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High-temperature thermodynamic properties of Ln_2BaO_4 (Ln = Nd, Gd, Dy, Ho, Er) compounds

Z.S. Vakhovskaya [*], A.L. Voskov, M.L. Kovba, I.A. Uspenskaya

Department of Chemistry, Moscow State University, Vorob'evy Gory, Moscow 119899, Russia

Abstract

The temperature dependence of the Gibbs energies of formation of Ln_2BaO_4 (Ln = Nd, Gd, Dy, Ho, Er) from simple oxides was determined by the electromotive force method with a fluorine-ion electrolyte in the temperature range 1010–1190 K.

Keywords: Standard Gibbs energies of formation; EMF; Ln_2BaO_4

1. Introduction

Ever since the discovery of high-temperature superconductivity of the ceramic materials, research in the area of synthesis of new superconductors and improving their superconductive (J_c) properties are unabating. A study of thermodynamic properties in ceramic systems is essential for the optimization of a synthesis of superconducting materials as well as for the evaluation of their stability to phase and chemical transformation. Recently, precursor mixtures utilizing Ln_2BaO_4 (Ln = Nd, Sm) (rather than $Ln_4Ba_2Cu_2O_5$) and $LnBa_2Cu_3O_z$ have been reported to enhance significant improvement of superconductivity [1,2]. The purpose of this work was to determine the thermodynamic properties of Ln_2BaO_4 (Ln = Nd, Gd, Dy, Ho, Er).

The thermodynamic properties of Ln_2BaO_4 (Ln = Nd, Sm, Eu and Gd) were studied by the electromotive force (EMF) method with a fluorine-ion electrolyte [3]. The thermodynamic function values recommended in ref. [3], however, raise certain questions. First, measurements were performed in the temperature range 900–1175 K. According to ref. [4], reproducible EMF values cannot be obtained for the BaZrO + ZrO_2 electrode at these temperatures. Secondly, the enthalpies of formation of Ln_2BaO_4 reported in this work −(93–110) kJ/mol were several times higher than those characteristic of similar complex oxides −(20–40) kJ/mol [5].

2. Experimental

According to the preliminary X-ray data, Ln_2BaO_4 exists in equilibrium with BaF_2 and Ln_2O_3 at temperatures below 1300 K. Bearing this in mind, the thermodynamic properties of Ln_2BaO_4 in the temperature range 1010–1190 K were determined by measuring the EMF (E) of the galvanic cell

$$(-)\mathrm{Pt},\ O_2\,|Ln_2BaO_4,\ BaF_2,\ Ln_2O_3|\ BaF_2\,|CaO,\ CaF_2|\ \mathrm{Pt},\ O_2(+) \qquad \text{(I)}$$

We used the $CaO–CaF_2$ equilibrium mixture as a reference electrode instead of $BaO–BaF_2$ (thermodynamic function calculations would be simpler with the latter) because barium oxide was exceedingly hygroscopic and reactive toward platinum contacts at high temperatures and could form BaO_{1+x} solid solutions in an oxygen atmosphere.

The $Ln_2BaO_4 + Ln_2O_3$ equilibrium electrode mixture was prepared in a solid-state reaction from $BaCO_3$ (pure for analysis) grade and Ln_2O_3 (99.99%). The reagents were preliminarily calcined, $BaCO_3$ at 400 °C and Ln_2O_3 at 900 °C. A mixture of Ln_2O_3 and barium carbonate was then ground in an agate mortar and pressed into pellets. Annealing was performed in three stages with regrinding the samples and

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[*] Corresponding author.
E-mail address: vz@td.chem.msu.su (Z.S. Vakhovskaya).

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pressing them into pellets, 48 h at 950 °C, 144 h at1150 °C and 72 h at 1400 °C. The X-ray patterns obtained with the use of a STOE Powder Diffraction System showed that the product contained the Ln_2BaO_4 phase and corresponding rare-earth oxide.

The apparatus and the procedure for measurements were described in ref. [6]. The temperature dependence of the EMF of cell (I) was measured in a flow of oxygen purified from traces of moisture and CO_2. The EMF reached equilibrium in about 10 h after introducing oxygen in the beginning of measurements and in 3–4 h after changing temperature during experiments. The cell operation time was no longer than 4 days; after this, its EMF irreversibly decreased, probably because of changes in the electro physical properties of the BaF_2 electrolyte as a result of the formation of BaO_{1+x}.

