 mg) were weighed, spread in an alumina crucible with a flat bottom (11 mm o.d., 9 mm i.d. 20 mm height), and loaded into the reaction chamber. The electrochemical oxygen pump was heated up to 1073 K. After the closed system was evacuated using a rotary pump, Ar gas (above 99.99% purity) was circulated at a flow rate of 900 cm³/min in the direction indicated by the arrow in Fig. 1. The potentiostatic operation was carried out so that the chemical potential of the oxygen at the solid electrolyte/Ar interface ($x=L$), $\mu(\text{O}_2)^L$, was maintained at a constant value. The emf, $E(m)$, between the leads for emf measurements is related to $\mu(\text{O}_2)^L$ by⁽⁸⁾

$$E(m) = (1/4F) \{ \mu(\text{O}_2)^L - \mu(\text{O}_2)^0 \} \\ = -(RT/4F) \ln \{ 0.21 \times P^* / P(\text{O}_2)^L \} \quad (1)$$

under the condition: $\bar{t}_{\text{ion}} \approx 1$, where $\mu(\text{O}_2)^0$ and $\mu(\text{O}_2)^L$ are the oxygen chemical potentials in air and at the electrolyte/Ar interface, respectively, $P^* = 101325$ Pa, $P(\text{O}_2)^L$ is the oxygen partial pressure corresponding to $\mu(\text{O}_2)^L$, F is the Faraday constant, and $\bar{t}_{\text{ion}}$ is the average ionic transference number of the electrolyte.

Because the potentiostatic operation was performed under the conditions: $E(m) = -140$ mV, $P(\text{O}_2)^L / P^* = 4.9 \times 10^{-4}$ was attained. The electric current passing through the oxygen pump was converted to the corresponding voltage, and input via GP-IB into a personal computer (PC-9800) at an interval of 0.425 s. The average value of the 40 signals was obtained as the measured value of the current.

Since the oxygen in the closed system was electrochemically evacuated through the electrolyte, the chemical potential of the oxygen in the circulating Ar gas, $\mu(\text{O}_2)^G$, approached $\mu(\text{O}_2)^L$. The electric current decreased with time and reached a constant value, I_∞ . After confirming the base current, I_∞ , the reaction chamber was heated and successively cooled at a constant rate of $R = 2$ K/min. $P(\text{O}_2)^L / P^* = 4.9 \times 10^{-4}$ at 1073 K corresponds to $P(\text{H}_2)^L / P(\text{H}_2\text{O})^L < 10^{-7}$, e.g., $P(\text{H}_2)^L / P^* = 10^{-8}$ for $P(\text{H}_2\text{O})^L / P^* = 10^{-1}$, where $P(\text{H}_2)^L$ and $P(\text{H}_2\text{O})^L$ are the partial pressures of H₂ and H₂O gases at the electrolyte/Ar interface. As the $P(\text{H}_2)^L$ was

sufficiently low and the value of $P(\text{H}_2\text{O}) / P(\text{H}_2)$ was variable, the oxygen partial pressure in the circulating gas, $P(\text{O}_2)$ was independent of the temperature in the sample chamber. When the oxide sample is reduced by heating it, for instance $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$, the oxygen within it is released into the system, and $\mu(\text{O}_2)^G$ becomes larger than $\mu(\text{O}_2)^L$. The oxygen is electrochemically pumped out of the system. As the reaction is terminated and $\mu(\text{O}_2)^G$ decreases to its starting value $\mu(\text{O}_2)^L$, the electric current, I , diminishes until it reaches the base current I_∞ . The amount of oxygen released or taken in by the sample, with the reaction, $N(\text{O})$ in mol is related to the ionic charge, Q_{ion} , and expressed by^{(5)(6)†}

$$N(\text{O}) = Q_{\text{ion}} / 2F = (1/2F) \int (I - I_\infty) dt. \quad (2)$$

(Experiment 2) When a preselected phase Pr_{*n*}O_{2*n*-2} was attained in the oxygen analyzer using the same technique as described in experiment 1, the chamber with the sample was quenched in ice-water. Several phases of Pr_{*n*}O_{2*n*-2} prepared in this manner were maintained in a desiccator, the humidity in which was less than 5%. These powders reacted very slowly with water vapor and formed Pr(OH)₃ over time. These phases were identified using a powder X-ray diffraction (XRD) apparatus (Shimadzu Co. Ltd., XD-5A, Cu:K_α spectrum), and the difference in the speed of Pr(OH)₃ formation was examined.

