

Formation of diffusionlessly transformed tetragonal phases by rapid quenching of melts in $\text{ZrO}_2\text{-RO}_{1.5}$ systems (R = rare earths)

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Rare-earth (Nd, Sm, Er, Yb, Sc)-doped zirconia was melted using an arc-imaging furnace, and rapidly quenched with a hammer and anvil apparatus (cooling rate $>10^5 \text{ K sec}^{-1}$). These $\text{ZrO}_2\text{-RO}_{1.5}$ samples were investigated by X-ray diffraction and transmission electron microscopy. The existing region of metastable tetragonal zirconia is from 2 to 14 mol % of $\text{RO}_{1.5}$ regardless of the species of dopants, $\text{RO}_{1.5}$. In the lattice parameters of the tetragonal phases, the unit cell volume corresponds to the ionic radii of dopants, whereas the tetragonality (c/a) is independent of the species of dopants, but dependent on the content of dopants.

1. Introduction

The stress-induced transformation of metastable tetragonal phase into monoclinic symmetry is important for the toughness of yttria-stabilized zirconia ($\text{YO}_{1.5}\text{-ZrO}_2$) [1, 2]. It is, however, believed that two kinds of tetragonal phase exist at least in the system $\text{ZrO}_2\text{-YO}_{1.5}$ [3, 4]. One, t-phase, is the tetragonal phase which is an equilibrium phase at a high temperature. The other, t'-phase, is a metastable tetragonal phase which is transformed from the high temperature cubic phase without diffusion. It has been reported that the t-phase is transformable and the t'-phase is non-transformable when an external stress is applied [4]. The systematic studies on the formation and transformation of these tetragonal phases, however, have not yet been accomplished.

In most previous work, tetragonal phases have been prepared by solid state reactions such as sintering. In the case of solid state reactions, however, the formation region of the tetragonal phases are limited by the solubility limit at the temperature of sintering. In addition, samples prepared by such methods might have complicated microstructures and contents of stabilizing agents such as Y_2O_3 , CaO and MgO due to incomplete reactions and/or incomplete quenching. Recently tetragonal phases have often been prepared from melts [3–5]. The melts themselves are homogeneous, however, the solidification and successive cooling cause inhomogeneous precipitation in compositions and microstructures. Therefore, the cooling rate must be well considered during the sample preparation. Our previous studies [6–8] revealed that the tetragonal phase with homogeneous $\text{YO}_{1.5}$ content and microstructure could be obtained by rapid quenching of melts in the $\text{ZrO}_2\text{-YO}_{1.5}$ system, which was the t'-phase. Our recent work [9] indicated that the t'-phase could also be obtained by rapid quenching

in the $\text{ZrO}_2\text{-ErO}_{1.5}$ system. The present study deals with the t'-phases formed by rapid quenching of melts in the ZrO_2 -other $\text{RO}_{1.5}$ systems.

2. Experimental procedure

$\text{ZrO}_2\text{-RO}_{1.5}$ samples containing 0 to 20 mol % $\text{RO}_{1.5}$ were prepared by rapid quenching of their melts. The starting materials were high-purity ZrO_2 (99.9%, Soekawa Rikagaku Co. Ltd. Tokyo, Japan) and $\text{RO}_{1.5}$ (R is a rare earth element; neodymium, samarium, erbium, ytterbium, (99.9%, Shin-etsu Chemical Co. Ltd. Tokyo, Japan) or scandium (99.98% Mitsubishi Metal Co. Ltd. Tokyo, Japan) powders.

The powders were mixed in an agate mortar with methanol for 1.5 h, and pressed into a pellet of 3 mm in height and 2 mm in diameter. The pellet was melted in air using an arc-imaging furnace and then rapidly quenched with a copper-made hammer-anvil apparatus [6, 7, 10, 11]. Films of about 15 mm in diameter and 20 μm in thickness were obtained, where the cooling rate was estimated to be higher than 10^5 K sec^{-1} [7, 11]. The chemical analysis of the samples was conducted by ICP emission spectroscopy.

The existing phases in the films were studied by an X-ray diffraction (RU-200, Rigaku Electric Co. Ltd, Tokyo, Japan, $\text{CuK}\alpha$ 40 kV, 80 mA) at room temperature, where the quenched films were directly pasted on the holder for the X-ray diffraction in order to avoid the stress-induced transformation during grinding.