3. Results and discussion

The EMF value was considered equilibrium if it remained constant for several hours and was reproducible in thermal cycling in subsequent experiments. The results obtained are shown in Fig. 1; they were treated by the method of least squares on the assumption of a linear dependence of EMF on temperature:

Nd	$E(\pm 3.3)$ (mV) = $(188 \pm 24) + (17 \pm 22) \times 10^{-3} T$ (K)	T = 1040–1170 K
Gd	$E(\pm 1.4)$ (mV) = $(127 \pm 13) + (30 \pm 12) \times 10^{-3} T$ (K)	T = 1010–1140 K
Dy	$E(\pm 2.8)$ (mV) = $(63 \pm 20) + (92 \pm 17) \times 10^{-3}$T (K)	T = 1040–1170 K
Ho	$E(\pm 5.5)$ (mV) = $(58 \pm 23) + (93 \pm 22) \times 10^{-3}$T (K)	T = 1010–1190 K
Er	$E(\pm 2.9)$ (mV) = $(31 \pm 16) + (119 \pm 14) \times 10^{-3} T$ (K)	T = 1045–1185 K

For the passage of 2 F of electricity, the half-cell and the overall potential-forming reaction in galvanic cell (I) should be written as

$$\begin{array}{l} BaF_2 + Ln_2O_3 + 0.5O_2 + 2e^- \rightarrow Ln_2BaO_4 + 2\tilde{F}^- \\ \quad \text{(working electrode)} \\ CaF_2 + 0.5O_2 + 2e^- \rightarrow CaO + 2\tilde{F}^- \\ \quad \text{(reference electrode)} \\ \hline \quad CaF_2 + Ln_2BaO_4 = CaO + BaF_2 + Ln_2O_3 \end{array} \tag{1}$$

The thermodynamic functions of formation of Ln_2BaO_4 from simple oxides were calculated by combining the temperature dependences of the Gibbs energies (kJ/mol) of reaction (1)

$$\Delta_r G_{(1)} = -nFE_{(I)}$$

and the exchange reaction (2)

$$\begin{array}{l} CaF_2 + BaO = CaO + BaF_2 \\ \Delta_r G_{(2)} = -(66.7 \pm 2.6) + (7.0 \pm 2.7) \times 10^{-3} T \end{array} \tag{2}$$

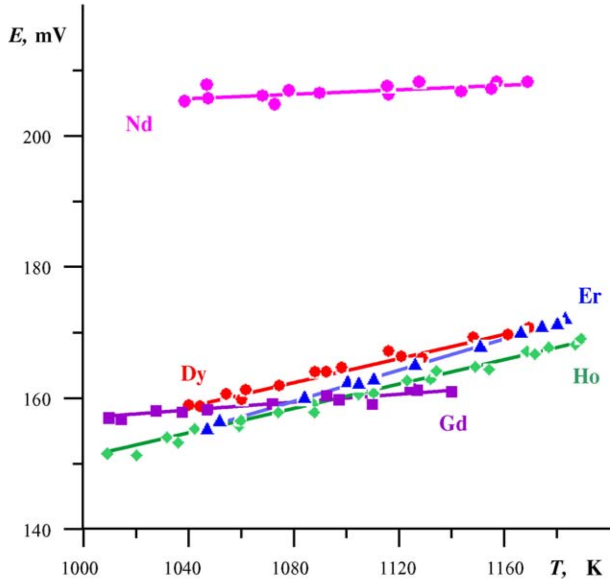

Fig. 1. Temperature dependences of EMF of electrochemical cell (I).

To reduce systematic errors, we used the Gibbs energy of this reaction calculated in ref. [7] from the results of EMF measurements for the cell

$$(-)Pt, O_2\,|BaO, BaF_2|\,CaF_2\,|CaO, CaF_2|\,Pt, O_2(+) \tag{II}$$

rather than from the handbook data on reaction (2).

Accordingly, for the reaction

$$BaO + Ln_2O_3 = Ln_2BaO_4 \tag{3}$$

Nd	$\Delta_f G^\circ_{ox}(\pm 0.6)$ (kJ/mol) = $-(30.4 + 8.6) + (10.3 + 7.0) \times 10^{-3}\, T$
Gd	$\Delta_f G^\circ_{ox}(\pm 0.3)$ (kJ/mol) = $-(42.2 + 6.5) + (12.8 + 5.1) \times 10^{-3}\, T$
Dy	$\Delta_f G^\circ_{ox}(\pm 0.5)$ (kJ/mol) = $-(54.5 + 7.9) + (24.8 + 6.1) \times 10^{-3}\, T$
Ho	$\Delta_f G^\circ_{ox}(\pm 1.1)$ (kJ/mol) = $-(55.5 + 8.4) + (24.9 + 7.0) \times 10^{-3}\, T$
Er	$\Delta_f G^\circ_{ox}(\pm 0.6)$ (kJ/mol) = $-(60.7 + 7.1) + (30.0 + 5.5) \times 10^{-3}\, T$

