

## Determination of solid solubility limit of GeO<sub>2</sub> in 2 mol % Y<sub>2</sub>O<sub>3</sub>-stabilized tetragonal ZrO<sub>2</sub> by Raman spectroscopy

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At atmospheric pressure, pure ZrO<sub>2</sub> exists as three polymorphs. On cooling from the melt, the high-temperature form of cubic (c) ZrO<sub>2</sub> transforms to tetragonal (t) symmetry at ~2370 °C and then to monoclinic (m) form at ~1200 °C. c-ZrO<sub>2</sub> has a fluorite-type structure, where Zr ions are in eightfold coordination with their nearest oxygen ions. The tetragonal form represents a slightly distorted fluorite structure, where the Zr ion is associated with two sets of four oxygen ions at distances of 0.2065 (Zr-O) and 0.2455 nm (Zr-O'), respectively [1]. It is well known that for ZrO<sub>2</sub> to be utilized for technical applications c-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> should be stabilized at an ambient temperature by the formation of solid solutions which prevent deleterious tetragonal to monoclinic phase transformation. The most widely used alloying oxides for this purpose are CaO, MgO, Y<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>, among others. Since the technically important properties such as phase stability, fracture toughness, and ionic conductivity depend on the content of the stabilizing oxides in the high-temperature polymorphs, the solid solubility limits of alloying oxides have been one of the prime research interests of c- and t-ZrO<sub>2</sub>.

Recently Yashima *et al.* [2] reported the determination of the phase boundary between t-ZrO<sub>2</sub> + c-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> in the system Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> by using Raman spectroscopy. They decided on the composition at which one of six distinctive Raman modes for t-ZrO<sub>2</sub> became extinct with an increase in Y<sub>2</sub>O<sub>3</sub> content as the boundary. Within t-ZrO<sub>2</sub> solid solubility limits, however, such extinction cannot be expected since the solid solutions should retain the characteristic Raman spectra of t-ZrO<sub>2</sub>.

Li *et al.* [3] suggested that the stabilization of t-ZrO<sub>2</sub> in the system GeO<sub>2</sub>-ZrO<sub>2</sub> is achieved by shortening the cation-O bond length of t-ZrO<sub>2</sub> while lengthening the cation-O' bond as a result of the substitution of Ge<sup>4+</sup> for Zr<sup>4+</sup>. It can then be expected that solubility limits of GeO<sub>2</sub> in t-ZrO<sub>2</sub> solid solutions will be determined by observing shifts of the Raman modes corresponding to the stretching of Zr-O and Zr-O' bonds with increasing GeO<sub>2</sub> content in t-ZrO<sub>2</sub>, since Raman spectroscopy is sensitive to the changes in the bond lengths and angles between cation and anion. In the present study, the solid solubility limit of GeO<sub>2</sub> in 2 mol % Y<sub>2</sub>O<sub>3</sub>-stabilized t-ZrO<sub>2</sub> (2Y-TZP) was estimated by

using Raman spectroscopy and the result was compared with the limit determined by X-ray powder diffraction.

Specimens were prepared by adding 99.99% pure GeO<sub>2</sub> into 2Y-TZP powder (Tosoh Inc., Tokyo, Japan). The mixing was performed by ball milling for 24 h. After drying, the mixed powders were calcined for 5 h at 1000 °C, followed by attrition milling for 1 h. Zirconia balls were used in both the milling processes. Pellets of each composition for Raman spectroscopy were isostatically pressed at 350 MPa and then sintered for 3 h at 1350 °C. Specimens for X-ray diffraction (XRD) were obtained by heating the attrited powders for 3 h at 1350 °C.

Raman spectra were obtained by a double monochromator (Jobin Yvon U1000, Longjumeau, France) in a back-scattering geometry. The spectra were excited with an Ar-ion laser operating at 514.5 nm wavelength. The spectra of each specimen were taken three times over the range 100-900 cm<sup>-1</sup>, scanning at 1.0 cm<sup>-1</sup> step-size with an integration time constant of 1 s. XRD data were obtained from the powder specimens, mixed carefully with Si internal standard (SRM 640b), using an automated X-ray diffractometer (Philips, EA Almelo, Netherlands) with CuK<sub>α</sub> radiation, λ (CuK<sub>α1</sub>) = 0.154060 nm. A scan speed of 0.5° 2θ/min was employed in the 65° to 120° 2θ range. After K<sub>α2</sub> peak stripping, the peak positions were determined by profile refinement using the built-in PC-APD program. Details of the lattice parameter refinement procedure have been described elsewhere [4].

Fig. 1 shows the Raman spectra of 2Y-TZP as a function of the GeO<sub>2</sub> content. The Raman data exhibits six distinct peaks of t-ZrO<sub>2</sub> [5]. Among these peaks, only the 261 cm<sup>-1</sup> mode continuously shifts to a higher wave number as the GeO<sub>2</sub> content increases. This peak corresponds to the Zr-O' stretching mode [6]. Accordingly, the cation-O' bond length in t-ZrO<sub>2</sub> decreases with GeO<sub>2</sub> alloying. This contradicts the rationalization of the GeO<sub>2</sub> alloying effect on the stabilization of t-ZrO<sub>2</sub> [3], implying that changes in the cation-oxygen bond lengths are not a measure of the phase stability of t-ZrO<sub>2</sub>.