(Experiments 2 and 4) The commercial Pr₆O₁₁ powders 3N, the Pr₇O₁₂ powders obtained in the second heating run of experiment 1, and those of Pr(OH)₃ prepared in experiment 2, were placed in the oxygen analyzer. The applied voltage, $E(m) = -1.3$ or -1.4 V corresponds to $P(\text{O}_2)^L / P^* < 10^{-25}$. As the $P(\text{O}_2)^L$ was very small and the Ar+1% H₂ gas mixture was circulated, the ratio of $P(\text{H}_2) / P(\text{H}_2\text{O})$ was maintained constant, i.e., 2×10^3 or 2×10^4 . In experiment 2, the Pr(OH)₃ powders were heated to 1073 K, and the decomposition to Pr₂O₃ was monitored in the oxygen analyzer. In experiment 4, all samples were heated, annealed at 873 K for 24 h, and the sample chamber quenched in ice-water. The Pr₂O₃ phases obtained were analyzed by powder XRD to identify whether the phases had A- or C-type structure. Since C-Pr₂O₃ turns to A-Pr₂O₃ by strongly pressing with pestle, the powder needed to be handled with the greatest possible care.

IV. Experimental Results and Discussion

(Experiment 1) The current-temperature-time (I - T - t) curves for two commercial Pr₆O₁₁ powders, obtained in the 1st heating run, are shown in Fig. 3. For sample 3N, five peaks appeared corresponding to the phase transitions: Pr₆O₁₁ ($n=12$) $\rightarrow$ Pr₅O₉ ($n=10$) $\rightarrow$ Pr₃O₁₆ ($n=9$) $\rightarrow$ Pr₇O₁₂ ($n=7$) $\rightarrow$ σ -PrO_{*x*} ($n \approx 5$) $\rightarrow$ Pr₂O₃ ($n=4$). The Pr₂O₃ phase, annealed at 1323 K for 5 h, was quenched with the

† A similar oxygen analyzer based on this principle is available from Toray Co., Ltd., Ohtsu-city, Shiga, Japan.

Fig. 3 Comparison of the current-temperature-time profiles obtained when commercial Pr_6O_{11} powders, 3N and 5N (20 mg) were heated from room temperature under the conditions of $E(m) = -140$ mV and $R = 2$ K/min.

sample chamber into ice-water. The powder XRD analysis revealed that the phase was A- Pr_2O_3 and did not involve C- Pr_2O_3 . In sample 5N, another peak appeared at the lower temperature on the I - T - t curve. This was attributed to the PrO_2 which was present in the starting powder. The large peak for $\sigma\text{-PrO}_x \rightarrow \text{Pr}_2\text{O}_3$ was followed by a very small peak. The XRD analysis revealed that the A- Pr_2O_3 obtained after annealing at 1323 K for 5 h involved a small amount of C- Pr_2O_3 . Since 5N involved more $\text{Pr}(\text{OH})_3$ than 3N did, we propose a first hypothesis that substances related to H_2O increase the relative stability of C- Pr_2O_3 to A- Pr_2O_3 .

The present potentiostatic operation established the conditions, $P(\text{O}_2)^L/P^* = 4.9 \times 10^{-4}$ and $P(\text{H}_2\text{O})^L/P(\text{H}_2)^L > 10^7$. As seen from Fig. 3, the starting temperatures for $\text{Pr}_9\text{O}_{16} \rightarrow \text{Pr}_7\text{O}_{12}$ were nearly equal. This proved

Fig. 4 Superposition of the current-temperature-time profiles obtained by 10 heating runs of 3N compared with those by 17 heating runs of 5N, under the condition of $E(m) = -140$ mV. (a) 3N, (b) 5N. Annealing time at 1323 K is 3 h, except for the 9th heating run of 3N and the 15th heating run of 5N, i.e., 24 h. Before the final run of 3N and the penultimate run of 5N, the pumping capacity of oxygen-pump was enhanced.

that the decomposition of the H₂O vapor released from the samples was negligible and did not disturb the $P(\text{O}_2)$ in the circulating Ar gas. After maintaining at 1323 K for 3 h, the samples were cooled again to 673 K and the phases oxidized to Pr₅O₉. After 8 h, the samples were heated again to 1323 K, (2nd heating run). This treatment was continued until the I - T - t curve was no longer dependent on the heating run number. The dependence of the I - T - t curves for Pr₇O₁₂ → σ -PrO_x → A-Pr₂O₃ on the heating run number is shown in Fig. 4. As shown in this figure, only during the 1st heating run of 5N, the starting temperature T_{de} for Pr₇O₁₂ → σ -PrO_x became lower. The H₂O contained in Pr_nO_{2n-2} may increase the relative thermal stability of σ -PrO_x to Pr₇O₁₂. The T_{de} values for σ -PrO_x → A-Pr₂O₃ in 3N and 5N obtained in the 2nd heating run, were similar. As heating and cooling were repeated, the T_{de} shifted toward a higher temperature and approached a constant value as shown in Fig. 4 by the final run. That is, there was no significant difference between 3N and 5N. In Fig. 4, in order to determine more precise values of T_{de} in the final runs, the annealing period at 1323 K before the final heating run of 3N and that before the penultimate run of 5N were extended to 24 h.