Lattice parameters of tetragonal and cubic phases in the films were calculated by X-ray diffraction using (400) and (004) peaks. The (400) and (331) peaks of silicon were used as internal standards. For comparison, both the tetragonal and the cubic phases were indexed on the basis of the face-centred lattice.

The film of the $\text{ZrO}_2\text{-4 mol % ErO}_{1.5}$ sample was broken by applying a mechanical stress, and this

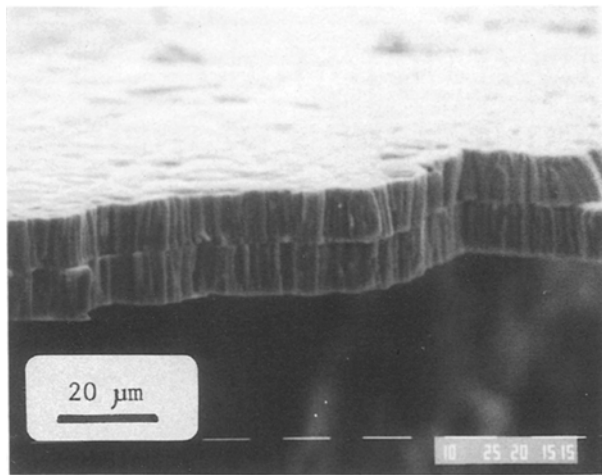


Figure 1 The fracture surface of rapidly quenched 4 mol % ErO_{1.5}-ZrO₂. The film consists of two layers caused by the solidification process.

fracture surface was observed by scanning electron microscopy (SEM), (JSM-T200, JEOL Co Ltd., Tokyo, Japan). The films of ZrO₂-ErO_{1.5} samples were observed by transmission electron microscopy (TEM), (H700, Hitachi Co. Ltd., Tokyo, Japan, 200 kV) after thinning by ionic bombardment of argon.

3. Results and discussion

3.1. Composition and microstructure

The chemical analyses (Table I) indicated that the starting ZrO₂ contained 1.1 mol % HfO₂ and that it did not change during melting and quenching. Similarly, the contents of rare earth oxides also did not change during melting and quenching. The impurity of SiO₂ might be increased by grinding the samples using an agate mortar.

The photograph of the typical fracture surface of ZrO₂-4 mol % ErO_{1.5} film (Fig. 1) reveals that it consists of two layers. This structure was caused by the quenching process: the molten sphere on a copper-made anvil in an arc-imaging furnace was splattered by a copper-made hammer, and then solidified from the surfaces in contact with the hammer and the anvil simultaneously.

The TEM photograph (Fig. 2) shows zirconia containing 8 mol % ErO_{1.5} to be tetragonal, because the

observed field was completely covered by the dark field images of (2 1 1) and (3 2 1). Another independent field image was too dark to be taken. This seems to be caused by the orientation of tetragonal domains upon the transformation from cubic into t'-phase due to external stresses applied during quenching as pointed out by Shibata *et al.* [12].

3.2. Phases present in rapidly quenched samples

Fig. 3 shows the existing phases in ZrO₂-RO_{1.5} samples. Pure zirconia (ZrO₂-0 mol % RO_{1.5}) was monoclinic with baddeleyite structure [13]. The ZrO₂-2 mol % RO_{1.5} samples contained two phases of monoclinic and tetragonal [14].

The volume fraction of the monoclinic phase (V_m) was calculated by the calibration method by Toraya *et al.* [15, 16]

$$V_m = 1.311 X_m / (1 + 0.311 X_m)$$

$$X_m = \{ (I_m(111) + I_m(11\bar{1})) / (I_m(111) + I_m(11\bar{1}) + I_t(111)) \}$$

where $I_m(111)$ is the integrated intensity of (111) reflection of monoclinic phase, $I_m(11\bar{1})$ the integrated intensity of (11 $\bar{1}$) reflection of monoclinic phase and $I_t(111)$ the integrated intensity of (111) reflection of tetragonal phase. The values of V_m were about 0.90 regardless of the R ion in any ZrO₂-2 mol % RO_{1.5} samples. ZrO₂-4 mol % RO_{1.5} samples were mostly tetragonal, and had values of V_m of less than 0.05. Samples containing from 6 to 10 mol % RO_{1.5} were completely tetragonal. The ZrO₂-12 mol % RO_{1.5} samples were mostly tetragonal, but contained a small amount of cubic phase. Samples containing 14 mol % or above RO_{1.5} consisted of the face centred cubic phase (fluorite structure) [17]. It should be noted that the existing phases in ZrO₂-RO_{1.5} (R is Nd, Sm, Y, Er, Yb) are independent of the species of dopants: R ions, that is, the compositional region of tetragonal phase is also independent of R ions. The results in Fig. 3 are in disagreement with previous reports [5, 17-20]. For example, the monoclinic phase region of the present work was smaller than that of previous workers [5, 18-20]. According to Scott [19], ZrO₂-4 or 5 mol % YO_{1.5} samples prepared by arc-melting and cooling were mixtures of monoclinic and tetragonal phases.

