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$CeO_{1.5}$-stabilized tetragonal ZrO_2

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Ceria-stabilized tetragonal zirconia polycrystals show high toughness and high resistance to the low-temperature ageing degradation. However, ceria is less effective in stabilizing tetragonal zirconia compared to yttria and other trivalent oxides. The tetravalent oxide of CeO_2 can be easily reduced to the trivalent $CeO_{1.5}$, but phase separations occur leading to the destabilization of the tetragonal phase or the stabilization of the cubic phase. A procedure of high-temperature sintering and low-temperature reduction has been developed for preparing $CeO_{1.5}$-stabilized tetragonal zirconia. It was found that 9 mol% $CeO_{1.5}$ could stabilize the tetragonal zirconia to room temperature and that the stability region in the $CeO_{1.5}$–ZrO_2 system was extended to the lower dopant content region. The $CeO_{1.5}$-stabilized tetragonal zirconia had a lower tetragonality and lower transformability compared to the CeO_2-stabilized tetragonal zirconia with the same dopant mole percentage. The changes in the phase composition, tetragonality and stability caused by the reduction of CeO_2 to $CeO_{1.5}$ have been discussed in relation to the changes of oxygen stoichiometry, which is considered of the first-order importance in the stabilization of polymorphous zirconia.

1. Introduction

Ceria-doped tetragonal zirconia polycrystals show high toughness and high resistance to low-temperature ageing degradation, and is a candidate ceramic for structural applications [1–4]. However, compared to yttria and other trivalent oxides, the tetravalent ceria is less effective in stabilizing the tetragonal zirconia (t-ZrO_2) as well as the cubic zirconia (c-ZrO_2), e.g. a higher mole per cent of ceria must be added to zirconia to stabilize it in the t- or c-phases to lower temperatures. For example, at room temperature, 6 mol% $YO_{1.5}$-doped ZrO_2 is in the t-phase while 6 mol% CeO_2-doped ZrO_2 is in monoclinic (m) phase. Usually, only at CeO_2 contents higher than 12 mol%, can the doped ZrO_2 exist in the t-phase [1, 2].

It has been recognized that the oxygen stoichiometry is of first-order importance in the stabilization of polymorphous zirconia [5, 6]. The lesser effect of ceria in stabilizing t-ZrO_2 can be understood because the ceria is a tetravalent oxide which introduces much fewer oxygen vacancies into the zirconia lattice, although appreciable non-stoichiometry in ceria exists at higher temperatures [7]. For the trivalent oxides-doped ZrO_2, it has been observed that the tetragonal stability region and the tetragonality of c/a are only dependent on the dopant content, but almost independent of their species [8, 9]. On the other hand, adding pentavalent oxides, such as Ta_2O_5 or Nb_2O_5 to the trivalent $YO_{1.5}$-doped ZrO_2 to compensate for the oxygen vacancies, would cause destabilization of the t-phase [10, 11].

Because ceria can be easily reduced from CeO_2 to $CeO_{1.5}$, we expect that by sintering or heat treatment in reducing atmospheres, the stability of the CeO_2-doped t-ZrO_2 would be increased due to the valence change of Ce(IV) to Ce(III). In a previous study, it was found that reduction heat treatment significantly affected the phase structure and stability of the ceria–yttria-doped zirconia [12]. After the reduction heat treatment in charcoal at 900 °C, the t-m metastable phase boundary at room temperature was greatly shifted to the lower ceria content region and the stability of the t-phase increased. However, at high temperatures (> 1000 °C), the reduction of CeO_2 to $CeO_{1.5}$ resulted in phase separations, leading to either destabilization of the t-ZrO_2 [13-15] or stabilization of the c-ZrO_2 [12]. Hence, it seemed impractical to prepare $CeO_{1.5}$-stabilized t-ZrO_2 by the conventional sintering or heat treatment according to the phase diagrams of the ZrO_2-$CeO_{1.5}$ system [16, 17].

