

Distribution Coefficients of Rare-Earth Oxides in Zirconium Dioxide Melt Crystallization

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Abstract—Using a modified cryoscopy method and phase diagram data for ZrO_2 – R_2O_3 (R = rare-earth element) systems, we have calculated distribution coefficients of rare-earth oxides in zirconia melt crystallization. We have obtained $k > 1$ for R = Gd–Lu, Sc, and Y, which corresponds to the presence of maxima in the melting curves of the solid solutions. The distribution coefficient as a function of the ionic radius of R^{3+} can be represented by the Gaussian $k(r) = 2.92\exp[-21.48(r - 0.84)^2]$, where r is the eight-coordinate ionic radius in Shannon's system.

Keywords: zirconia, rare-earth oxides, phase diagrams, modified cryoscopy method, fianites, distribution coefficient, heterovalent isomorphism

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INTRODUCTION

Zirconia (ZrO_2) is one of the most refractory metal oxides. On heating to 1443 K, its low-temperature (monoclinic) polymorph transforms into a tetragonal phase, which in turn transforms into a high-temperature (cubic) phase with the fluorite structure (sp. gr. $Fm\bar{3}m$, $Z = 4$) at ~ 2643 K. The ZrO_2 – R_2O_3 (R = rare-earth (RE) element) systems contain wide fields of cubic $Zr_{1-x}R_xO_{2-0.5x}$ solid solutions based on the high-temperature ZrO_2 polymorph [1], which exist at low temperatures as well. In a number of systems, the formation of such solid solutions is accompanied by maxima in their melting curves, that is, by high-temperature stabilization.

Single crystals of solid solutions based on the high-temperature (fluorite) phases of RE oxide-doped zirconia are well-known as fianites, which are used as diamond imitations in jewelry owing to their high refractive index and dispersion and are quantum electronic materials [2–5]. Partially stabilized two-phase zirconia with a relatively low stabilizer concentration is a material with an extremely high fracture toughness [3, 4, 6]. ZrO_2 -based fluorite solid solutions offer high oxygen ion conductivity, which makes these materials a working medium for solid oxide fuel cells [7, 8]. Their high ionic conductivity correlates with their low thermal conductivity [9, 10], so films of ZrO_2 -based solid solutions are used to produce heat-insulating (thermal barrier) coatings, which combine high heat resistance, very low thermal conductivity, and high strength [11].

Knowledge of impurity distribution coefficients in melt crystallization is crucial for the ability to prepare highly homogeneous materials with tailored composition, including high-quality optical materials. Such information is important in the fabrication of ceramics, because rejection of components to grain boundaries has a significant effect on the electrical conductivity of the material.

Information about distribution coefficients in the systems under consideration has so far been insufficient [3, 12].

Equilibrium thermodynamic distribution coefficients k can be evaluated from phase diagram data [13].

The purpose of this work was to calculate RE oxide distribution coefficients in zirconium dioxide melt crystallization by a modified cryoscopy method. Previously, such calculations were performed for HfO_2 – R_2O_3 system [14].

The modified cryoscopy method builds on the limiting van't Hoff equation:

$$m = [RT_0^2/\Delta H](k - 1), \quad (1)$$

where ΔH is the enthalpy of fusion of the host component, T_0 is its melting point, R is the gas constant, k is the impurity distribution coefficient, and m is the slope of the liquidus. This equation is valid in the case of infinite dilution.

In the modified cryoscopy method, m is found not by precisely measuring low values of temperature depression on the addition of low impurity concentrations but by fitting liquidus curves in a wide concentra-

Table 1. Fitting of the liquidus curves of fluoride solid solutions in the $ZrO_2-R_2O_3$ systems to Eq. (2)