(Experiment 2) While the Pr_nO_{2n-2} phases prepared in the oxygen analyzer were maintained in a dessicator at room temperature, they reacted very slowly with water vapor and formed Pr(OH)₃. In order to prepare Pr(OH)₃ as a starting phase, the strength ratio of the XRD peak of Pr(OH)₃ involved in various Pr_nO_{2n-2} to that of the bulk powder was first examined as a function of time. The speed of Pr(OH)₃ formation was fastest for A-Pr₂O₃; the pure phase was obtained in 800 h, when it reacted with H₂O vapor in equilibrium with water. σ -PrO_x relatively quickly formed Pr(OH)₃, however this involved the other Pr_nO_{2n-2} phases. For C-Pr₂O₃, Pr₇O₁₂, and Pr₅O₉, the speeds of Pr(OH)₃ formation were too low. Thus, only the Pr(OH)₃ prepared from A-Pr₂O₃ could be the starting material. The Pr(OH)₃ powders were placed in the oxygen analyzer, and decomposed to Pr₂O₃ in an Ar+1%H₂ gas mixture by heating. The potentiostatic operation with $E(m) = -1.3$ V established the conditions: $P(\text{O}_2)^{\text{L}}/P^* < 10^{-25}$ and $P(\text{H}_2)^{\text{L}}/P(\text{H}_2\text{O})^{\text{L}} = 2 \times 10^3$. Therefore, most of the evolved H₂O gas was decomposed at the inner wall of the electrolyte, and the oxygen electrochemically pumped out of the system. The I - T - t curve shown in Fig. 5 has two peaks, the ratio of the ionic charges being nearly 2:1. This proves that the following reactions occurred⁽⁹⁾:

As seen from Fig. 5, under the experimental condition, the decomposition was completed at a temperature below 723 K.

In the experiments 1 and 3 under $P(\text{O}_2)/P^* = 4.9 \times 10^{-4}$, the evolved H₂O gas was not decomposed elec-

trochemically. As the reactions (3) and (4) might proceed at higher temperatures, the Pr₇O₁₂ phase, quenched with the sample chamber in the course of the heating run, was subjected to powder XRD analysis. It was confirmed that the reactions (3) and (4) were completed at 973 K under all the present experimental conditions.

(Experiment 3) The Pr(OH)₃ powder formed from A-Pr₂O₃ was placed in the oxygen analyzer, and heated to 1323 K under $P(\text{O}_2)/P^* = 4.9 \times 10^{-4}$. The I - T - t curve is not influenced by the H₂O vapor released from the sample, because the dissociation of H₂O into H₂ and O₂ is negligible under this atmosphere. As the H₂O released from Pr(OH)₃ enhanced the pressure of the circulating gas, the stopcock was opened one time at a temperature around 873 K, so that the system could be maintained around atmospheric pressure. As the temperature was increased, Pr₇O₁₂ was formed and followed by the phase transitions: Pr₇O₁₂ → σ -PrO_x → A-Pr₂O₃. The results are shown in Fig. 6(a). In another experiment, while the system was evacuated, the reaction chamber with Pr(OH)₃ was first heated to 773 K, maintained for 3h and therefore the Pr(OH)₃ was decomposed as shown in Fig. 5. The chamber was cooled to room temperature, then Ar gas introduced. After the base-current I_{∞} was confirmed, the heating and cooling runs were started. The results are shown in Fig. 6(b). In both experiments, the period of annealing at 1323 K was extended to 24 h, so that the final I - T - t curves were attained in the 3rd heating runs.

