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Critical evaluation of thermodynamic properties of rare earth sesquioxides (RE = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y)

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ABSTRACT

In order to develop the thermodynamic database containing rare earth sesquioxides (RE_2O_3), accurate thermodynamic descriptions of all stable and metastable RE_2O_3 phases are required. Rare earth sesquioxides have five polymorphs, which are (from low to high temperature) the cubic phase (C), the monoclinic phase (B), the hexagonal phase (A), the high temperature hexagonal phase (H), and the high temperature cubic phase (X). However, the thermodynamic property data of all polymorphs available in the literature are insufficient. In particular, the thermodynamic data for the phases stable only at high temperatures and for metastable phases are not well investigated. In this study, all ΔH^o_{298K}, S^o_{298K}, C_P (or heat content) and phase transition temperature (T_{tr}) data available in the literature for each rare earth sesquioxide were collected and critically evaluated based on the sample preparations, experimental procedures and characterization techniques. Relationships between ΔH^o_{298K}, S^o_{298K}, and T_{tr} against the ionic radii of the entire rare earth cations were then established and missing thermodynamic information was predicted based on the general trends. In these ways, the accurate and consistent Gibbs energies of all stable and metastable RE_2O_3 phases (RE = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) were prepared. These Gibbs energy data can be readily used for the development of a comprehensive thermodynamic database containing rare earth oxides.

1. Introduction

RE_2O_3 (rare earth sesquioxides) typically include the whole series of lanthanide sesquioxides from La_2O_3 to Lu_2O_3 and two rare earth like sesquioxides, Y_2O_3 and Sc_2O_3. The "sesquioxide" simply indicates the oxide which has two moles of cations and three moles of oxygen anions in each mole of oxide. RE_2O_3 have a wide range of applications because of their unique physical and chemical properties. One of the most important applications is to use RE_2O_3 as ZrO_2 stabilizers. ZrO_2 is commonly used as heat resistant material on gas engine turbines to protect Ni- based superalloy. The most widely used RE_2O_3 stabilized ZrO_2 system is YSZ (yttrium stabilized zirconia), which was originally developed by NASA in the mid 1970s. Nowadays, a lot of efforts have been poured into researching of more advanced alternative RE_2O_3-stabilized-ZrO_2 aiming lower thermal conductivity and better durability [1]. Several candidates are Gd_2O_3, Sm_2O_3 and Nd_2O_3 sesquioxides [1]. Rare earth metals and oxides are highly desired in battery, advanced ceramics and military industries. Although rare earth oxides have a wide range of strategic and critical applications, the thermodynamic properties and phase diagrams are still not well determined. For example, neither the Gibbs energies for all stable nor metastable RE_2O_3 are accurately established.

Several years ago, a comprehensive review of thermodynamic properties of RE_2O_3 was performed by Zinkevich [2], who studied standard enthalpy, entropy, C_p and phase stabilities. Some of the thermodynamic properties of metastable phases were also deduced from the calculated phase diagrams of binary RE'_2O_3-RE''_2O_3 systems. Clear disagreements between some assessed results by Zinkevich and experimental data regarding transition temperatures of RE_2O_3 were found. Some of the transition enthalpy and temperature of metastable RE_2O_3 were not clearly reported in the work of Zinkevich. Furthermore, the experimental transition enthalpy of A → H transition adopted by Zinkevich was questionably large, which can induce significantly unreliable estimation of the Gibbs energy of A and H phases. Therefore, it is necessary to critically review all the thermodynamic properties of RE_2O_3 again to produce a more unequivocal and consistent thermodynamic data for the entire RE_2O_3.