The objectives of the present work were firstly to develop a procedure for preparing the $CeO_{1.5}$-stabilized t-ZrO_2, and secondly, to study the phase structure and stability in the $CeO_{1.5}$-stabilized t-ZrO_2 in comparison to the CeO_2- and $YO_{1.5}$-doped ZrO_2 systems.

2. Preparation of the $CeO_{1.5}$-stabilized t-ZrO_2

The sintering temperatures for zirconia ceramics are usually higher than 1200 °C, while the temperatures for reducing ceria are much lower (> 400 °C) [17, 18]. Hence, a two-stage heat-treatment procedure was developed here to prepare the $CeO_{1.5}$-stabilized t-ZrO_2, e.g. sintering the CeO_2-doped ZrO_2 at high temperature in an oxidative atmosphere (usually in air) and then *in situ* reducing CeO_2 at a lower temperature in a reducing atmosphere. The high-temperature sintering oxidation atmosphere guarantees the densification of the CeO_2-doped zirconia in the single t-phase region at $CeO_2 < 20$ mol % according to the ZrO_2-CeO_2 phase diagram [19, 20]. The low reduction temperature is necessary to suppress the diffusional phase separation. It should be chosen as low as possible but still high enough to retain the CeO_2-doped zirconia in the t-phase to avoid the possible macro- or micro-cracking resulting from the t-m phase transformation.

It has been observed that the single t-phase is retained in the CeO_2-doped ZrO_2 after reduction heat treatments at temperatures below 1000 °C [12, 14, 15, 21, 22]. As the t-m transition temperature for pure ZrO_2 is about 1100 °C and this temperature is decreased by doping, we expected at 900 °C, the CeO_2-doped ZrO_2 specimens at $CeO_2 > 3$ mol % to be metastably retained in the single *t*-phase. Therefore, in the present work, the sintering temperature was selected as 1400 °C as usual, and the reducing temperature as 900 °C.

The CeO_2-doped ZrO_2 powders with 3, 6, 9, 12, 16 and 20 mol % CeO_2, derived by the coprecipitation method, were pressed into pellets 10 mm diameter and 1 mm thick. The pellets were sintered at 1400 °C for 4 h in air in a quartz glass tube, then cooled to 900 °C and reduced for 4 h in flowing hydrogen (purity $> 9.9999\%$). After the reduction, the glass tube was sealed and withdrawn from the furnace and rapidly cooled to room temperature. This procedure prevented the reoxidation of the specimens during cooling. Detailed heat-treatment specifications are shown in Fig. 1. For comparison, a set of specimens was heat treated in air with the same temperature programme.

3. Characterization of the $CeO_{1.5}$-stabilized t-ZrO_2

3.1. X-ray photoelectron spectroscopy (XPS)

The valence states of cerium and zirconium in the reduced and unreduced specimens were analysed by XPS (VG MII). In all the reduced specimens, Ce(IV) is reduced to Ce(III) while the zirconium ion is in its full oxidation state of Zr(IV). The chemical states of cerium and zirconium are independent of the CeO_2 content. Examples of the Ce 3d and Zr 3d spectra are given in Fig. 2 for specimens with 12 mol % CeO_2. The experimental details are the same as given elsewhere [14, 23]. For the unreduced specimen, Ce 3d and Zr 3d spectrum (a) resembles those of CeO_2 and ZrO_2, respectively, indicating that both cerium and zirconium are in the Ce(IV) and Zr(IV) states. For the reduced specimen, the Ce 3d spectrum (b) is greatly changed, which is characteristic of that of pure Ce_2O_3, indicating that the heat treatment at 900 °C for 4 h in hydrogen has sufficiently reduced the CeO_2 to $CeO_{1.5}$, that is, Ce(IV) to Ce(III). On the other hand, the Zr 3d spectrum (b) shows little change. This suggests that the zirconium is not reduced at 900 °C and is retained in the Zr(IV) state. These results are in good agreement with previous studies [14, 23].