R^{3+}	m , K/mol	a , K/mol ²	b , K/mol ³	Fitting range, x	Correlation coefficient, R^2	Ref.
La	-731	-25560	89708	0-0.24	0.9995	[18]
Pr	-1860	3116	-2382	0-0.35	0.9997	[18]
Nd	-1100	583	391	0-0.35	0.998	[18]
Sm	-101.7	-2362	2706	0-0.35	0.998	[18]
Gd	28.5	-434	-485	0-0.75	0.9993	[18]
Dy	353	-1182	61.3	0-0.80	0.9985	[18]
Ho	626	-1743	462	0-0.82	0.9991	[18]
Er	763	-1965	604	0-0.82	0.9989	[18]
Yb	845	-1775	383	0-0.80	0.9976	[18]
Sc	2020	-12886	20353	0-0.30	0.9982	[19]
Y	917	-2367	927	0-0.83	0.9988	[18]
	312	-719	-367	0-0.70	0.972	[17]

tion range and subsequently differentiating the resultant analytical expressions. Such calculations were performed for the MF_2-RF_3 systems [13] and a number of systems based on cadmium and lead fluorides [15, 16].

An adequate use of Eq. (1) for calculating distribution coefficients implies that there are reliable experimental phase diagram data, in particular, those on liquidus curves. Since the $ZrO_2-R_2O_3$ systems are among the most refractory oxide systems, they are difficult to study. A solution was found by using solar furnaces for heating and optical pyrometers for recording signals [17-19]. The most detailed systematic studies of phase equilibria in the $ZrO_2-R_2O_3$ systems were carried out by Rouanet [18], and his data were used in this work.

Liquidus curves were analyzed in a wide concentration range by least squares fitting with cubic polynomials. In this process, the melting point of ZrO_2 (2983 K) was fixed by increasing its weight by ten times. Primary data were obtained by digitizing plots reported by Rouanet [18] and Shevchenko et al. [19]. In addition, we used experimental data reported by Noguchi et al. [17].

The data for the $ZrO_2-R_2O_3$ systems are well represented by equations of the form

$$T = 2983 + mx + ax^2 + bx^3, \quad (2)$$

where x is the mole fraction of R_2O_3 . The coefficients m , a , and b and the correlation coefficient are given in Table 1.

Differentiating the equations for $x = 0$, we obtain the slope of the liquidus (depression) at an infinitely low impurity concentration: $(dT/dx)_{x=0} = m$. The melting point T_0 of ZrO_2 was taken to be 2983 K [18, 20]. Note that, in the case of the yttrium-group rare

earths, fitting was carried out for the entire liquidus curve, including a broad concentration range (Table 1). In the case of the cerium-group rare earths, the situation is more complex: in the $ZrO_2-R_2O_3$ systems, the ordered phase with the pyrochlore structure reaches melting across the liquidus and solidus curves. This process corresponds to a type B_1VII bifurcation [21, 22]. The situation in the $ZrO_2-Pr_2O_3$ system is close to a transition state. Note that the liquidus curves of the phase diagrams for $R = Pr, Nd$, and Sm have inflections, which sharply restricts the concentration range where the liquidus curve can be adequately represented by a cubic polynomial.

Two values of the enthalpy of fusion ΔH of ZrO_2 were reported in the literature: 87.15 [23] and 68.72 kJ/mol [20]. We took the later one, 68.72 kJ/mol [20], that is, $\Delta S = 23.05$ J/(mol K). The low entropy of fusion is typical of compounds with the fluorite structure [13]. The 20% difference between the ΔH values characterizes the accuracy in calculated values of k .

The calculated distribution coefficients are presented in Table 2. It should be noted that, in the case of the praseodymium oxide and neodymium oxide systems, we obtained physically meaningless results: negative k values. It seems likely that this is related to the complex behavior of the liquidus curves in the systems under consideration and the limited information about the temperature depression at low R_2O_3 concentrations (the first points studied by Rouanet [18] corresponded to 5 mol % R_2O_3). For the $ZrO_2-Y_2O_3$ system, we obtained significantly different k values using data reported by Noguchi et al. [17] and Rouanet [18]. The origin of the discrepancy is not yet clear.