The purpose of this study is to obtain a set of consistent thermodynamic data for all stable and metastable RE_2O_3 (entire lanthanide sesquioxides from La_2O_3 to Lu_2O_3 and two rare earth like sesquioxides, Y_2O_3 and Sc_2O_3). There are five solid polymorphs and one liquid phase for each RE_2O_3. In this study, the literature data were analyzed and categorized into three parts: (1) the phase transition temperatures, (2)

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the standard enthalpies of formation, standard entropies and heat capacity functions, and (3) the enthalpies and entropies of transitions. In the first part, the thermal stability and phase transition of each RE_2O_3 was discussed. The best set of transition temperature values for stable and metastable RE_2O_3 phases were determined. In the second part, the ΔH°_{298K} and S°_{298K} of stable RE_2O_3 phases were assessed based on the numerous experimental data. In the third part, the enthalpy and entropy of stable and metastable phase transitions were assessed from direct experimental data and indirect phase diagram data.

2. Temperatures of polymorphic phase transitions

The stable crystal form of the RE_2O_3 at room temperature is varied with the atomic number of RE. Lanthanide oxides from La_2O_3 to Nd_2O_3, generally named as the light RE_2O_3, are stable in form of hexagonal structure (A phase); Sm_2O_3 to Gd_2O_3, named as the middle RE_2O_3, are stable in either monoclinic (B phase) or cubic structure (C phase); Tb_2O_3 to Lu_2O_3, named as the heavy RE_2O_3, are stable only in cubic form (C phase). The Pm_2O_3, which positions between the light and middle RE_2O_3, is stable in C phase. That is, three stable RE_2O_3 phases C, B and A exist at room temperature depending on the RE_2O_3. These phases stable at room temperature transform to high temperature hexagonal phase (H phase), and high temperature cubic phase (X phase) at about 2400 K. Foex and Traverse [3] reported that these two high temperature phases are not quenchable to room temperature.

Ideally, the polymorphic transition of RE_2O_3 occurs in the sequence of C→B→A→H→X→L from room temperature to high temperature. However, some transitions are inviable at atmospheric pressure especially when ionic radius of RE [4] becomes small (ionic radius of rare earth cation becomes smaller with increasing atomic number of RE). According to experimental data, phase transition of the light RE_2O_3 (RE = La to Nd) follows the sequence of A→H→X→L. The middle RE_2O_3 (RE = Sm to Gd) and Pm_2O_3 obey the ideal transition sequence of C→B→A→H→X→L; and RE_2O_3 from Tb_2O_3 to Dy_2O_3 generally obey the ideal transition without A phase, C→B→H→X→L; Ho_2O_3 and Y_2O_3 have the transition sequence without A or X phases, C→B→ H→ L; RE_2O_3 from Er_2O_3 to Yb_2O_3 transform in the order of C→H→L; Lu_2O_3 and Sc_2O_3 maintain C structures until their meltings.

The importance of proper understanding of polymorphic transition urged many investigations starting from Goldschmidt et al. [5] in 1925. They presented the stable polymorphs of RE_2O_3 at room temperature. In 1961, Warshaw and Roy [6] studied the C→B transition temperatures of selective RE_2O_3 (RE = La–Nd, Sm–Gd, Tb, and Dy) using classical quenching technique with XRD (X ray diffraction) phase analysis. The first comprehensive study for the phase transitions of the entire lanthanide RE_2O_3 series from room temperature to melting temperature was carried out by Foex and Traverse [3] using *in situ* thermal and XRD analysis. In their study, the T_{tr} (transition temperature) and T_{fus} (fusion temperature) were plotted depending on the atomic number of the RE to present the provisional phase transition diagram of RE_2O_3. A few years later, Tresvyatkii et al. [7] measured the T_{tr} of some RE_2O_3 (RE = La to Nd, Sm, Gd, Tb to Er, Yb and Y) using DTA (differential thermal analysis) and XRD methods. The reversibility of the phase transitions with increasing and decreasing temperature was demonstrated in their work. Coutures et al. [8] carried out selective binary phase diagram studies of the La_2O_3–RE_2O_3 systems (RE = Nd, Gd, Sm, Dy, Ho, Tm, Er, Yb, and Y) using TA (thermal analysis) and XRD methods. They produced the phase diagrams at high temperatures mainly involving H, X and liquid phases. The T_{tr} of pure RE_2O_3 could be extracted from these binary phase diagrams. The results of Coutures et al. [8] are in excellent agreement with their previous work by Foex and Traverse [3]. The most recent comprehensive study of T_{tr} of RE_2O_3, excluding Pm_2O_3 and Eu_2O_3, was performed by Shevthenko and Lopato [9] in 1985 using DTA method in controlled gaseous environment up to 2873 K and TA method in air using solar radiation heating up to 3273 K. All the results from these four most comprehensive investigations and some fragmental studies are discussed below, and compared for each phase transition in the following Sections 2.2–2.6. The best and most reliable set of data were selected in this work and hypothetical transition temperatures for metastable phases were predicted. Some necessary comparisons between this work and the previous assessment from Zinkevich [2] were also made.