The obtained enthalpy terms of mixed oxides as a function of rare-earth ionic radii in six-coordination are shown in Fig. 2. There is a visible similarity between the functional dependence $\Delta_f H^\circ(Ln_2BaO_4) = f(r_{Ln})$ and $\Delta_f H^\circ(Ln_2O_3) = f(r_{Ln})$ (Ln = Er, Ho, Tb, Dy, Gd, Nd, Pr). So it is possible to predict the standard enthalpies of formation for uninvestigated compounds Tb_2BaO_4 and Pr_2BaO_4: −47.9 and −26.7 kJ/mol, respectively.

The reaction's entropies determine the temperature dependences of the standard Gibbs energies of formation. According to our results, dependence $\Delta_f S_{ox} = f(r_{Ln})$ is monotonous within the accuracy of experiment. As known, in spite of invariability of structural type $CaFe_2O_4$ there are some distortions of LnO_6–octahedron in Ln_2BaO_4 from La to Er. So, it is reasonable to suppose that such distortions should be reflecting on the values of formation entropy.

As mentioned above, the thermodynamic properties of the Ln_2BaO_4 (Ln = Nd and Gd) were reported only in one paper [3]. The authors used the same EMF method with a fluorine-ion electrolyte as we did but measured the EMF of

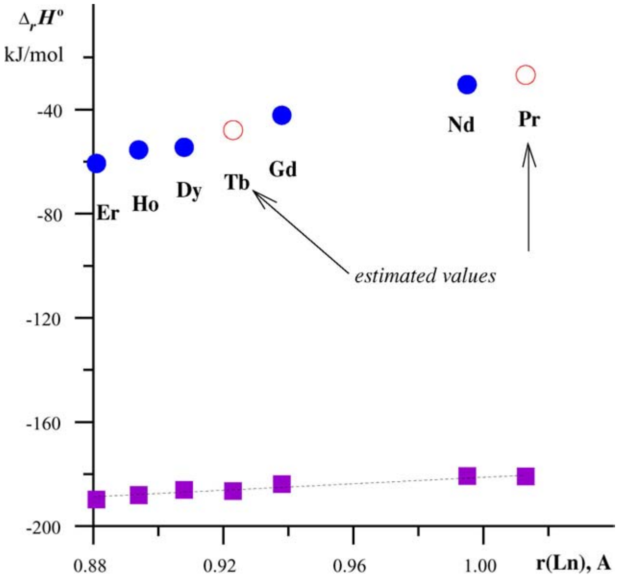

Fig. 2. Standard enthalpy of formation of Ln_2BaO_4 from constituent oxides (circle) and $\Delta_f H^\circ$ (Ln_2O_3)/10 from the elements as a function of rare-earth ionic radii in six-coordination, r(Ln) (square).

the cell

$$(-)\mathrm{Pt, O_2}\ |\mathrm{Ln_2BaO_4, Ln_2O_3, BaF_2}|\ \mathrm{CaF_2}$$
$$|\mathrm{BaZrO_3, ZrO_2, BaF_2}|\ \mathrm{Pt, O_2}(+) \qquad \text{(III)}$$

The temperature dependences of the standard Gibbs energy of formation of Ln_2BaO_4 (Ln = Nd and Gd) from simple oxides obtained in ref. [3] had the form

Nd	$\Delta_f G^\circ_{ox}$ (kJ/mol) = −112.14 + 19.2 × $10^{-3}T$
Gd	$\Delta_f G^\circ_{ox}$ (kJ/mol) = −128.84 + 32.0 × $10^{-3}T$

These data are substantially different from those obtained in this work. According to our results and [3], the Gibbs energy of formation of Ln_2BaO_4 (Ln = Nd and Gd) from the oxides at 1100 K equal −19.1, −28.4 and −91.0, −93.6 kJ/mol, respectively. We made an attempt to reproduce measurements performed in ref. [3] with a ($BaZrO_3$, ZrO_2, BaF_2) reference electrode at 1050–1150 K, but the EMF values were unstable and substantially different from those reported in ref. [3]. Note large negative value of $\Delta_f H_{ox}$ at high temperatures is not peculiar for similar compound. For example, $\Delta_f H^\circ_{ox}$ (Y_2BaO_4) = −33.9, −46 and −30.9 kJ/mol [8–10].

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