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Oxygen-induced structural change of zirconia by adding rare earth oxides with solid state method

Wen-Ku Chang[a,*], Andy A. Wang[b], Yuan-Haun Lee[a]

[a]*The Graduate Institute of Materials Science and Engineering, National Taiwan University, Taipei 10764, ROC*
[b]*Chemical Engineering Department, Nan Ya Junior College, Chung Li 10764, ROC*

Abstract

The crystal structures of zirconia by doping such rare earth oxides, as Pr_2O_3, Nd_2O_3, Sm_2O_3, Dy_2O_3, Ho_2O_3 and Yb_2O_3 ($RO_{1.5}$), were obtained by using powder X-ray diffraction method. These ZrO_2-$RO_{1.5}$ samples were prepared by solid state reaction methods. The existing regions of stabilized zirconia were strongly influenced by the species and contents of dopants. The lattice parameters of the cubic phases were dependent on the contents of dopants, and the differential of lattice parameters corresponds to the ionic radii of dopant. The density of the three phases of zirconia revealed a linear relation with the contents of dopants, and the slopes of the density of three phases in each system ZrO_2-$RO_{1.5}$ also indicated linear relations with atomic weight of R^{3+} ion.

Keywords: Stabilized zirconia; Powder X-ray diffraction; Solid state reactions; Lattice parameters

1. Introduction

Pure zirconia (zirconium dioxide, ZrO_2) has three phases of different crystal structures under atmospheric pressure: monoclinic zirconia remains stable up to 1443 K [$P2_1/c$, $Z=4$] [1,2], tetragonal zirconia from 1443 to 2643 K [$P4_2/nmc$, $Z=2$] [3] and cubic zirconia [$Fm3m$, $Z=4$] [4] at higher temperatures up to the melting point at 2950 K. The tetragonal and cubic phases of pure zirconia can be stabilized at room temperature by adding suitable oxides such as MgO, CaO, Y_2O_3 and certain lanthanide oxides. Previous studies [5–7] indicated that the calcium stabilized zirconia could also be obtained and it remains stable up to room temperature by adding CaO and $CaCl_2$ in zircon ($ZrSiO_4$). This new process which is different from the conventional one decreases the dissociation temperature of zircon from 1676 °C to 800 °C. However, the resulting phases were difficult to separate from its mixture composition, but can be identified by XRD method. So, we studied the zirconia ceramics, including the refinement of the original observed XRD data to identify crystal structures of *c*, *t* and *m* in ZrO_2 solid solution, and determination of their relative phases percentage by Rietveld analysis (1969) [8].

The effect of additive ionic radius on lattice parameters of HfO_2 and ZrO_2 solid solutions has been studied extensively by many researchers. Trubelja and Stubican [9] investigated the ionic conductivity of HfO_2-$RO_{1.5}$ solid solutions ($R=Sc^{3+}$, Y^{3+} and La^{3+} cations) and showed that the activation enthalpy for conduction increased with dopant radius. Kim et al. [10] determined the lattice parameters of the fluorite-type HfO_2 and ZrO_2 solid solutions formed by doping with Ho_2O_3 and Y_2O_3 to clarify the relative ionic radii of Ho^{3+} and Y^{3+} in cubic (CN=8). Yoshimura et al. [11] studied the formation of non-diffusion transformed tetragonal phases by rapid quenching of melts in ZrO_2-$RO_{1.5}$ systems ($R=Nd^{3+}$, Sm^{3+}, Er^{3+}, Yb^{3+}, Sc^{3+}).

The purpose of this study is to compare the influence of the ionic radius of rare-earth cations in the lattice by determining the lattice parameters of the ZrO_2 solid solutions formed (solid state reaction method) by doping with Pr_2O_3, Nd_2O_3, Sm_2O_3, Dy_2O_3, Ho_2O_3 and Yb_2O_3 in composition ranges from 0 to 25 mol%. The powder XRD data of ZrO_2-$RO_{1.5}$ solid solutions were obtained from analysis using the Rietveld method.

