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Proposal structure of $PR_{88}O_{160}$ phase in binary, rare earth higher oxides

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Abstract

Using Kang–Eyring's fluorite-type module theory and experimental diffraction data we propose a structure model of the $Pr_{88}O_{160}$ phase and interpret the solid eutectic reaction of the $Pr_{88}O_{160}$ phase by comparison of the proposal structure with the determined structures of Pr_9O_{16}, $Pr_{40}O_{72}$, and $Pr_{24}O_{44}$.

Keywords: $Pr_{88}O_{160}$ phase; Structure; Module theory

1. Introduction

In 1966, Hyde et al. [1] showed that the tensimetric isobaric data for praseodymium oxides indicated a stable phase with a composition $PrO_{1.818}$ under oxygen partial pressures of 30–205 Torr in the temperature range 420–450 °C. This composition has not been prepared as a single phase because it is very easy to decompose to the $PrO_{1.778}$ and $PrO_{1.80}$ phases during heating up from the α-phase, but it also is easy to transform into $PrO_{1.833}$ as it is cooled down. Therefore, the eutectic reactions of the $PrO_{1.818}$ always occur as Fig. 1 shown.

Turcotte et al. had given the structural information of this phase from high temperature X-ray diffraction [2]. Tuenge and Eyring [3] presented the electron diffraction pattern of $PrO_{1.818}$ phase showing a completely different structure from $CeO_{1.818}$ and $TbO_{1.818}$ phases (Fig. 2). Since 1966, there has been no successful resolution of the structure of this phase in harmony with the thermodynamic and diffraction data. In this paper, we use Kang–Eyring fluorite-type module theory to propose the structure of this phase and to understand the thermodynamic features.

2. Modeling process

Based on Kang–Eyring module theory [4], the composition of any rare earth higher oxides should have the formula as follows:

$$(\theta + \tau)R_4O_7 + \nu R_4O_6 + \delta R_4O_8$$

in which R_4O_7, R_4O_6, and R_4O_8 are the compositions of modules with one, two, or none oxygen atoms missing, respectively. θ and τ are the numbers of the U- and V-type module with one oxygen missing, respectively. ν and δ are the numbers of modules with two or no oxygen missing, respectively.

If n designates the number of the fluorite-type modules in an unit cell of the homologous series phase and m is the number of times in which the eight oxygen sites have equally been vacant, then the composition of the homologous series should be $R_{4n}O_{8n-8m}$, where $n = (\theta + \tau + \nu + \delta)$ and $8m = (\theta + \tau + 2\nu)$.

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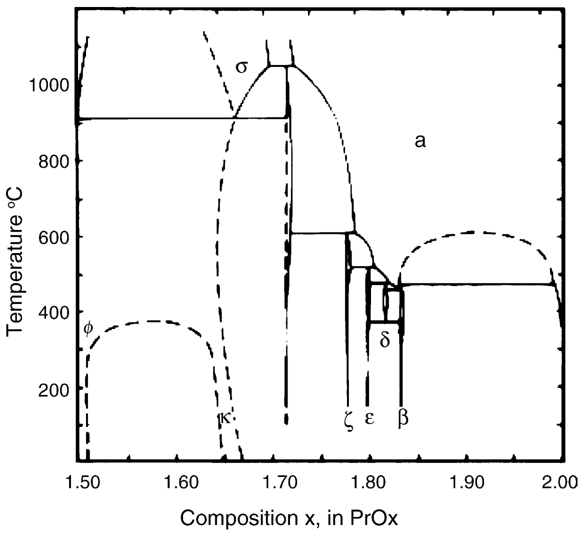

Fig. 1. PrO_x phase diagram.

This is called the modular generic formula and composition. If we use the number of each type of atom contained in a crystallographic unit cell as the generic chemical formula, it would be R_nO_{2n-2m} since there are four atoms in each fcc unit cell. This formula rationalizes all of the experimentally discovered homologous phases.

Based on the electron diffraction and gravimetric data, this phase should have 88 modules ($n = 88$) and eight times of the eight oxygen sites to be equally vacant ($m = 8$). It contains 16 oxygen vacancies in a crystallographic unit cell. Therefore, the module content would be 24F32U32V. It is impossible to contain any W modules because this phase is more oxidized than the ε-phase, PrO_{1778} having no W modules in its structure. The W module may appear if it is directly related to the ε-phase Pr_7O_{12} ($PrO_{1.714}$), for example, $n = 19$ and 62.