Since the starting Pr(OH)₃ was prepared from A-Pr₂O₃, any Pr_nO_{2n-2} that appeared should not involve a superlattice structure. As a result, the T_{de} value for σ -PrO_x → A-Pr₂O₃ in the 1st heating run was not larger than that in the final heating run, being on the contrary, much lower. In particular, the T_{de} value shown in Fig. 6(b) was lowest among all the starting materials. In this experiment, the Pr(OH)₃ had been decomposed and the H₂O vapor excluded. Considering that the sample had been annealed at 773 K, we propose the second hypothesis that the substances related to H₂O dissolved in the bulk powder, for example H and OH, decrease the relative thermal stability of C-Pr₂O₃ to A-Pr₂O₃. Continued heating may have decreased the concentration of the

Fig. 5 Current-temperature-time profile obtained by heating Pr(OH)₃ powder (19.86 mg). $E(m) = -1.300$ V, the circulating gas: Ar+1%H₂. The Pr(OH)₃ was prepared from A-Pr₂O₃.

Fig. 6 Superposition of the current-temperature-time profiles obtained by heating $\text{Pr}(\text{OH})_3$ three times, under the condition of $E(m) = -140$ mV. (a) without vacuum treatment, $\{\text{Pr}(\text{OH})_3: 19.97 \text{ mg}\}$, (b) with vacuum treatment at 773 K, $\{\text{Pr}(\text{OH})_3: 19.98 \text{ mg}\}$. Annealing time at 1323 K was 24 h.

substances and the T_{de} for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ moved toward a higher temperature, as shown in Figs. 4 and 6. The phase of $\text{A-Pr}_2\text{O}_3$ was confirmed by powder XRD analysis after the experiments.

Hypotheses one and two may appear inconsistent. However, the 2nd and 3rd heating runs in Fig. 6(a) show that the current peak for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ tends to diverge. The amount of sample spread in the crucible was small and the particles were virtually isolated. The H_2O vapor generated by the decomposition of $\text{Pr}(\text{OH})_3$ was circulated through the system. As a result, it is implied that the relative stability of $\sigma\text{-PrO}_x$ was different in the particulate form, that is, the part near the surface and the bulk. Thus, the first hypothesis can be refined to state that the substances related to H_2O near the surface of particles increase the relative stability of $\text{C-Pr}_2\text{O}_3$ to $\text{A-Pr}_2\text{O}_3$.

(Experiment 4) The Pr_2O_3 phase prepared around 873 K reportedly consisted of a mixture of A- and C-type phases⁽¹⁰⁾. Because $\sigma\text{-PrO}_x$ has a C-type-like structure, the relative stability of $\text{C-Pr}_2\text{O}_3$ to $\text{A-Pr}_2\text{O}_3$ should be similar to that of $\sigma\text{-PrO}_x$ to $\text{A-Pr}_2\text{O}_3$. Thus, Pr_2O_3 phases were prepared from several starting materials, by annealing at 873 K for 24 h in the oxygen analyzer with a highly reduced atmosphere. The powders were quenched with the sample chamber into ice-water and analyzed by powder XRD. As seen from Fig. 7(a), the Pr_2O_3 prepared from the commercial Pr_6O_{11} powder 3N had a C-type structure; the additional peak interpreted as diffraction

Fig. 7 X-ray diffraction patterns for Pr_2O_3 powders prepared from different starting phases, by annealing at 873 K for 24 h in the oxygen analyzer. $E(m) = -1.40$ V, the circulating gas: $\text{Ar} + 1\% \text{H}_2$, ○: $\text{A-Pr}_2\text{O}_3$, unmarked: $\text{C-Pr}_2\text{O}_3$, *: additional peak. The starting phase are: (a) commercial Pr_6O_{11} with additional peaks, (b) $\text{Pr}(\text{OH})_3$ prepared from $\text{A-Pr}_2\text{O}_3$ without an additional peak, (c) Pr_7O_{12} without an additional peak.

due to a superlattice structure was observed around $2\theta = 29^\circ$. That is, the structure suppressed the phase transition: $\text{C-Pr}_2\text{O}_3 \rightarrow \text{A-Pr}_2\text{O}_3$. Pr_2O_3 phases were also prepared several times from Pr_7O_{12} which did not involve this structure; some of the phases obtained had only the C-type structure. Sometimes, the peak due to (111) diffraction of $\text{A-Pr}_2\text{O}_3$ appeared around $2\theta = 31^\circ$ as shown in Fig. 7(c). When the $\text{Pr}(\text{OH})_3$ formed from $\text{A-Pr}_2\text{O}_3$ was used as the starting phase, the additional peak around $2\theta = 29^\circ$ did not appear in the XRD pattern, as seen from Fig. 7(b). The peak due to the diffraction of $\text{A-Pr}_2\text{O}_3$ in the mixed phases became predominant. Considering that the Pr_2O_3 had been annealed at 873 K, substances related to H_2O might dissolve in the bulk, then acted to decrease the relative stability of $\text{C-Pr}_2\text{O}_3$.