Table 1
Summary of the C→B phase transition temperatures. ASS: assessment; DT: decrease temperature; DTA: differential thermal analysis; EST: estimation; IT: increase temperature; QM: quenching method; TA: thermal analysis; XRD: X-ray diffraction; UNK: unknown method.

Sesquioxides	Ionic radii, Å	T_{trans}, K	Techniques	References
Y_2O_3	0.892	2756	EST	This work
Sc_2O_3	0.73	5099	EST	This work
La_2O_3	1.061	(−786)	EST	This work
Ce_2O_3	1.034	(−369)	EST	This work
Pr_2O_3	1.013	(−21)	EST	This work
Nd_2O_3	0.995	285	EST	This work
Pm_2O_3	0.982	973	QM, XRD	Chikalla, 1972 [10]
		457	EST, ASS	Zinkevich, 2007 [2]
		973	ASS	This work
Sm_2O_3	0.964	1173–1273	QM, XRD	Roth, 1960 [11]
		1153	QM, XRD	Warshaw, 1961 [6]
		676	EST, ASS	Zinkevich, 2007 [2]
		1153	ASS	This work
Eu_2O_3	0.950	1323	QM, XRD	Curtis, 1959 [13]
		1348	QM, XRD	Roth, 1960 [11]
		1373	QM, XRD	Warshaw, 1961 [6]
		894.5	EST, ASS	Zinkevich, 2007 [2]
		1348	ASS	This work
Gd_2O_3	0.938	1523	QM, XRD	Roth, 1960 [11]
		1508	QM, XRD	Warshaw, 1961 [6]
		1561	UNK	Kolitsch, 1995 [16]
		1425	EST, ASS	Zinkevich, 2007 [2]
		1561	ASS	This work
Tb_2O_3	0.923	2113	QM, XRD	Warshaw, 1961 [6]
		1829	XRD, IT	Foex, 1966 [3]
		1679	XRD, DT	Foex, 1966 [3]
		1823	EST, ASS	Zinkevich, 2007 [2]
		1823	ASS	This work
Dy_2O_3	0.908	2223	TA	Foex, 1966 [3]
		2223	DTA	Tresvyatkii, 1971 [7]
		2140	TA	Coutures, 1976 [8]
		2253	DTA	Shevthenko, 1985 [9]
		2263	EST, ASS	Zinkevich, 2007 [2]
		2238	ASS	This work
Ho_2O_3	0.894	2456	TA	Foex, 1966 [3]
		2463	DTA	Tresvyatkii, 1971 [7]
		2459	TA	Coutures, 1976 [8]
		2463	DTA	Shevthenko, 1985 [9]
		2458	EST, ASS	Zinkevich, 2007 [2]
		2460	ASS	This work
Er_2O_3	0.881	2593	DTA	Tresvyatkii, 1971 [7]
		2593	EST, ASS	Zinkevich, 2007 [2]
		2600	ASS	This work
Tm_2O_3	0.869	2913	EST	This work
Yb_2O_3	0.858	3195	EST	This work
Lu_2O_3	0.848	3315	EST	This work