2. Experimental

The samples used for data collection were all prepared from high-purity zirconia (99.9%) and $RO_{1.5}$ ($R=Pr^{3+}$, Nd^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+} and Yb^{3+}(99.9%)). The

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*Corresponding author.

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zirconia-$RO_{1.5}$ (ZrO_2-x mol% $RO_{1.5}$; x=0~25) solid solutions were prepared by solid state reaction. They were manually mixed as methanol slurries with a pestle in an agate mortar for 1 h. The mixed powder was pressed into pellets (20 mm in diameter and 5 mm in height) by a press at 100 Kg/cm^2. These samples were then fired at 1673 K in air for 10 h in an electric furnace. The fired product was crushed and ground in an alumina mortar and then pressed again into pellets at about 100 Kg/cm^2. These samples were fired at 1923 K in air with $MoSi_2$ furnace to homogenize the $RO_{1.5}$ contents and then cooled with a cooling rate of 20 K min^{-1}. The existing phases in the quenched pellets were directly pasted on the holder for the X-ray diffraction in order to avoid the stress-induced transformation during grindings [11]. The X-ray diffraction patterns of the sintered samples were collected with an X-ray diffractometer (Phillips) under the following experimental conditions: with CuKα radiation, monochromator, step-scan mode, step width=0.04° in 2θ, fixed time=6 s, 2θ range=25~120°. X-ray powder diffraction patterns were refined and analyzed by the multiphase Rietveld method (Rietveld analysis program RIETAN, Izumi, 1995) to determine the amounts of different phases as well as their lattice parameters and unit-cell density.

3. Results and discussion

Fig. 1 shows the results of the ZrO_2-5 mol% $SmO_{1.5}$ sample diffraction pattern by the multiphase Rietveld analysis method, and shows that the fit of the calculated to the observed diffraction is good. Crosses indicate the observed data and a solid line indicates the pattern calculated using the structural model (monoclinic ZrO_2, the space group $P2_1/c$; tetragonal ZrO_2, the space group $P4_2/nmc$). The obtained R factors are correspondingly small (R_{wp}=4.29, R_p=3.24, monoclinic phase R_I=1.04; tetragonal phase R_I=0.55). The amounts of the different polymorphs at each contents were estimated from the scale factors obtained in the final refinements, using the equation: [12]

$$X_p = \frac{S_p Z_p M_p V_p}{\sum_q S_q Z_q M_q V_q}$$

where X_p is the mass fraction of the pth phase, Z_p is the number of formula units each of mass M_p in the unit-cell volume V_p, and S_p is the Rietveld scale factor for the pth phase. Detailed results of different contents and species of dopants from the quantitative phase analysis are shown in Fig. 2a Fig. 2b. The amounts of monoclinic phase decrease when the contents of rare earth oxides increase. On the other hand, the amounts of stabilized phases (tetragonal and cubic phases) increase with increasing rare earth oxide contents.

Fig. 3a Fig. 3b shows the lattice parameters of tetragonal and cubic phases in ZrO_2-$RO_{1.5}$ samples at room temperature. In this case of solid state reaction which has been reported the formation region of the tetragonal phases are limited by the solubility limit at the temperature of sintering [9]. In addition, samples prepared by such methods might have complicated microstructures and contents of stabilizing agents due to incomplete reactions and/or incomplete quenching. Therefore, the lattice parameters of tetragonal phases vary irregularly with the $RO_{1.5}$

