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Systematics of the phase behavior in lanthanide sesquioxides

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Abstract

The crystal structures of the lanthanide (Ln) sesquioxides, Ln_2O_3, are systematized according to the radius ratio η between the lanthanide ion crystal radius and the "equivalent formula unit radius" which is derived from the unit cell volume of the sesquioxide. New criteria for the stability range of each structure are given quantitatively. These criteria were used to correlate the phase transformations of lanthanide sesquioxides with two critical values of η: $B \rightarrow A$ occurs at $\eta = 2.26$; $C \rightarrow B$ occurs at $\eta = 2.42$. The $C \rightarrow B$ phase transformation pressure in Eu_2O_3 was estimated. The polymorphism of lanthanide sesquioxides at any temperature and pressure can be estimated using these new systematic critical values.

1. Introduction

Understanding the polymorphic relationships among the lanthanide sesquioxides is fundamental to any study involving these compounds and is of special importance when one considers the use or reaction of a lanthanide sesquioxide at elevated temperature and/or pressure. Polymorphism is common to these sesquioxides, and no fewer than five distinct crystalline types have been described. Below about 2000 °C three types, designated as A, B, and C, are commonly observed, while above that temperature types designated as H and X are formed [1]. In the present paper we shall address only the phase behavior of the structure types A, B and C and present new systematics to correlate them.

The phase transformation from C type to B type to A type as the temperature increases is well known for several of the lanthanide sesquioxides. This same order of phase transformations can be observed at a constant temperature with decreasing atomic number of the lanthanide. The $C \rightarrow B \rightarrow A$-type phase transformations occur with an increase in coordination number (CN) and with an increase in density, both at odds with the usual expectations for phase changes occurring with increasing temperature. This work attempts to solve these apparent problems.

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It is clear that the radius of a lanthanide ion is critical to the polymorphic relationship of its sesquioxides. As stated by Roth and Schneider [2], the sesquioxides of the larger lanthanide cations crystallize in the hexagonal structure (A type), those of the smallest cations form the cubic structure (C type), and the sesquioxides of the intermediate cations crystallize in the monoclinic structure (B type). Such a statement is correct qualitatively but is not quantitatively applicable. Thus, it would be useful for a systematic study of the polymorphism in the lanthanide sesquioxides to yield new quantitative criteria for predicting the phase behavior of these materials.

2. Method

The three crystal structures observed below 2000 °C in the lanthanide sesquioxides are designated as the A, B, and C types. Details of the crystallography are given in the following.

The hexagonal, A-type sesquioxide is described by space group $P\bar{3}m1$ (D_{3d}^3) (*International Tables for Crystallography* number 164) with one formula unit per unit cell ($Z=1$). The two lanthanide atoms in the unit cell are both seven coordinated, with four oxygen atoms closer than the other three, and are located in the 2d Wyckoff positions of $3m$ (C_{3v}) site symmetry.

The monoclinic, B-type sesquioxide, with six formula units per unit cell ($Z=6$), is described by space group $C2/m$ (C_{2h}^3) (*International Tables for Crystallography* number 12). The lanthanide atoms are seven and six coordinate and are located in three different 4i positions of m (C_s) site symmetry.

The b.c.c., C-type sesquioxide is described by space group $Ia3$ (T_h^7) (*International Tables for Crystallography* number 206). The unit cell contains 32 lanthanide atoms and 48 oxygen atoms ($Z=16$). The lanthanide atoms are all six coordinate and are located in the 8a positions of 3 (S_6) site symmetry and in the 24d positions of 2 (C_2) site symmetry.

We first arrange all lanthanide sesquioxides, Ln_2O_3(Ln = lanthanide), according to their crystal structure. In this way, all Ln_2O_3 crystals are distributed among the three possible crystal structures. The experimental data on the polymorphism and structures for the lanthanide sesquioxides were taken from Eyring's work [1].

The formula volume V_0 of each sesquioxide can be calculated from the experimental lattice parameters listed in ref. 1 and knowledge of the number of formula units per unit cell. For the A-type structure, $V_0=\sqrt{3}a^2c/2$, for the B-type structure, $V_0=(abc \sin \beta)/6$, and for the C-type structure, $V_0=a^3/16$. The results of our calculations are given in Table 1.

We define an "equivalent formula unit radius" R_m as

$$R_m=[(3/4\pi)V_0]^{1/3} \qquad (1)$$

where V_0 is the formula volume. The physical meaning of R_m is similar to the Wigner–Seitz radius. The values of R_m for each compound are listed in Table 1.

TABLE 1.