TABLE I Inductively coupled plasma emission spectroscopy of melted ZrO₂-RO_{1.5} samples. The pure zirconia contained 1.1 mol % HfO₂. No compositional change occurred during melting.

I		m/o	pure ZrO ₂	Er	Sc	Nd	Sm	Yb	Yb
				10.0	10.0	10.0	10.0	10.0	14.0
II	ZrO ₂	w/o	97.3	82.8	-	-	-	-	-
	HfO ₂	w/o	1.86	1.59	-	-	-	-	-
	RO _{1.5}	w/o	-	14.4	5.69	13.5	13.3	14.8	20.0
	SiO ₂	w/o	0.02	0.04	-	-	-	-	-
III	ZrO ₂	m/o	98.89	89.0					
	HfO ₂	m/o	1.11	1.0					
	(Zr, Hf)O ₂	m/o	100.0	90.0					
	RO _{1.5}	m/o		10.0	10.0	10.5	10.0	10.0	13.8

I Initial stabilizer contents.

II The contents after melting and quenching determined by ICP method, --- : not analysed.

III Mole fraction calculated from II.

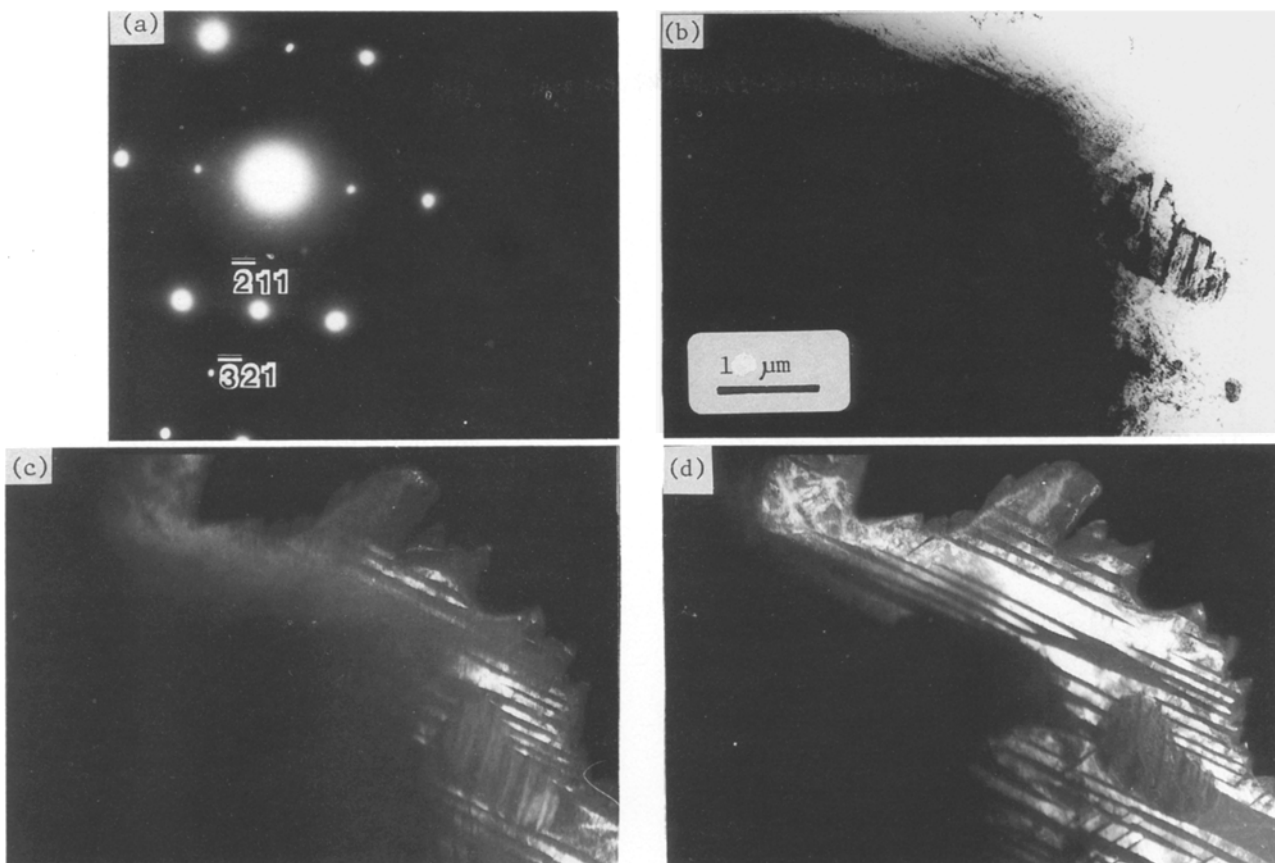


Figure 2 (a) Electron diffraction and (b) microstructure of rapidly quenched 8 mol % $\text{ErO}_{1.5}\text{-ZrO}_2$. Dark field micrographs taken by (c) $(\bar{3}21)$ and (d) $(\bar{2}11)$ reflections of the same area as (b).

According to Sakuma *et al.* [5], the value of V_m of arc-melted and cooled 2 mol % $\text{Y}_2\text{O}_3\text{-ZrO}_2$ ($= 3.9$ mol % $\text{YO}_{1.5}\text{-ZrO}_2$) samples was about 0.6. However, as shown in Fig. 4, the V_m of 4 mol % $\text{RO}_{1.5}\text{-ZrO}_2$ is almost 0 in the present study. A part of the monoclinic phase in the 2 or 3 mol % Y_2O_3 samples in the previous works might be formed by the stress-induced transformation during grinding to prepare the X-ray diffrac-