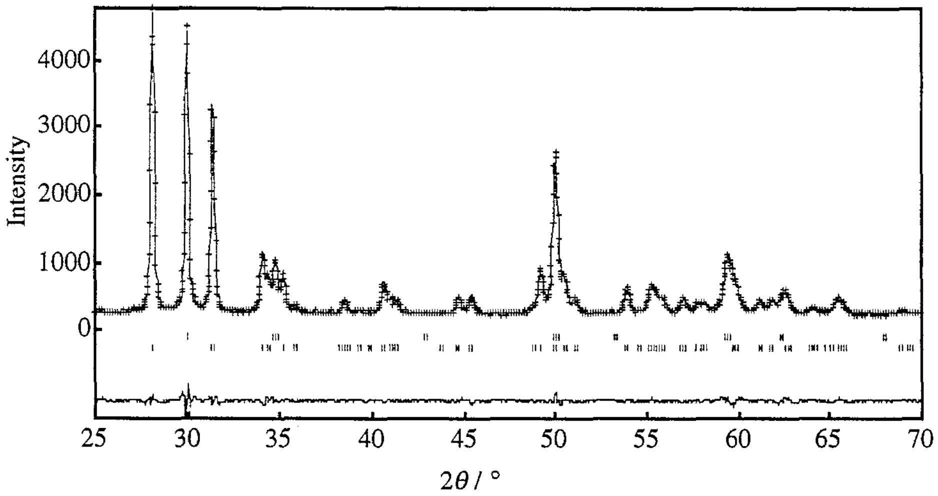

Fig. 1. Output from the Rietveld analysis of the powder X-ray diffraction pattern of ZrO_2-5 mol% $SmO_{1.5}$. The observed data are indicated by crosses and the calculated profile by a solid line. The short vertical bars below the pattern represent the positions of all possible Bragg reflections; the line below the short vertical bars is the difference between the observed and calculated patterns.

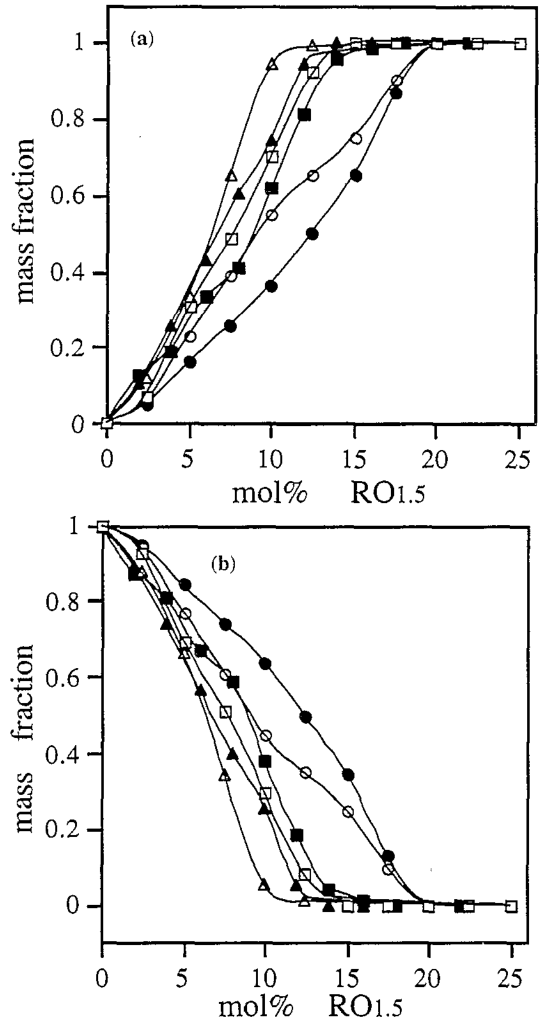

Fig. 2. (a) Mass fraction of stabilized phase zirconia in various contents of dopants (△: Yb, ▲: Dy, □: Sm, ■: Ho, ○: Nd, ●: Pr). (b) Mass fraction of monoclinic phase zirconia in various contents of dopants (△: Yb, △: Dy, □: Sm, ■: Ho, ○: Nd, ●: Pr).