All the specimens reduced changed in colour from the original pale yellow to the greenish blue, which corresponds to the colour of ceria and ceria-doped zirconia reduced in hydrogen at temperatures around 1000 °C [14, 18, 24]. Sectional observation shows the colour change occurs throughout the bulk, which demonstrates that the reduction of CeO_2 to $CeO_{1.5}$ has proceeded homogeneously.

3.2. Phase composition

Fig. 3 shows the phase compositions of the pellets determined by X-ray diffraction (XRD) on the as-heat-treated surfaces. For the specimens heat treated in air, e.g. the CeO_2-ZrO_2 system, the t-phase could be stabilized at room temperature only at $CeO_2 > 12$ mol %. This is inconsistent with the previous results [1, 2]. However, for the specimens reduced, for example the $CeO_{1.5}$-ZrO_2 system, the stable region of the t-phase is extended to the lower dopant concentration region. For instance, the t-phase is retained fully at 9 mol % $CeO_{1.5}$ and 80% t-phase is retained at 6 mol % $CeO_{1.5}$. The line

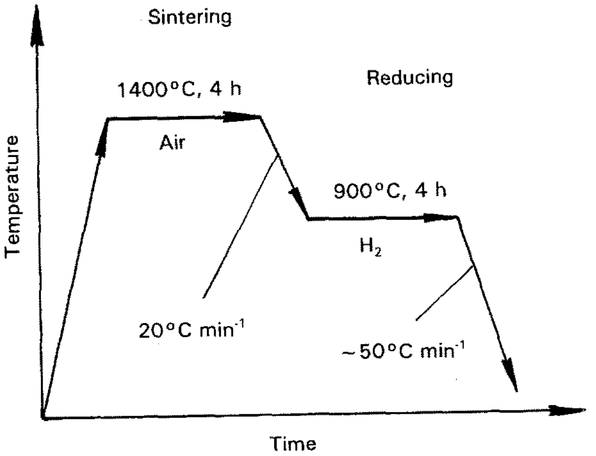

Figure 1 Specifications of the heat-treatment procedure for preparing the $CeO_{1.5}$-doped tetragonal zirconia.

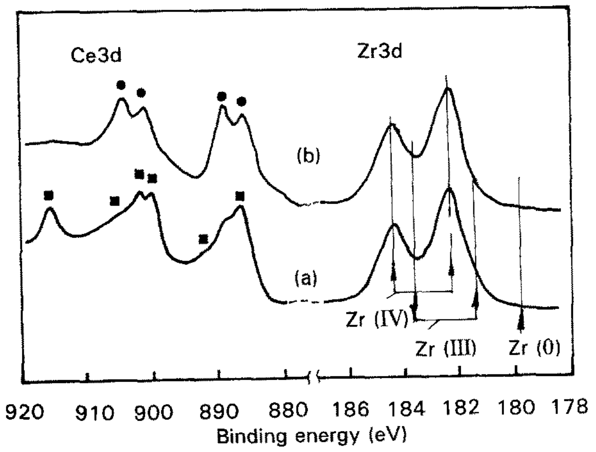

Figure 2 Ce 3d and Zr 3d XPS spectra for 12 mol % CeO_2-doped ZrO_2, (a) unreduced and (b) reduced, as specified in Fig. 1. (■) Ce(IV), (●) Ce(III).