tion sample. In the present study, therefore, quenched samples were not ground in preparing samples for the X-ray study. In fact, some parts of tetragonal phases transformed into monoclinic symmetries by grinding $\text{ZrO}_2\text{-4 mol % RO}_{1.5}$ samples [21].

In samples $\text{ZrO}_2\text{-ScO}_{1.5}$, as shown in Fig. 3, the monoclinic phase region was almost the same as those in other rare-earth containing samples. However, the tetragonal region (2 to 16 mol % $\text{ScO}_{1.5}\text{-ZrO}_2$ region) was larger than these in $\text{ZrO}_2\text{-other rare-earth oxides}$ samples (2–14 mol % $\text{RO}_{1.5}\text{-ZrO}_2$). This wide region of tetragonal phases corresponds to the fact that the tetragonal single-phase region of less than 8 mol % Sc_2O_3 (less than 14.7 mol % $\text{ScO}_{1.5}$) in the phase diagram of $\text{ZrO}_2\text{-ScO}_{1.5}$ [22] is wider than that

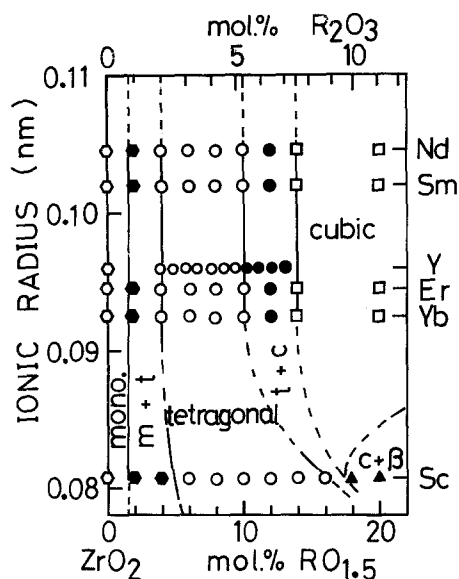


Figure 3 The phase relationship as a function of the species of $\text{RO}_{1.5}$ and their contents. The phase boundary between monoclinic and tetragonal phases is independent of the species of $\text{RO}_{1.5}$; \circ monoclinic, \bullet monoclinic + tetragonal, \circ tetragonal, \bullet tetragonal + cubic, \square cubic, \blacktriangle cubic + β -phase.