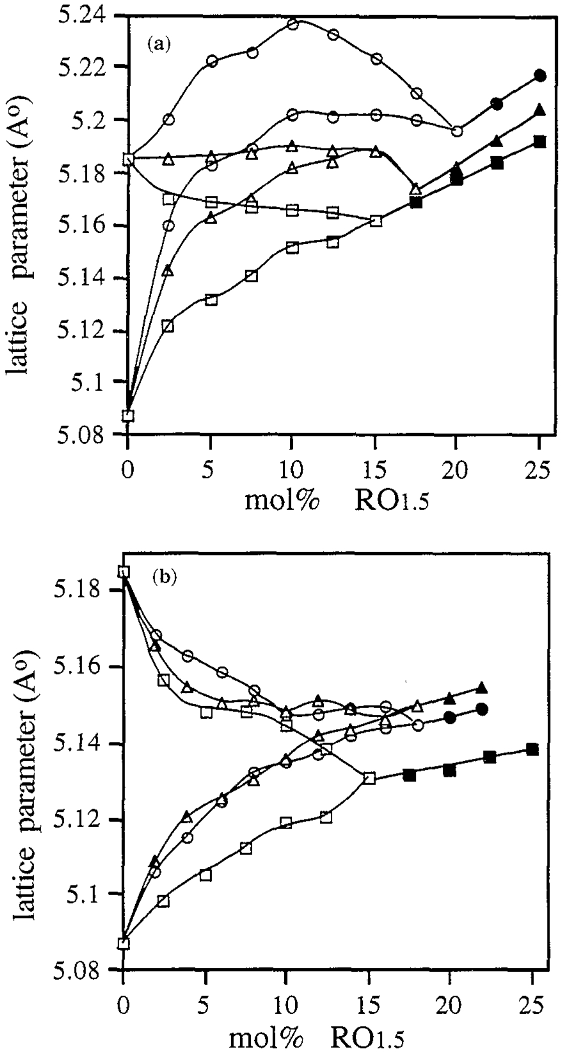

Fig. 3. (a) Lattice parameter of c,t-phases ZrO_2 solid solutions as a function of dopant content. (○●: Pr, △▲: Nd, □■: Sm, unfilled symbols: t-phases, filled symbols: c-phases). (b) Lattice parameter of c,t-phases ZrO_2 solid solutions as a function of dopant content. (△▲: Dy, ○●: Ho, □■: Yb, unfilled symbols: t-phases, filled symbols: c-phases).

content. This suggests that specimens have not been equilibrated. However, the lattice parameters of cubic phases vary continuously with the $RO_{1.5}$ content. This suggests that ZrO_2 and $RO_{1.5}$ form a complete solid solution and chemical homogeneity in the cubic phase region. The slopes of the lattice parameters of the cubic phase in ZrO_2-$RO_{1.5}$ system indicated two-section linear relations with ionic radii of R^{3+} as shown in Fig. 4. The slope of the lattice parameters of cubic phase in first section, where the ionic radii are smaller, is smaller than the second section.

the slope of first section $= 0.00974X$(ionic radius [nm]) $- 0.000765$ (nm/mol%)

the slope of second section $= 0.03714X$(ionic radius [nm]) $- 0.003259$ (nm/mol%)

The ionic radii are proposed by Shannon [13]. According to Yoshimura et al., similar results of the slopes of lattice parameter were obtained by rapid quenching of melts in ZrO_2-$RO_{1.5}$ systems.

the slope of first section $= 0.00872X$(ionic radius [nm]) $- 0.000654$ (nm/mol%)

the slope of second section $= 0.02456X$(ionic radius [nm]) $- 0.002059$ (nm/mol%)

However, the data reported by Kim et al. showed larger lattice parameters than the previous data.

Fig. 5a Fig. 5b Fig. 5c show the linear relations between the content of dopants and the density of unit cell in each ZrO_2-$RO_{1.5}$ system. The unit cell density is calculated by the atomic weight in unit cell and the lattice parameters by Rietveld refinement. It revealed that the

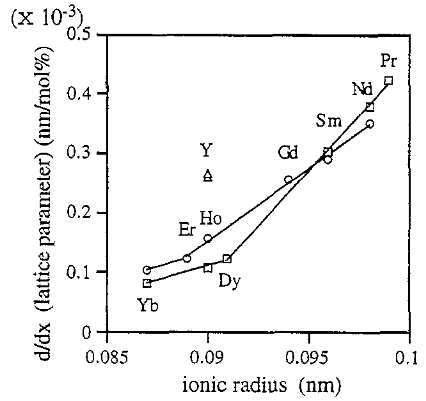

Fig. 4. The relationship of the lattice parameter of the cubic phase against content of dopant and ionic radius of R^{3+}. (□: present work, ○: Yoshimura et al. [11], △: Kim et al. [10])

density of the unit cell is dependent on both atomic weight and the dopant content. By least squares calculation, the slopes of the density in each phase indicated linear relations with atomic weight of R^{3+} as shown in Fig. 6.