The symmetry environment of cations in a scheelite-type ZrGeO<sub>4</sub> is exactly the same as that in a

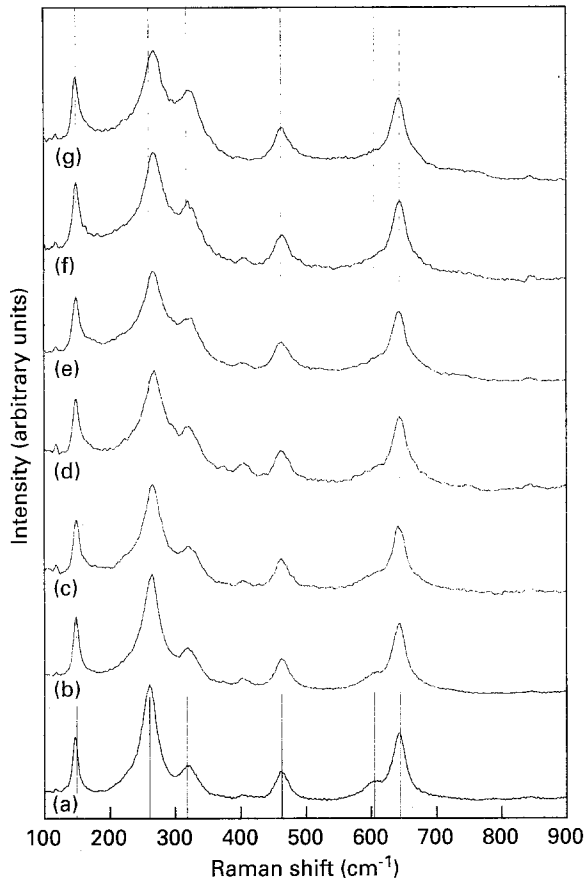


Figure 1 Raman spectra of 2 mol%  $Y_2O_3$ -stabilized  $t-ZrO_2$  containing (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5 and (g) 6 mol% of  $GeO_2$ .

distorted fluorite-type  $t-ZrO_2$  and the germanium ions, whose ionic size is smaller than that of the zirconium ion, are considered as only tetrahedrally coordinated to form isolated  $GeO_4$  groups in  $ZrGeO_4$  [7]. This might also be true for  $Ge^{4+}$  in 2Y-TZP so that the shift of  $261\text{ cm}^{-1}$  mode towards higher frequencies in Fig. 1 is related to the tetrahedral coordination of  $Ge^{4+}$  to oxygen ions. It has been reported that the substitution of  $Nb^{5+}$  and  $Ta^{5+}$  for  $Zr^{4+}$  in 3Y-TZP also results in the four-fold coordination of the pentavalent ions since the ionic sizes of  $Nb^{5+}$  and  $Ta^{5+}$  are smaller than that of  $Zr^{4+}$  [8]. However, the pentavalent ion doping causes the shifts of  $261$ ,  $609$ , and  $642\text{ cm}^{-1}$  modes towards higher frequencies. The  $642\text{ cm}^{-1}$  and the additional  $609\text{ cm}^{-1}$  modes correspond to the stretching of the Zr–O bond [6]. The decrease in Zr–O bond length with increasing  $Nb^{5+}$  and  $Ta^{5+}$  content was attributed to a change in local bond structure due to annihilation of oxygen vacancies created by the  $Y^{3+}$  doping in  $t-ZrO_2$  [8]. In Fig. 1 it is noteworthy that the intensity of the  $609\text{ cm}^{-1}$  band diminishes as the  $GeO_2$  content increases. The same trend was observed with  $Nb_2O_5$  alloying [8]. On the other hand, no such decrease in intensity was detected as the contents of cations such as  $Y^{3+}$  and  $Ce^{4+}$  [8, 9] increased, which form an eight-fold coordination in  $t-ZrO_2$ . This suggests that the decrease in the  $609\text{ cm}^{-1}$  line intensity in addition to the shift of  $261\text{ cm}^{-1}$  mode towards higher wave numbers might be characteristic of  $t-ZrO_2$  solid solutions containing tetrahedrally coordinated cations.