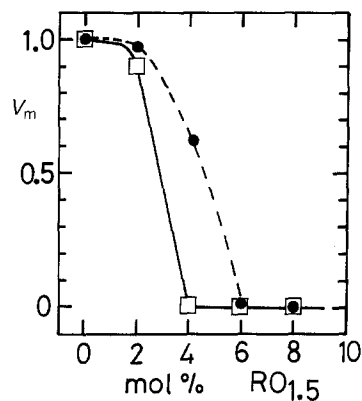


Figure 4 Volume fraction of monoclinic phase (V_m) as a function of $\text{RO}_{1.5}$ content of the rapidly quenched $\text{ZrO}_2\text{-RO}_{1.5}$ (present work) and arc-melted $\text{ZrO}_2\text{-YO}_{1.5}$ [5]. (\bullet Sakuma *et al.*, \square present work).

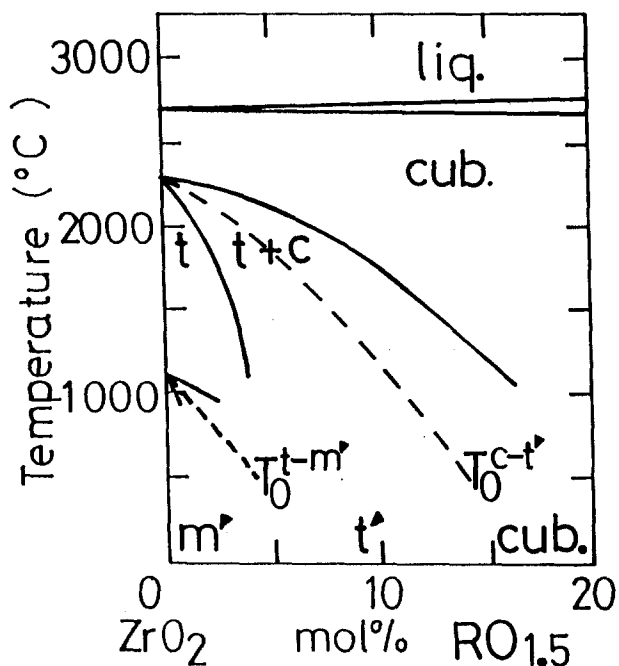


Figure 5 Schematic phase diagram. Phase boundaries (—) and T_0 lines (---). From these phase relations, the formation of phases in rapidly quenched $ZrO_2-RO_{1.5}$ can be understood.

of $ZrO_2-RO_{1.5}$ which is less than 5 mol% in the systems $Er_2O_3-ZrO_2$ [23] or $Y_2O_3-ZrO_2$ [19]. Samples containing 18 or 20 mol% $ScO_{1.5}$ consisted of two phases of β [18] and cubic.

The formation of these phases can be explained by the schematic phase boundaries and T_0 lines [24] in the system $ZrO_2-RO_{1.5}$ without any compositional change due to diffusions (Fig. 5) during cooling. The melts of $ZrO_2-RO_{1.5}$ crystallize firstly into a cubic phase below the solidification temperature and then this cubic phase transforms into tetragonal phase below the equilibrium temperature ($T_0^{c-t'}$) between cubic and tetragonal (t') phase [3], although the exact location of the $T_0^{c-t'}$ line has not yet been found. The cubic phase of $ScO_{1.5}$ -rich samples might transform exceptionally into the β -phase below a certain temperature in the system $ZrO_2-ScO_{1.5}$. The tetragonal phases transform into monoclinic phases below the equilibrium tem-

perature ($T_0^{t-m'}$ between tetragonal (t or t') and monoclinic (m') phases [24].*

3.3. Lattice parameters of quenched samples

Fig. 6 shows the lattice parameters of tetragonal and cubic phases in $ZrO_2-RO_{1.5}$ samples at room temperature. Their lattice parameters vary continuously with $RO_{1.5}$ content. It indicates that ZrO_2 and $RO_{1.5}$ form a complete solid-solution in the compositional range studied. It seems that the tetragonal phase continuously changes to the cubic phase with $RO_{1.5}$ content as a single solid-solution phase. This continuous behaviour of lattice parameters indicates that no phase decomposition due to the diffusion processes occurred in the rapidly quenched $ZrO_2-RO_{1.5}$ samples studied. (This is the characteristic feature of the present study and contrasts with the previous works reported using no rapid quenching.) They cannot be explained by the previous equilibrium phase diagrams containing two-phase regions ($c + t$ and $t + m$), but can be understood using the phase relation diagram in the system $ZrO_2-RO_{1.5}$ (Fig. 5).