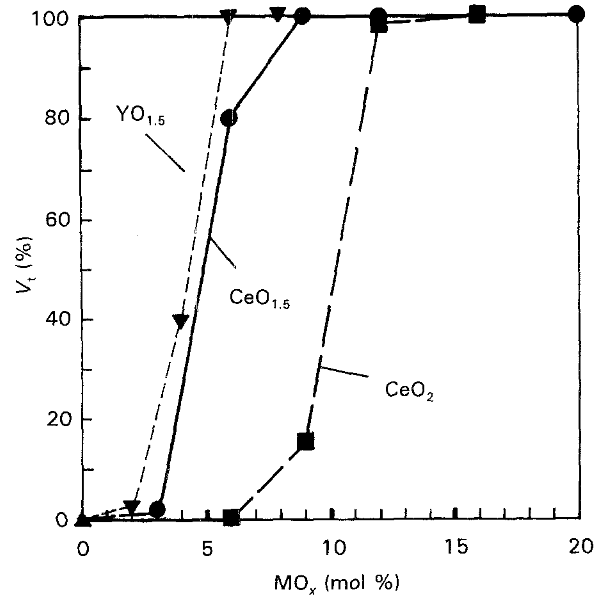

Figure 3 Volume fraction of tetragonal phase versus dopant content for CeO_2-, $CeO_{1.5}$- and $YO_{1.5}$-doped ZrO_2; $YO_{1.5}$ data after [24].

of volume fraction of t-phase versus dopant content for $CeO_{1.5}$-doped ZrO_2 is much nearer that for $YO_{1.5}$-doped ZrO_2 [24]. This implies that at the same mole percentage, $CeO_{1.5}$ can stabilize the t-ZrO_2 more effectively than CeO_2.

3.3. Tetragonality

The tetragonality of c/a of the tetragonal phase versus dopant concentration for CeO_2-, $CeO_{1.5}$- and $MO_{1.5}$-doped ZrO_2 systems is compared in Fig. 4. The tetragonality linearly decreases with increasing dopant concentration. The decrease in tetragonality due to the trivalent oxides $MO_{1.5}$, where M can be yttrium, scandiun, neodymium, samarium, gadolinium and ytterbium, is consistent and more pronounced than that due to the tetravalent oxide CeO_2. When CeO_2 is reduced to $CeO_{1.5}$, the decrease in tetragonality due to $CeO_{1.5}$ is greatly increased. For example, at 12 mol %, the c/a for CeO_2-doped t-ZrO_2 is about 1.018, while for $CeO_{1.5}$-doped t-ZrO_2 it is decreased to 1.012. However, $CeO_{1.5}$ is still less effective than the gonality. On the line extrapolation, the tetragonality would be unity at dopant content of 17 mol % for $MO_{1.5}$-ZrO_2 systems, while for $CeO_{1.5}$-ZrO_2 system, it is unity at a much higher concentration of 30 mol %. It is obvious that the role of $CeO_{1.5}$ deviates from those of the intrinsic trivalent oxides. The origin for this deviation will be discussed later.

3.4. Transformability

The transformability of CeO_2- and $CeO_{1.5}$-stabilized t-ZrO_2s was compared by determining the m-phase fraction on the ground and liquid-nitrogen (78 K) quenched surfaces of the specimens of 12 mol % $CeO_{1.5}$-doped t-ZrO_2 and 12 mol % CeO_2-doped t-ZrO_2. Grinding was manually performed on SiC paper (120 mesh). The XRD results are shown in Fig. 5.

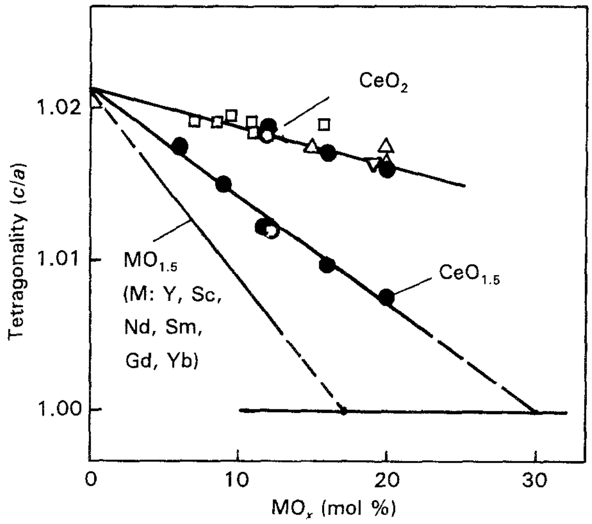

Figure 4 Tetragonality versus dopant content for CeO_2-, $CeO_{1.5}$- and $MO_{1.5}$-doped ZrO_2. (●) Present work, (□) after [2], (○) after [12], (△) after [19], (▽) after [20] and $MO_{1.5}$ after [8, 9].