Formula unit volume V_0, equivalent formula unit radius R_m, cationic crystal radius R^{3+} and radius ratio η for three lanthanide sesquioxide crystal structures

Ln	A-type structure				B-type structure				C-type structure			
	V_0 (Å^3)	R_m (Å)	R^{3+} (Å)	η	V_0 (Å^3)	R_m (Å)	R^{3+} (Å)	η	V_0 (Å^3)	R_m (Å)	R^{3+} (Å)	η
La	82.30	2.70	1.24	2.18								
Ce	79.42	2.67	1.21	2.21								
Pr	77.52	2.65	1.20	2.21					86.69	2.75	1.13	2.43
Nd	76.21	2.63	1.19	2.21					85.02	2.73	1.12	2.44
Pm	74.53	2.61	1.18	2.21					82.96	2.71	1.11	2.44
Sm					74.80	2.61	1.13	2.31	81.70	2.69	1.10	2.45
Eu					73.12	2.59	1.12	2.31	80.25	2.68	1.09	2.46
Gd					72.08	2.58	1.11	2.32	79.00	2.66	1.08	2.46
Tb					71.20	2.57	1.09	2.36	77.17	2.64	1.06	2.49
Dy					69.90	2.56	1.08	2.37	75.81	2.63	1.05	2.50
Ho					68.47	2.54	1.07	2.37	74.58	2.61	1.04	2.51
Er					67.56	2.53	1.06	2.39	73.33	2.60	1.03	2.52
Tm					66.43	2.51	1.05	2.39	72.08	2.58	1.02	2.53
Yb					65.22	2.50	1.04	2.40	70.98	2.57	1.01	2.54
Lu					64.56	2.49	1.03	2.42	70.12	2.56	1.00	2.56

We took the ionic radii for all lanthanide cations, Ln^{3+}, from Shannon's crystal radii (CR) [3] and designate them here as R^{3+}. According to Shannon the cationic radius is dependent on the CN. Thus, in the C-type and A-type structures, we used the values of CR corresponding to CNs of 6 and 7 respectively. For the B-type structure we used a value of the cationic radius interpolated for a CN of 6.5, because both 6 and 7 are operative CNs in this structure. These CR values are tabulated in Table 1 under R^{3+}. According to Roth and Schneider [2], the CR is the critical factor in determining which of the three crystal structures is the stable structure. Examination of the data in Table 1 confirms that their statement is qualitatively correct.

Finally we divided the "equivalent formula unit radius" by the crystal radius R^{3+} to yield a dimensionless parameter η:

$$\eta = R_m / R^{3+} \qquad (2)$$

After this normalization or scaling of the radii, we found a clear, quantitative correlation between the value of η and the exhibited crystal structure.

3. Results and discussion

Using our parameter η and the experimental crystal structure data for the lanthanide sesquioxides, the room temperature and pressure (RTP) section of a generalized phase diagram for the lanthanide sesquioxides was constructed and is reproduced in Fig. 1. In this representation it becomes clearly evident that the A-type crystal structure is stable when $\eta < 2.25$, the B-type structure is stable when $2.30 < \eta \leqslant 2.42$, and the C-type structure is stable when $2.43 \leqslant \eta$. Therefore it is likely that the B → A and C → B phase transformations in the lanthanide sesquioxides occur at certain constant critical radius ratios:

$$\eta = 2.26 \pm 0.04 \qquad \mathrm{B} \rightarrow \mathrm{A}\ \text{transformation} \tag{3a}$$

$$\eta = 2.42 \pm 0.02 \qquad \mathrm{C} \rightarrow \mathrm{B}\ \text{transformation} \tag{3b}$$

The effect of the number of 4f electrons on the value of η can also be seen in Fig. 1. Within each structure type, η increases with the number of 4f electrons, consistent with the well-known lanthanide contraction.

Our scaling of R^{3+} has produced a quantitative description for the phase behavior of all lanthanide sesquioxides and determined the critical values for their phase transformations as given by eqns. (3a) and (3b). Such a scaling method is very helpful to understand the nature of the phase transformations and to predict when they occur.

A number of investigators have studied the effects of both temperature and pressure on the polymorphism of the lanthanide sesquioxides. Both temperature and pressure separately can induce C → B → A transformations. As mentioned in the introduction to this paper, the density of the Ln_2O_3 compounds increases from C to B to A, which is at odds with the usual expectation for a phase change occurring with an increase in temperature. To understand better the nature of these phase transformations, we need to examine the change in the characteristics of the chemical bonding involved.

The C → B → A transformation sequence is accompanied by a change in the characteristics of the chemical bonding involved, especially for the M—O bonds. Shannon has summarized the effects of covalence on the interatomic

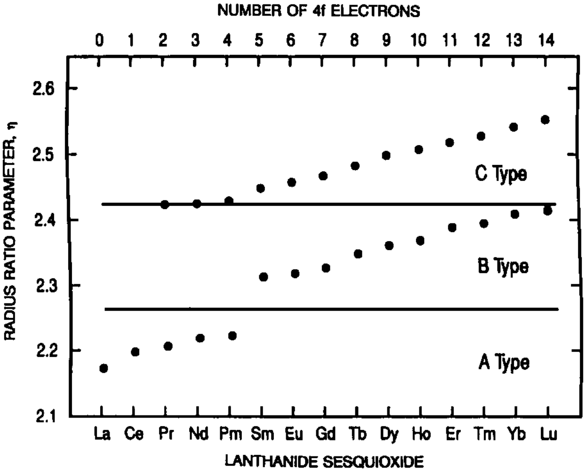

Fig. 1. Plot of the η value for the lanthanide sesquioxides according to their crystal structure and number of 4f electrons.