The lattice parameters of tetragonal phases containing from 4 to 10 mol% $RO_{1.5}$ showed linear relations, and the a -axis and c -axis approach each other rapidly in samples containing from 10 to 14 mol% $RO_{1.5}$ except for $ZrO_2-ScO_{1.5}$. The lattice parameters of tetragonal phases containing from 4 to 16 mol% $ScO_{1.5}$ gave a linear relation. These results are in good agreement with the solid solutions in the system $ZrO_2-YO_{1.5}$ [18–20] and in the $ZrO_2-YbO_{1.5}$ system [18].

The lattice parameters of the tetragonal phase of pure zirconia, c_0 , a_0 , c_0/a_0 , $(a_0^2 c_0)^{1/3}$ and $a_0^2 c_0$, which are obtained by the extrapolation of the linear relations between the lattice parameters and $RO_{1.5}$ contents from 4 to 10 mol% $RO_{1.5}$ must be unique for any $RO_{1.5}$ system. These lattice parameters of pure zirconia and the slopes of lines were calculated by a least square method with their intercepts constrained to the same value. As shown in Table II, the estimated lattice parameter values of the tetragonal phase of pure zirconia are in good agreement with the lattice parameters of pure ZrO_2 , which were obtained by the linear

TABLE II The lattice parameters of the tetragonal phase of pure zirconia, a_0 , c_0 , c_0/a_0 , $(a_0^2 c_0)^{1/3}$ and $a_0^2 c_0$. Data (a) are obtained by the extrapolation of the linear relations between the lattice parameters and $RO_{1.5}$ content from 4 to 10 mol% in the samples rapidly quenched from melts. Data (b) are obtained by the extrapolation of the linear following relations between the lattice parameters and temperatures after Aldebert and Traverse [25] c axis (tetragonal phase of pure zirconia) = $5.2048 + 0.00005835 \times (\text{Temperature } ^\circ\text{C})$, and a axis (tetragonal phase of pure zirconia) = $5.0677 + 0.00006222 \times (\text{Temperature } ^\circ\text{C})$. Data (c) are obtained from the lattice parameter after Teufer [26] and above coefficients of thermal expansion, da/dT and dc/dT .

Reference	a_0 (nm)	c_0 (nm)	c_0/a_0	$(a_0^2 c_0)^{1/3}$ (nm)	$a_0^2 c_0$ (nm ³)
(a) Present work	0.50831	0.51851	1.0202	0.51169	0.1340
(b) Aldebert and Traverse [25]	0.5068	0.5205	1.027	0.5113	0.1337
(c) Teufer [26]	0.5072	0.5199	1.025	0.5114	0.1337

* In the $ZrO_2-RO_{1.5}$ phase diagram, the monoclinic phase region is below 1150°C. In this lower temperature region, the diffusion rate of cations is so low that the equilibrium phase decomposition by the eutectoid reaction, $t \rightarrow m + c$, cannot be accomplished. Therefore, the monoclinic phase is not an equilibrium monoclinic phase decomposed from the high temperature tetragonal phase, but is formed by the diffusionless transformation from the frozen tetragonal phase. This monoclinic phase should be called the m' -phase.