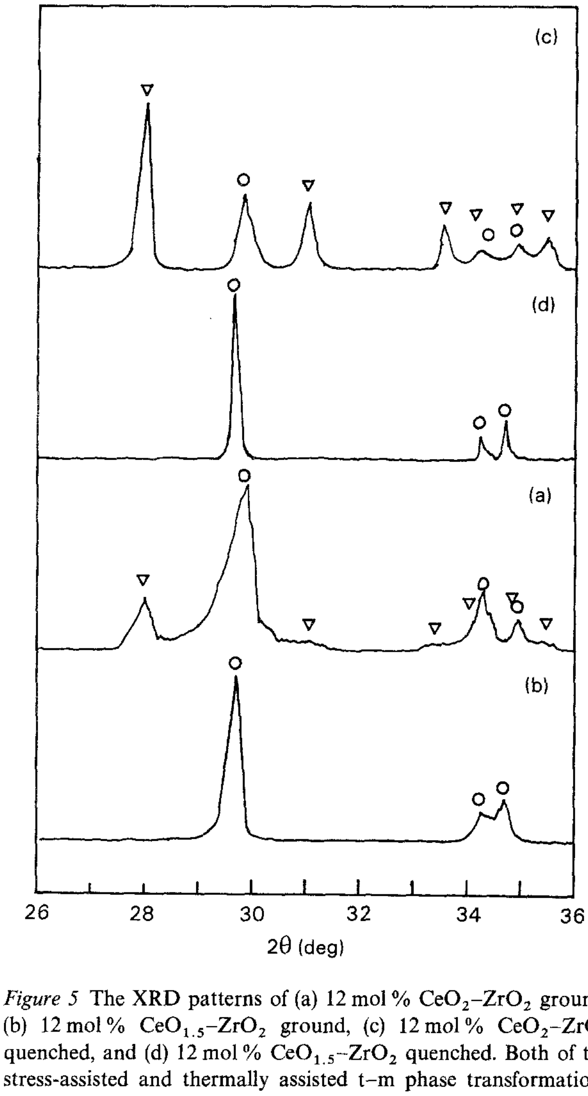

Figure 5 The XRD patterns of (a) 12 mol % CeO_2–ZrO_2 ground, (b) 12 mol % $CeO_{1.5}$–ZrO_2 ground, (c) 12 mol % CeO_2–ZrO_2 quenched, and (d) 12 mol % $CeO_{1.5}$–ZrO_2 quenched. Both of the stress-assisted and thermally assisted t–m phase transformations are seen to be suppressed due to the reduction of CeO_2 to $CeO_{1.5}$ by comparing (a) and (b), and (c) and (d) (▽) m-phase, (○) t-phase.

For the unreduced specimen, grinding induces about 30% t-m phase transformation at the surface, an asymmetrical broadening of the $(1\,1\,1)_t$ line, and the intensity reversal of $(0\,0\,2)_t$ and $(2\,0\,0)_t$ lines (Fig. 5a), as observed previously [25, 26]. For the reduced specimen, however, grinding causes no t-m phase transformation and no intensity reversal, although a slight asymmetrical broadening of the $(1\,1\,1)_t$ line remains (Fig. 5b). Similarly, upon liquid-nitrogen quenching, about 75% t-phase transforms to m-phase in the unreduced specimen (Fig. 5c), while no phase transformation at all was found in the reduced specimen (Fig. 5d). The suppression of both the stress-assisted and thermally-assisted phase transformations in 12 mol% $CeO_{1.5}$-doped t-ZrO_2 indicates that the transformability of the CeO_2-doped t-ZrO_2 is decreased by the reduction of CeO_2 to $CeO_{1.5}$.