4. Conclusions

The existing region of stabilized phases by solid state reaction method is dependent on the species of rare earth oxides and the dopant content, but is independent of the species and dependent on the dopant content by arc melted method [11]. The amounts of Zr^{4+} ion substituted by the R^{3+} ion increase with decreasing the ionic radii of dopant. The slope of lattice parameters of cubic phase showed two-section linear relation with ionic radius, which is

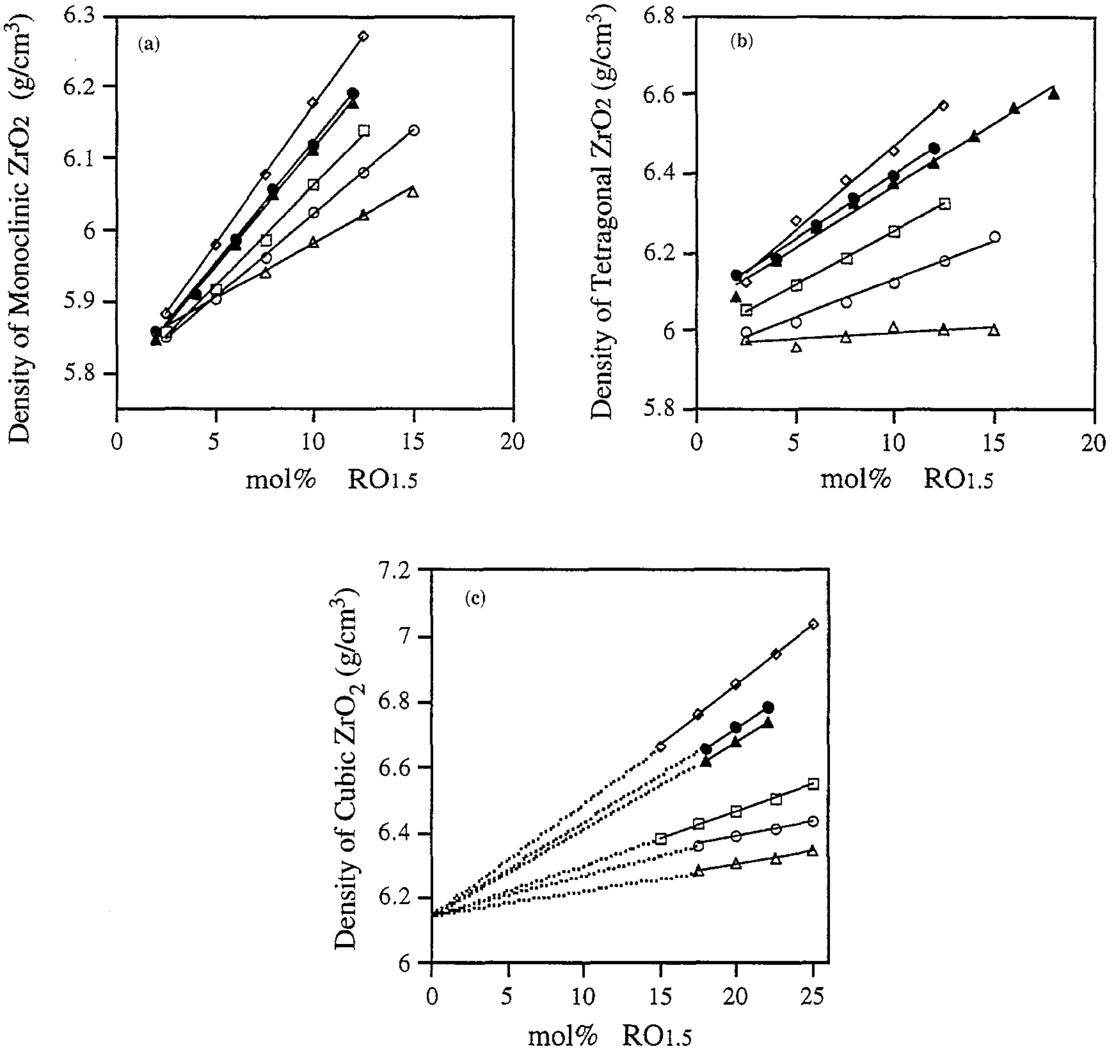

Fig. 5. (a) The relationship between the content of dopants and the density of monoclinic ZrO_2. (◇: Yb, ●: Ho, ▲: Dy, □: Sm, ○: Nd, △: Pr). (b) The relationship between the content of dopants and the density of tetragonal ZrO_2-$RO_{1.5}$. (◇: Yb, ●: Ho, ▲: Dy, □: Sm, ○: Nd, △: Pr). (c) The relationship between the content of dopants and the density of cubic ZrO_2-$RO_{1.5}$. (◇: Yb, ●: Ho, ▲: Dy, □: Sm, ○: Nd, △: Pr).

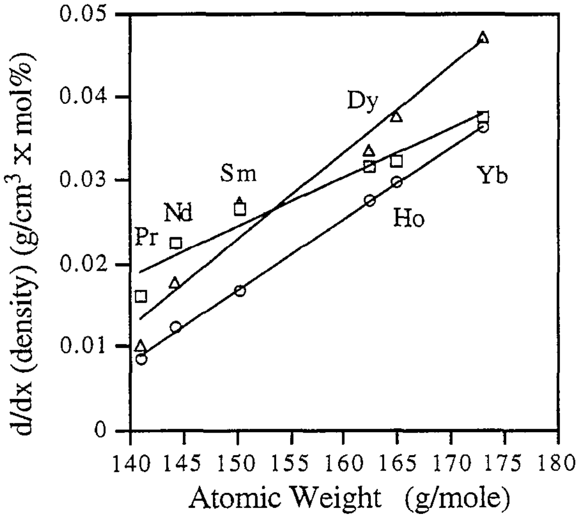

Fig. 6. The relationship between the slopes of the density against the $RO_{1.5}$ content and the atomic weight. (□: monoclinic phase, △: tetragonal phase, ○: cubic phase).