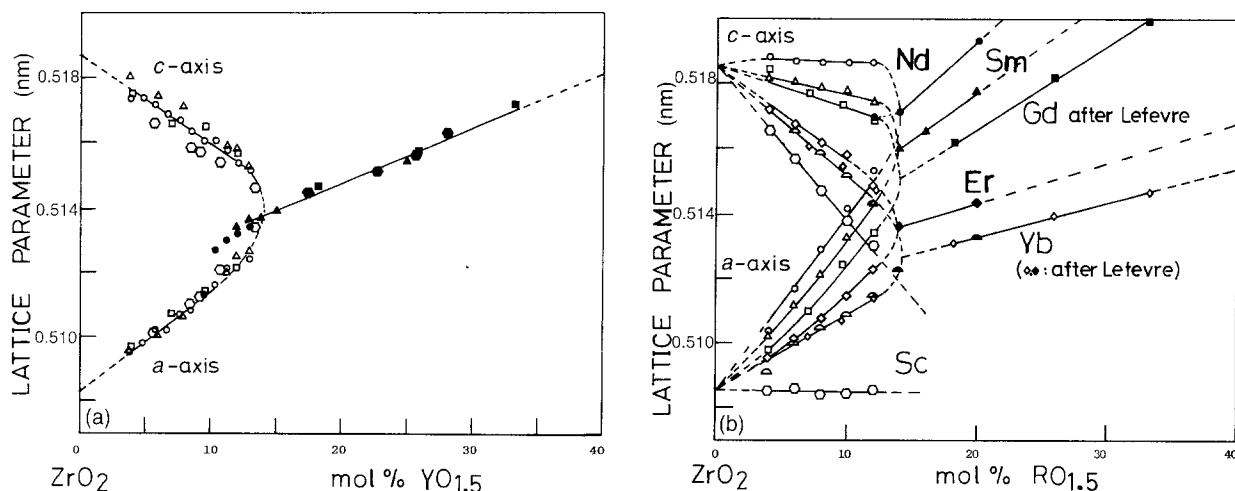


Figure 6 The lattice parameters of rapidly quenched (a) ZrO_2 - $YO_{1.5}$ or (b) $RO_{1.5}$. Open symbols from data of tetragonal phases, and full symbols from data of cubic phases. (\square \blacksquare Lefevre, \triangle \blacktriangle Scott, \circ \bullet Suto *et al.*, \circ \bullet Noma *et al.* in (a)).

extrapolation from the measured values from 1135 to 2025°C for pure ZrO_2 by Aldebert and Traverse [25] or a value at 1250°C for pure ZrO_2 by Teufer [14, 26], particularly, in the unit cell volume. However, the present data showed larger a_0 , smaller c_0 , and that smaller tetragonality (axial ratio c_0/a_0) than the previous data. The present data which were determined from the systems of many R ions seem to be more reliable than them.

Fig. 7 shows the linear relations between the ionic radii of R ions and the slopes of the a axis and c axis

$$\text{the slope of } a\text{-axis} = 0.0228 \times (\text{ionic radius [nm]}) - 0.00184 \text{ (nm mol}^{-1}\text{)}$$

$$\text{the slope of } c\text{-axis} = 0.0206 \times (\text{ionic radius [nm]}) - 0.00219 \text{ (nm mol}^{-1}\text{)},$$

where the ionic radii are what were proposed by Shannon [27], and the coordinate number of R^{3+} ions was assumed to be seven, because the coordinate number of 6 mol % $YO_{1.5}$ -containing tetragonal zirconia was 6.5 or 7 according to the EXAFS study by Morikawa *et al.* [28].

As shown in Fig. 8, the cube roots of the unit cell

volumes of tetragonal phases in the system ZrO_2 - $RO_{1.5}$ gave linear relations with $RO_{1.5}$ content for all R ions. The slopes of the cube root of unit cell volume of tetragonal phases in each system ZrO_2 - $RO_{1.5}$ also indicated linear relations with ionic radii of R^{3+} ions as shown in Fig. 7. These linear relations clearly indicate that the lattice parameters of tetragonal phases are dependent on both the ionic radii and the dopant content. The behaviour of the cube root of unit cell volumes can be explained by an ion packing model [29] of the fluorite structure where the Zr^{4+} ion is substituted by the R^{3+} ion.

Fig. 9 shows the tetragonality of samples containing $RO_{1.5}$. The tetragonality of ZrO_2 from 4 to 10 mol % $RO_{1.5}$ gave a linear relation with the $RO_{1.5}$ content

$$c/a \text{ (tetragonality)} = 1.0204 - 0.0011678$$

$$\times (RO_{1.5} \text{ mol } \%)$$

The value of 1.020 is the tetragonality of the tetragonal phase for pure ZrO_2 obtained by the extrapolation of the linear relation. The tetragonality decreases with the $RO_{1.5}$ content, and then rapidly approaches 1.000 of the cubic one in the compositional

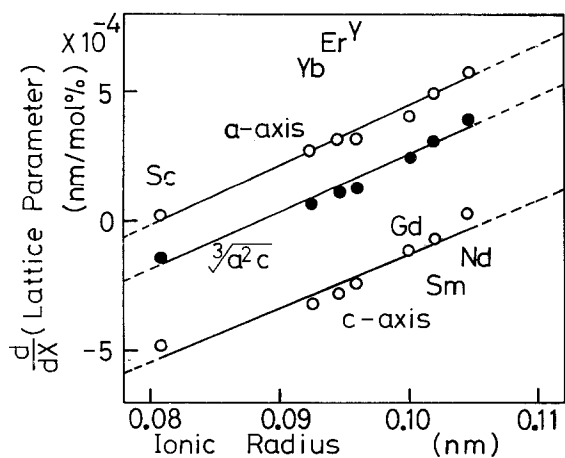


Figure 7 The relationship between the slopes of lattice parameters against the $RO_{1.5}$ content and the ionic radii of R^{3+} ions. They show linear relations.