4. Discussion

First we recall that the oxygen vacancy is of first-order importance in stabilizing the tetragonal, as well as cubic, zirconias. The tetravalent CeO_2 can introduce few oxygen vacancies into the zirconia lattice for electroneutrality. Its effect may mainly come from its larger ion size compared with the host zirconium ion ($r_{Ce(IV)} = 0.097$ nm, and $r_{Zr(IV)} = 0.084$ nm). When CeO_2 is reduced to $CeO_{1.5}$, large quantity of stoichiometric oxygen vacancies are introduced into the ZrO_2 lattice. The ionic formula becomes $(Zr^{4+},Ce^{3+})_1(O^{2-},V_a^0)_2$ from $(Zr^{4+},Ce^{4+})_1(O^{2-})_2$, similar to that of $YO_{1.5}$ doping, $(Zr^{4+},Y^{3+})_1(O^{2-},V_a^0)_2$. Therefore, the stabilization of t-phase by $CeO_{1.5}$ should correspond to that by $YO_{1.5}$, approximately, considering that the t-m equilibrium depends primarily on the number of oxygen vacancies and is independent of what has caused the vacancies.

Based on the above considerations, the difference in the tetragonality versus dopant content between the CeO_2- and $CeO_{1.5}$-doped ZrO_2 systems can be attributed to the difference in the oxygen vacancies in the two systems. Because the tetragonality is decreased when CeO_2 is reduced to $CeO_{1.5}$, the t-m transformation temperature, M_s, would also be decreased. Therefore, at the same mole percentage, when the CeO_2-stabilized t-ZrO_2 with higher tetragonality, e.g. higher M_s, transforms to m-ZrO_2 above room temperature, the $CeO_{1.5}$-stabilized t-ZrO_2 could be retained to room temperature owing to its decreased tetragonality, e.g. lower M_s. Thus, the tetragonal stability region in $CeO_{1.5}$-doped ZrO_2 is extended to a lower dopant concentration compared to that in CeO_2-doped ZrO_2. The change in tetragonality can also account for the change in the transformability, as studied by grinding and liquid-nitrogen quenching. It is known that the transformability increases with tetragonality [10, 11]. The t-phase becomes unstable as c/a increases towards 1.020, which corresponds to the b/a ratio of m-ZrO_2 at room temperature. On the other hand, the t-phase becomes stable as c/a approaches unity, which corresponds to the cubic phase. We note that at 12 mol %, the tetragonality of CeO_2-ZrO_2 is about 1.018, while that of $CeO_{1.5}$-ZrO_2 is about 1.012. The 6 mol % $YO_{1.5}$-stabilized t-ZrO_2 has a tetragonality of 1.016, in which no t-m transformation could be induced by subzero-cooling, and grinding under the same conditions only causes a 5% t-m transformation [12, 26]. The tetragonality of