similar to the results by melted method. It suggests that ZrO_2 and $RO_{1.5}$ form a complete solid solution in the cubic phase region.

References

[1] J.D. McCullough and K.N. Trueblood, *Acta .Cryst.*, 12 (1959) 507–511.
[2] D.K. Smith and H. Newkirk, *Acta Cryst.*, 18 (1965) 983–991.
[3] G. Teufer, *Acta Cryst.*, 15 (1962) 1187.
[4] D.K. Smith and C.F. Cline, *J. Am. Ceram. Soc.*, 45 (1962) 249–250.
[5] W.K. Chang, Y.H. Lee and T.Y. Wung, *Advanced Materials*, in N. Mizutani et al. (eds.), Trans. Mat. Res. Soc. Jpn., Vol. 14A, 1993, pp. 459–462.
[6] Y.H. Lee, P.W. Wang and T.Y. Wung, *The Chinese Society for Materials Science*, C-927 (1989).
[7] W.K. Chang, Y.H. Lee and T.Y. Wung, *Chinese Ceramic Soc.*, 12 [3] (1993) 37–50.
[8] H.M. Rietveld, *J. Appl. Crystallogr.*, 2 (1969) 65–71.
[9] M.F. Trubelja and V.S. Stubican, *J. Am. Ceram. Soc.*, 74 [10] (1991) 2489–94.
[10] D.J. Kim, S.H. Hyun, S.G. Kim and M. Yashima, *J. Am. Ceram. Soc.*, 77 [2] (1994) 597–99.
[11] M. Yoshimura, M. Yashima, T. Noma and S. Somiya, *J. Mater. Sci.*, 25 (1990) 2011–2016.
[12] R.J. Hill and C.J. Howard, *J. Appl. Crystallogr.*, 20 (1987) 467–74.
[13] R.D. Shannon, *Acta Cryst. A*, 32 (1976) 751.