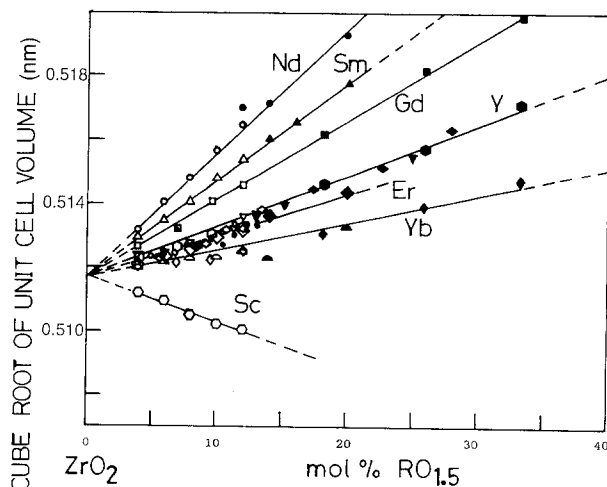


Figure 8 The cube root of unit cell volume as a function of $RO_{1.5}$ content in rapidly quenched ZrO_2 - $RO_{1.5}$.

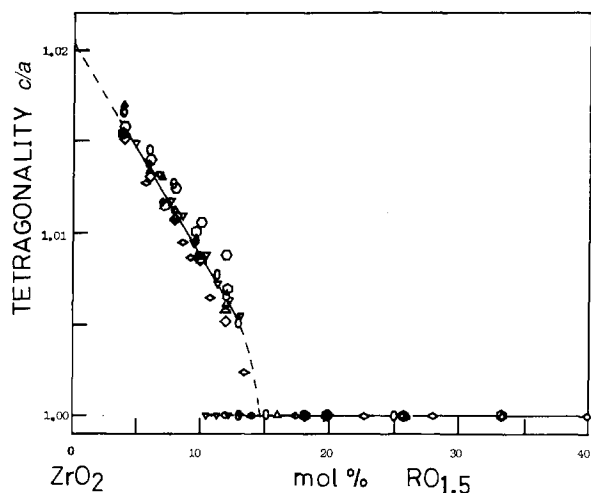


Figure 9 The relationship between the $RO_{1.5}$ composition and the tetragonality (axial ratio c/a) of rapidly quenched and arc-melted $ZrO_2-RO_{1.5}$ (O neodymium, \blacktriangle gadolinium (after Lefevre), \triangle samarium, \circ yttrium (after Lefevre), \emptyset yttrium (after Scott), \diamond yttrium (after Suto *et al.*), ∇ yttrium (after Noma *et al.*), \diamond erbium, \diamond ytterbium (after Lefevre), \triangle ytterbium, \circ scandium).

range from 10 to 14 mol % $RO_{1.5}$ ($R = Nd, Sm, Y, Er, Yb$). A similar rapid decrease in the tetragonality was found in pure zirconia at temperatures around $2000^\circ C$ by Aldebert and Traverse [25]. It should be noted that the tetragonality of $RO_{1.5}$ -containing ZrO_2 samples are almost independent of the species of dopants except for $ScO_{1.5}$, but dependent on the contents of the dopant. No change of axial ratio c/a of tetragonal zirconia with the substitution of ions with different ionic radii, suggests that R^{3+} ions dissolve randomly and isotropically in the lattice.

4. Conclusion

Rapidly quenched rare-earth (Nd, Sm, Er, Yb) oxides-doped zirconia formed monoclinic, tetragonal and cubic phases. The existing region of the tetragonal phase is 2 to 14 mol % $RO_{1.5}$, which is independent of the species but dependent on the dopant content. The lattice parameters of the tetragonal phases vary continuously with $RO_{1.5}$ content. The cube root of the unit cell volume and tetragonality (c/a) of the tetragonal phase which are calculated from the lattice parameters gave linear relations with the R^{3+} ion content. The slopes of the a axis, the c axis and the cube root of unit cell volume, correspond to the ionic radii of the dopants. The tetragonality c/a was independent of the species of dopant, but dependent on the content of dopant.

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