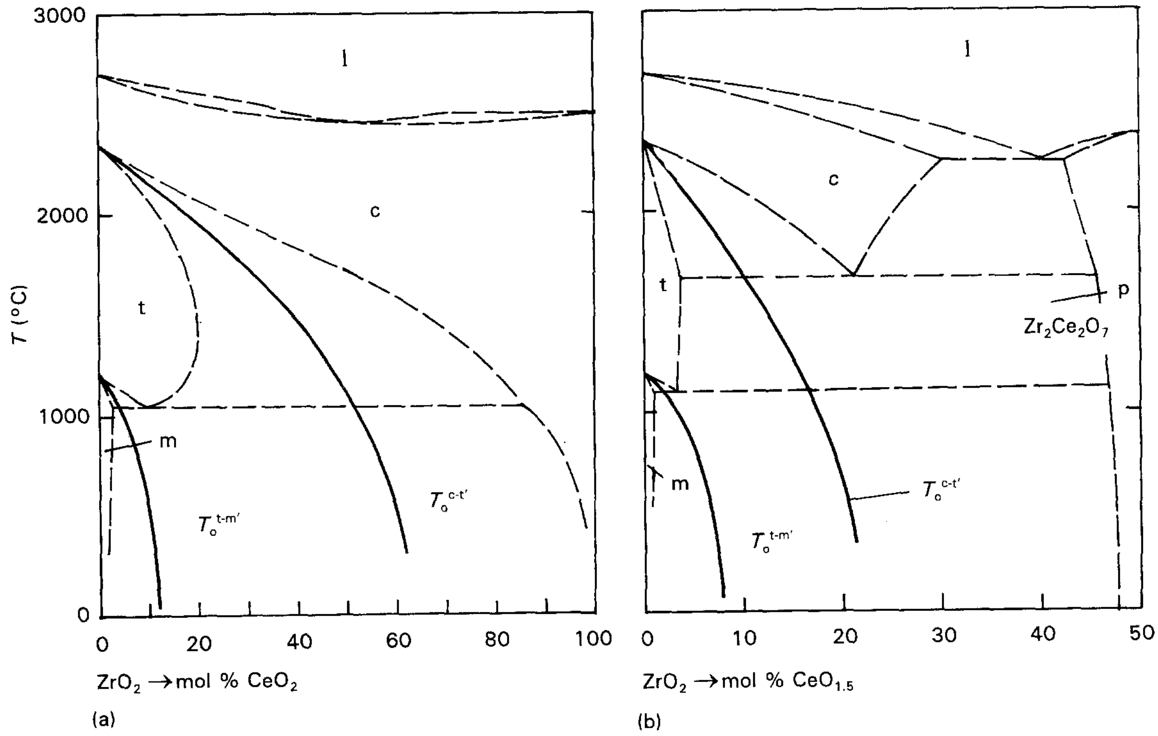

Figure 6 Schematic illustration of the metastable phase transformations of c–t′ and t–m′ in (a) CeO_2–ZrO_2 [8, 9] (a) and (b) $CeO_{1.5}$–ZrO_2. The left-shifted $T_0^{c-t'}$ and $T_0^{t-m'}$ lines in $CeO_{1.5}$–ZrO_2 are constructed based on the present data of the phase composition and tetragonality. The equilibrium phase diagram of $CeO_{1.5}$–ZrO_2 (– – –) is constructed referring to [16, 17]. Note that the concentration coordination for the $CeO_{1.5}$–ZrO_2 is twice as large as that for the CeO_2–ZrO_2.

12 mol % $CeO_{1.5}$-ZrO_2 (1.012) is much lower than that of 6 mol % $YO_{1.5}$-ZrO_2(1.016), so that the suppression of grinding-assisted and subzero-cooling-assisted t-m transformation is predictable.

In the present work, we have developed a procedure for preparing the $CeO_{1.5}$-doped tetragonal zirconia by suppressing the diffusional phase separation(s) in the $CeO_{1.5}$-ZrO_2 system. Another approach to access the diffusionless transformations is quenching the reduced $CeO_{1.5}$-ZrO_2 from the melt. A comparison of the diffusionless t-m′ and c-t′ transformations in the $CeO_{1.5}$- and CeO_2-ZrO_2 systems can be made based on the data obtained here. As shown in Fig. 6a, for the CeO_2-ZrO_2 system, the $T_0^{t-m'}$ line would join at 12 mol % CeO_2 at room temperature, while $T_0^{c-t'}$ line would be at a much higher CeO_2 concentration region, because the cubic ZrO_2 could be fully stabilized at room temperature only at $CeO_2 > 60$ mol % [19, 20]. In contrast, it is proposed in Fig. 6b that for the $CeO_{1.5}$-ZrO_2 system, the $T_0^{t-m'}$ line is shifted to the left and would join at < 9 mol % $CeO_{1.5}$ at room temperature, and the $T_0^{c-t'}$ line is also shifted to the left. Considering that in the $MO_{1.5}$-ZrO_2 systems, the cubic phase is stabilized at room temperature as the tetragonality approaches 1.005, the $T_0^{c-t'}$ line for $CeO_{1.5}$-ZrO_2 could be put at about 20 mol % at room temperature as the tetragonality approaches 1.005 at 20 mol % $CeO_{1.5}$, as shown in Fig. 4. In fact, after arc-melting and fast cooling in argon at $CeO_2 > 15$ mol %, the doped ZrO_2 specimens were fully retained in the cubic phase and the line for tetragonal fraction versus CeO_2 content agrees well with that observed for $CeO_{1.5}$-ZrO_2 [19]. After being reoxidized in air, both the t- and c-phases of the arc-melted specimens easily transformed to m- and t-phases respectively. It is certain that CeO_2, and even ZrO_2 partially, are reduced to $CeO_{1.5}$ and $ZrO_{1.5}$ during arc-melting in argon. These data support our present construction of the metastable phase diagram of the $CeO_{1.5}$-ZrO_2 system. A possible extension may be made to the $ZrO_{1.5}$-ZrO_2 system [27]. Owing to the easy redox reaction of CeO_2, it is expected that there will be uniquely redox-reaction-driven $c \leftrightarrows t$ and $t \leftrightarrows m$ transformations in the CeO_2-ZrO_2 system.