M–O distances [3]. According to Shannon, the covalence shortens the M–O bonds as the electronegativity of metal or oxygen decreases. From this point of view, this transformation sequence (C → B → A) represents an increase in covalence in the M–O bonding or a decrease in the electronegativity of metal or oxygen. Our previous study of the effect of pressure on C-type Eu_2O_3 showed that the electronegativity of Eu^{3+} decreases with pressure [4]. We argued that this change in the Eu^{3+} ion's electronegativity with increasing pressure is the driving mechanism for the C → B phase transformation in Eu_2O_3. Thus, it is likely that, with respect to the C-type structure, the B-type structure is a "high pressure phase" rather than a "high temperature phase". The C → B → A transformation sequence should be induced by increasing pressure, because increasing pressure favors higher densities [5]. The effect of temperature in a phase transformation can be modeled mathematically by the Clausius–Clayperon equation:

$$dP_t/dT = \Delta S/\Delta V \qquad (4)$$

The entropy increases and volume decreases in the C → B → A transformation sequence. Thus, with an increase in temperature, the transformation pressure could be lowered. It has been observed that pressure indeed induces a C → B phase transformation in some lanthanide sesquioxides and affects the C → B phase transformation temperature [6–8]. Thus, through our systematic study, we can understand better the nature of the phase transformations in lanthanide sesquioxides.

Equations (3a) and (3b) are very useful for predicting the transformation pressures P_t in the C → B → A phase transformation sequence, if the equation of state (EOS) or compressibility of the corresponding sesquioxides is known. As an example, we shall estimate here the transformation pressure for the C → B phase transformation in Eu_2O_3.

There are no EOS and compressibility data for C-type Eu_2O_3. We can only estimate its compressibility from the value of the bulk modulus of B-type Eu_2O_3 (see Appendix A). Applying eqn. (3b), we can obtain the critical value of R_m, which corresponds to the formula volume at which the C → B phase transformation occurs. For Eu_2O_3, $R_m = 2.638$ Å, and the corresponding transformation volume V_t is about 76.90 Å^3. There is an approximate relation:

$$V_t/V_0 \approx (1 - \gamma P_t) \qquad (5)$$

where V_0 is the formula volume of C-type Eu_2O_3 at room temperature and pressure, γ is its compressibility, and P_t is the transformation pressure. The value of P_t estimated from eqn. (5) is 3.5 GPa. The experimentally observed value is about 8 GPa which is probably not the equilibrium value but an overpressure [8]. Taking into account this fact and the crude approximation of γ, the agreement between the experimental and calculated values is quite satisfactory.

The polymorphism of the lanthanide sesquioxides at different temperatures can be examined through the use of eqns. (3) and (5). The method is that we first calculate the transformation pressure P_t, and then, through the

Clausius–Clayperon equation, we can estimate the transformation temperature at room pressure, because the volume and entropy changes between the two phases are available in most of the cases [1, 6].

Equations (3) and (5) thus provide a simple method to estimate phase transformation pressures at room temperature and phase transformation temperatures at ambient pressure. Such estimations combined with the Clausius–Clayperon equation allow one to predict quantitatively the polymorphism of the lanthanide sesquioxides at any pressure and temperature.

4. Conclusion

In the present work we establish new criteria for the polymorphism of the lanthanide sesquioxides. The ratio R_m/R^{3+} was used as a parameter, instead of just R^{3+}. With this parameter a quantitative description of the stability of each type of sesquioxide structure was given which can be used to estimate the polymorphism of lanthanide sesquioxides at any temperature and pressure.

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Appendix A

There are no experimental equation of state and compressibility data for C-type Eu_2O_3. We used the value of the bulk modulus B_0 of B-type Eu_2O_3 to obtain that for C-type Eu_2O_3 from

$$B_0V_0 = C \quad \text{(A1)}$$

where C is dependent on the structure type and ionic charge [A1]. Considering the similarity of the two structures (see Figs. 27(b) and 27(c) in ref. A2), we used an approximate relationship

$$(B_0V_0)_{\mathrm{B\ type}} \approx (B_0V_0)_{\mathrm{C\ type}} \tag{A2}$$

B_0 can be obtained from the shear modulus μ and Young's modulus Y through

$$Y = 9B_0\mu/(\mu + 3B_0) \tag{A3}$$

and the values of Y and μ as given in ref. A3. Thus, B_0 for B-type Eu_2O_3 is 91 GPa. Using eqn. (A2), one obtains for C-type Eu_2O_3 that B_0 is 83 GPa. Therefore, we estimate the compressibility γ of C-type Eu_2O_3 to be 1.2×10^{-2} GPa^{-1}.

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