From electron diffraction pattern, the intensities distribution of the diffraction spots seems to have similar symmetry as $Pr_{40}O_{72}$ and $Pr_{24}O_{44}$. Using the symmetry information and assembling rule of Kang–Eyring module theory, a proposal structure for this phase is given as Fig. 3. Fig. 4 shows the determined structures of Pr_9O_{16}, $Pr_{40}O_{72}$, and $Pr_{24}O_{44}$. In comparison with the structure of Pr_9O_{16}, $Tb_{11}O_{20}$, $Pr_{40}O_{72}$, and $Pr_{24}O_{44}$ [5–8], we may find that the structure of $Pr_{88}O_{160}$ phase have the basic structural characters of $Tb_{11}O_{20}$, $Pr_{40}O_{72}$, which means that a mosaic of the structure of $Tb_{11}O_{20}$ at center of the unit cell and the pair oxygen vacancies in $Pr_{40}O_{72}$ symmetrically distributed along 1/4 and 3/4 *c*-axis of the unit cell, where the glide plan located. Two isolated oxygen vacancies located near the origin and end of the *c*-axis of the unit cell. They are related each other by the inversion center of the unit cell. It may be seen as intergrowth of the pair oxygen vacancies and the mosaics in the structure of $Tb_{11}O_{20}$. That makes its unit cell so different from $Ce_{11}O_{20}$. $Tb_{11}O_{20}$, if it is oxidized, the pair oxygen vacancies will be single vacancy, and then the system will turn into the structure of $Pr_{24}O_{44}$.

A comparison of $Tb_{11}O_{20}$ with the $Pr_{88}O_{160}$ structures reveals that there are more cation having coordination numbers seven and six in $Pr_{88}O_{160}$ than in $Tb_{11}O_{20}$ phase, even the composition is the same. That may indicate a difference of valence variability between the praseodymium and terbium cations due to the electron configuration of these two rare earth elements. It seems the pairs of oxygen vacancies in PrO_x phase make a cation having six coordination environments, but the isolated oxygen vacancy in $Ce_{11}O_{20}$, $Tb_{11}O_{20}$ constructs a seven-coordination environment for Ce and Tb cation.

3. Summary

The fluorite-type module theory provides a basis for a comprehensive understanding of the relationship between the compositions and structures of the homologous series. Structure of the $Pr_{88}O_{160}$ phase is proposed based on the electron diffraction pattern and gravimetric data. The solid eutectic reactions between $PrO_{1.778}$, $PrO_{1.80}$, $PrO_{1.818}$, and $PrO_{1.833}$ have been elucidated by the structure feature of these phases.

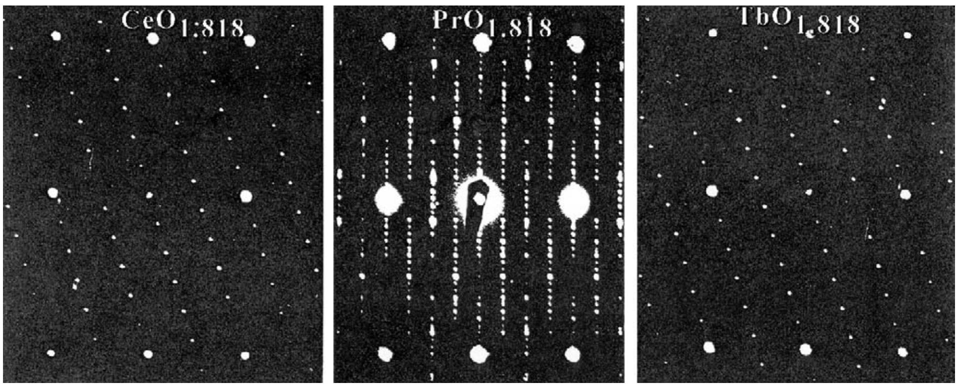

Fig. 2. The $CeO_{1.818}$, $PrO_{1.818}$, and $TbO_{1.818}$ phases demonstrated different diffraction patterns.