Of great interest is that $CeO_{1.5}$ is still less effective in stabilizing tetragonal ZrO_2 and in decreasing its tetragonality, compared with the other trivalent oxides. It has been proposed that this may arise from the possible ion-size effect, in that the Ce(III) ion is the largest compared with the other M(III) ions such as yttrium, neodymium, erbium, etc. EXAFS studies have shown that the location of the oxygen vacancy varies with the size of the dopant cations [28]. As the size of the dopant cations increases, the oxygen vacancy prefers to locate in the vicinity of the foreign cation. Another possible reason may be that the defects of Ce_{Zr} and V_a in the $CeO_{1.5}$-ZrO_2 system are ionized, which is different from the defects due to the intrinsic trivalent oxides, such as Y_{Zr} and V_a in the $YO_{1.5}$-ZrO_2 system. The ionized defects Ce'_{Zr} and $V_a^{\cdot\cdot}$ may be more tightly bonded together to form a complex defect such as $[Ce'_{Zr}][V_a^{\cdot\cdot}]$, so that the tetragonality changes differently in $CeO_{1.5}$-ZrO_2 from that in other $MO_{1.5}$-ZrO_2 systems. More detailed studies are needed to clarify the effect of intrinsity of the dopant valence on the tetragonality and the stabilization of the tetragonal and cubic zirconia ceramics.

5. Conclusion

A procedure of high-temperature sintering and low-temperature reduction has been developed from which $CeO_{1.5}$-doped tetragonal ZrO_2 has been successfully prepared. The CeO_2-doped ZrO_2 with 3–20 mol % CeO_2 were sintered in air at 1400 °C in the single t-phase region and then reduced in hydrogen at 900 °C at which CeO_2 could be sufficiently reduced to $CeO_{1.5}$, while the diffusional phase separation could be suppressed due to the low mobility of the cations. XPS has verified the reduction of CeO_2 to $CeO_{1.5}$. It was observed that 9 mol % $CeO_{1.5}$-doped ZrO_2 could be fully stabilized in the t-phase at room temperature. Compared to the CeO_2-doped ZrO_2 system, the tetragonal stability region in the $CeO_{1.5}$-ZrO_2 system was shifted to the left. The $CeO_{1.5}$-doped t-ZrO_2 reveals lower tetragonality and lower transformability compared to the corresponding CeO_2-doped t-ZrO_2 with the same dopant mole percentage. It is seen that due to the reduction of CeO_2 to $CeO_{1.5}$, both the metastable $T_0^{c-t'}$ and $T_0^{t-m'}$ lines were shifted to the lower dopant concentration region. The effects of reduction of CeO_2 to $CeO_{1.5}$ on the phase composition and stability have been explained, based on the first-order importance of the oxygen stoichiometry in the stabilization of polymorphous zirconia. The present work shows that the reduction heat treatment can be additional and/or alternative approach for controlling the structure and properties of zirconia ceramics.

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