The error of calculation by Eq. (1) includes the errors of determination of T_0 , ΔH , and m . Because of the high melting point of zirconium dioxide, which in

Table 2. Calculated distribution coefficients of RE oxides in ZrO₂ melt crystallization

R ³⁺	<i>r</i> , Å [24]	<i>k</i> ₁ (calculated from the ZrO ₂ –R ₂ O ₃ phase diagram)	±Δ <i>k</i> ₁	<i>k</i> ₂ (calculated using Eq. (3))
La	1.16	0.32	0.24	0.32
Pr	1.126	*		0.50
Nd	1.135	*		0.62
Sm	1.079	0.91	0.03	0.85
Eu	1.066			0.97
Gd	1.053	1.03	0.01	1.10
Tb	1.040			1.23
Dy	1.027	1.33	0.12	1.38
Ho	1.015	1.58	0.20	1.51
Er	1.004	1.70	0.25	1.64
Tm	0.994			1.75
Yb	0.985	1.78	0.27	1.86
Lu	0.977			1.95
Sc	0.87	2.87	0.66	2.86
Y	1.019	1.85 [18] 1.29 [17]	0.30 0.10	1.46

* Calculation from phase diagram data [18] yielded physically meaningless results.

addition depends significantly on oxygen partial pressure, this quantity is known with an accuracy near 3% [1, 20]. The largest error of calculation pertains to the enthalpy of fusion (see above). The error of calculation of *m* is difficult to evaluate. On the whole, we estimate the error of calculation of (*k* – 1) at 35%. The corresponding Δ*k*₁ values are given in Table 2.

The distribution coefficient as a function of the ionic radius of the rare-earth elements is well represented by the Gaussian (Fig. 1)

$$k(r) = 2.92 \exp[-21.48(r - 0.84)^2], \quad (3)$$

where *r* is the eight-coordinate “oxide” ionic radii of the rare-earth elements in Shannon’s system [24]. The correlation coefficient is 0.995. In our calculations, we used data for R = La–Sc. Data for the yttrium system were left out of consideration because of the large discrepancy between the values obtained by Noguchi et al. [17] and Rouanet [18].

The above relation has a certain physical meaning that stems from the theory of isomorphism energetics [15]. According to this relation, the ionic radius corresponding to the maximum in *k*(*r*) (that is, to an optimal capture of an isomorphous impurity during crystallization of the host) coincides with the ionic radius of Zr⁴⁺: *r* = 0.84 Å. This is atypical of heterovalent solid solutions with a variable number of ions per unit

cell [13, 15, 16]. A slight change in this quantity has no significant effect on the correlation coefficient of Eq. (3).

The systems with *k* > 1 (R = Tb–Lu, Sc, and Y) are characterized by the presence of maxima in the melting curves of solid solutions. This is characteristic of solid solutions with a variable number of ions per unit cell [25, 26].

At R = Gd, the distribution coefficient at infinite dilution is near unity. This corresponds to coincidence of the maximum with that of the pure component (tangential extremum, bifurcation point *B* [21]). At this point, the system is characterized by a horizontal tangent to both the liquidus and solidus curves at *x* = 0.

Note that the *k* values calculated here cannot be compared to data reported by Römer et al [12]: they determined the distribution coefficients of Nd³⁺, Sm³⁺, and Er³⁺ impurities for the crystallization of stabilized zirconia with the composition 88 mol % ZrO₂ + 12 mol % Y₂O₃, rather than pure ZrO₂.

The compositions corresponding to the maximum in the melting curves of solid solutions in binary systems melt congruently, which means that *k* = 1 at this point. Knowing the position of the maximum, the calculated *k* at *x* = 0 (Table 2), and the distribution coefficient at the highest concentration of the solid solution and the eutectic temperature, we can estimate the concentration dependence of *k* in the corresponding