As described earlier, when $\text{Pr}(\text{OH})_3$ was annealed at 773 K in a vacuum, the T_{de} value for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was lowest. Considering the similarity of the structures between $\sigma\text{-PrO}_x$ and $\text{C-Pr}_2\text{O}_3$, we can conclude that the substances related to H_2O dissolving in the bulk of C-type $\text{Pr}_n\text{O}_{2n-2}$ decreases the relative thermal stability to $\text{A-Pr}_2\text{O}_3$. It has been reported that the CaF_2 -related $\text{Pr}_n\text{O}_{2n-2}$ phases possess domain structures, and the interface energy has a large effect on the thermal stability of the bulk⁽¹¹⁾. The substances related to H_2O , e.g., H and OH dissolving near the interface of domains may change the interface energy and therefore the thermal stability of the bulk phase. When the vacuum treatment was not undertaken, the two current peaks for $\sigma\text{-PrO}_x \rightarrow \text{A-Pr}_2\text{O}_3$ was observed in the final heating run. The T_{de} value at lower temperature was nearly consistent with that for commercial powders 3N and 5N, and attributable to the properties of the bulk. We may infer that the T_{de} value at higher temperature came from H_2O , H, and OH near the surface of the particles, that is, the substances related to

Fig. 8 Results of evolved gas analysis for commercial Pr₆O₁₁ powder 3N, (47.51 mg).

H₂O near the surface of the particles increased the relative stability of C-type Pr_nO_{2n-2}. In the 1st heating run of commercial powders 5N, the large current peak for σ -PrO_x → A-Pr₂O₃ was followed a very small peak. The T_{de} value of the small peaks was the highest. Thus, we may infer that the substances related to H₂O near the surface of the particles functioned with the superlattice structure and the structure itself is closely related to H and OH.

When the Pr(OH)₃ prepared from A-Pr₂O₃ was decomposed, additional peaks was not observed in the XRD pattern of the Pr_nO_{2n-2} phases obtained. The formation or decomposition of Pr(OH)₃ is not the origin of the superlattice structure. It was found that H₂O vapor dissolves in CaF₂-related Pr_nO_{2n-2} as forms of H and OH during the annealing around 773 K. Thus, it may be inferred that the structure was induced by the dissolved H and OH during aging around room temperature and appeared on an early stage of the precipitation as Pr(OH)₃ or PrOOH. If it is true, the structure possibly presents near the surface of the particles and could function with the H and OH which dissolved or adsorbed near the surface. However, the superlattice structure, which increases the relative stability of C-type Pr_nO_{2n-2} is not the surface structure, because it could be reflected by additional peaks in powder XRD pattern. The effect on T_{de} for σ -PrO_x → A-Pr₂O₃ arises kinetically and not from a change in the thermodynamic properties, in view of the fact that the shape of the I - T - t curve for σ -PrO_x phase during the 1st heating run in Fig. 4 was different from the other ones.

(Experiment 5) The results of evolved gas analysis for commercial Pr₆O₁₁ powder 3N are shown in Fig. 8. The rod number of the powder was different from that used in the other experiment, and its XRD pattern exhibited very small additive peaks around $2\theta = 29^\circ$. A slight but clear evolution of H₂O accompanying the phase transition: σ -PrO_x → A-Pr₂O₃ can be observed in this

figure; an increase in $P(\text{H}_2)$ at 1323 K is attributable to the dissociation of H₂O induced with a decrease in $P(\text{O}_2)$. The results may imply that the superlattice structure in C-type Pr_nO_{2n-2} is closely related to the dissolved H and OH and disappears with evolution of H₂O vapor through this phase transition.

V. Conclusion

In order to clarify the effect of the substances related to H₂O present in Pr_nO_{2n-2} on the phase transition: σ -PrO_x or C-Pr₂O₃ → A-Pr₂O₃, five experiments were performed. Conclusions derived are:

- (1) H₂O vapor dissolves in CaF₂-related Pr_nO_{2n-2} as forms of H and OH, and decreases the relative thermal stability of the phase to A-Pr₂O₃.
- (2) A superlattice structure is induced near the surface of the particulate form by the dissolved H and OH during aging at a lower temperature, and suppresses kinetically the phase transition: σ -PrO_x or C-Pr₂O₃ → A-Pr₂O₃.
- (3) H, OH and H₂O function with the superlattice structure near the surface of the particulate form and suppress the phase transition kinetically.
- (4) The structure disappears through the phase transition, accompanying the evolution of H₂O vapor.

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