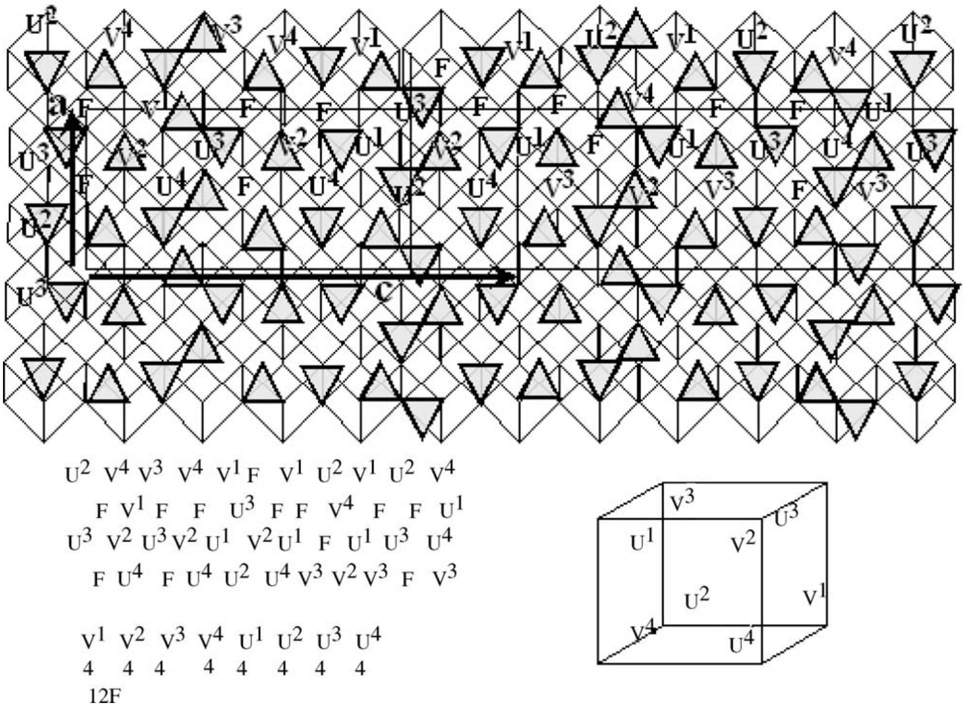

Fig. 3. A proposal structure of $Pr_{88}O_{160}$ phase.

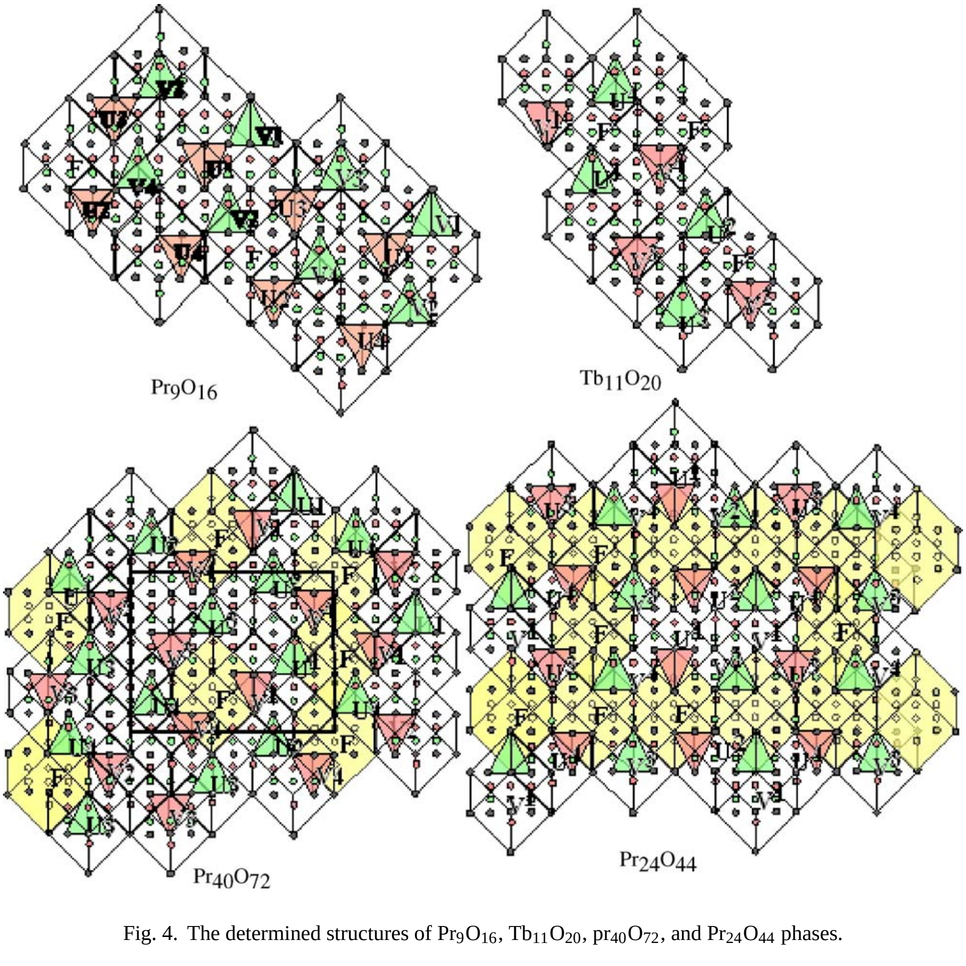

Fig. 4. The determined structures of Pr_9O_{16}, $Tb_{11}O_{20}$, $pr_{40}O_{72}$, and $Pr_{24}O_{44}$ phases.

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