The change in frequency of the  $261\text{ cm}^{-1}$  Raman mode in Fig. 1 is plotted as a function of mol%  $GeO_2$  in Fig. 2. As shown, the increase in the frequency of  $261\text{ cm}^{-1}$  mode terminates at about 3.5 mol%, and there is no shift with further increase in the amount of  $GeO_2$ . At this composition the cations become ordered, probably to form  $Zr_3GeO_8$  [6, 7], so that 3.5 mol%  $GeO_2$  can be considered the solid solubility limit of  $GeO_2$  in 2Y-TZP at  $1350\text{ }^\circ\text{C}$ . The plot of the full-width-at-half-maximum (FWHM) of the  $261\text{ cm}^{-1}$  line as a function of  $GeO_2$  content in Fig. 3 conforms to the result in Fig. 2. The Raman line continuously broadens with increasing  $GeO_2$  content and no further broadening occurs above 3.5 mol%  $GeO_2$ . The broadening of the Raman band occurs when disorder is introduced into the crystal structure [10]. Therefore, it is likely that an ordering of cations occurs at 3.5 mol%  $GeO_2$ . The measurements of  $a$  and  $c$  lattice parameters further support the determination of the solubility limit of  $GeO_2$  in 2Y-TZP by Raman spectroscopy. In Figs 4 and 5 the  $a$  and  $c$  lattice constants of 2Y-TZP linearly decrease and increase, respectively, as the  $GeO_2$  content increases up to 3.5 mol%, and the constants do not vary with additional increase in the content. The linearity, which corresponds to Vegard's law, shows that the solid solubility limit of  $GeO_2$  in 2Y-TZP is about 3.5 mol%. The identical results demonstrate that the Raman spectroscopy is a practical tool to determine the solubility limit because of its relatively simple procedures for specimen preparation and data analysis.

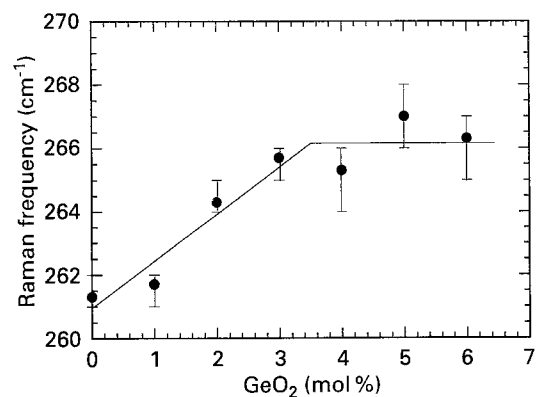


Figure 2 Shift of the  $261\text{ cm}^{-1}$  mode of  $t-ZrO_2$  Raman spectra as a function of  $GeO_2$  content.

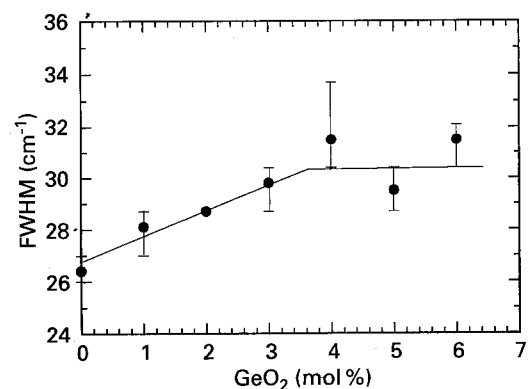


Figure 3 Full-width at the half-maximum of the  $261\text{ cm}^{-1}$  Raman line as a function of  $GeO_2$  content.

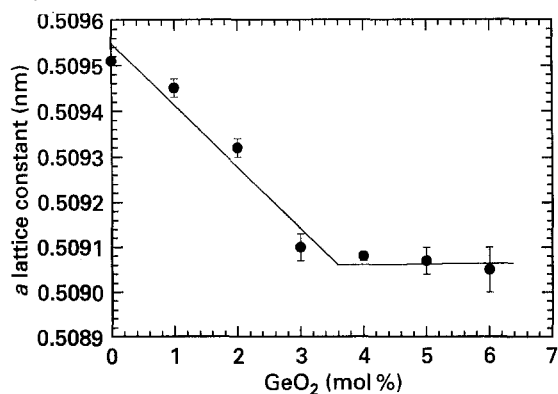


Figure 4 a lattice parameter of 2 mol % Y<sub>2</sub>O<sub>3</sub>-stabilized t-ZrO<sub>2</sub> as a function of GeO<sub>2</sub> content.

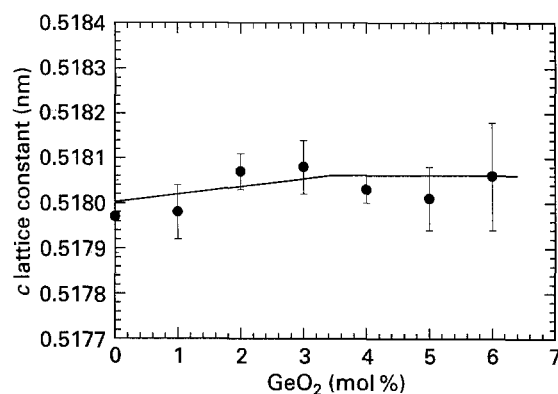


Figure 5 c lattice parameter of 2 mol % Y<sub>2</sub>O<sub>3</sub>-stabilized t-ZrO<sub>2</sub> as a function of GeO<sub>2</sub> content.

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