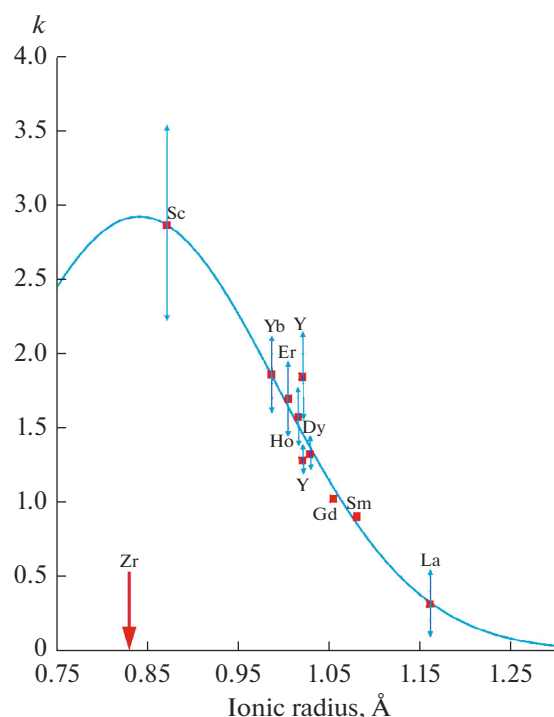


Fig. 1. Calculated distribution coefficient as a function of the ionic radius of R^{3+} for the RE oxide in zirconia crystallization [24]. The solid line represents Eq. (3).

systems ($k = x^S/x^L$, where x^S and x^L are the concentrations of the second component in the solid and liquid phases) [27, 28].

Note that the composition taken for stabilized zirconia (fianite) in the ZrO_2 – Y_2O_3 system differs from that of the maximum in melting curves; that is, the solid solution containing 8–10% yttria crystallizes not quite congruently. For the position of the maximum in the ZrO_2 – Y_2O_3 system, the data obtained by Noguchi et al. [17] and Rouanet [18] give the position of the maximum in the liquidus curve at $x = 0.20 \pm 0.02$. The interpolated equilibrium yttrium distribution coefficient at $x = 0.1$ is 1.1–1.3, depending on which data, those reported by Noguchi et al. [17] or Rouanet [18], are thought to be preferable. In crystal growth, this circumstance is compensated for by the fact that, at realistic crystallization rates, the effective distribution coefficient is closer to unity than the equilibrium one. Figure 2 shows the effective distribution coefficient as a function of crystallization rate for the composition 90 mol % ZrO_2 + 10 mol % Y_2O_3 [3].

Note that the k values obtained by us (Table 2) refer to ZrO_2 melt crystallization in an oxidizing atmosphere. Phase equilibria in the ZrO_2 – R_2O_3 systems depend significantly on oxygen partial pressure. A reducing atmosphere leads to the formation of a broad range of ZrO_{2-x} solid solutions and stabilizes the cubic phase to both higher and lower temperatures (the

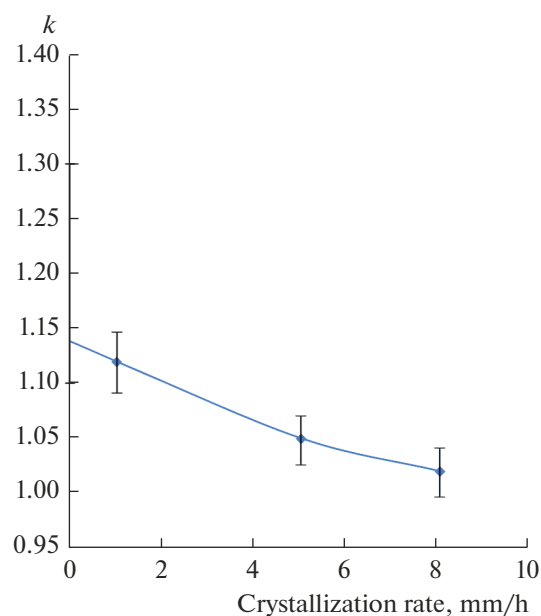


Fig. 2. Effective yttrium distribution coefficient as a function of crystallization rate for $Zr_{0.9}Y_{0.1}O_{1.95}$ according to data reported by Kuz'minov et al. [3].

maximum in the melting curve at 3073 K and the eutectoid equilibrium at 1733 K at the composition $ZrO_{1.86}$) [20].

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