Effect of Dopants on the Crystallite Growth of Superfine Zirconia Powder

J. L. Shi, Z. X. Lin & T. S. Yen

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, People's Republic of China

Abstract

Crystallites can grow in superfine zirconia powder during calcination. It is found that, in addition to calcination temperature and holding time, the crystallite size or crystallite growth rate can apparently also be affected by doping. Undoped powder has the largest crystallite size and the size decreases as the dopant content increases under the same calcination conditions. The effect of crystallite growth suppression is also dependent on dopant types, and it is explained by the dopants surface energy reduction effect, which is related to their ability to stabilize tetragonal and/or cubic phases of zirconia and to their surface-enriching and solute-dragging effects.

Während der Kalzinierung können in extrem feinem ZrO$_2$-Pulver Kristalle wachsen. Die Versuchsergebnisse zeigen, daß die Kristallitgröße neben der Kalzinierungstemperatur und der Haltezeit offensichtlich auch von einer Dotierung des Materials abhängt. Unter gleichen Kalzinierungsbedingungen weisen nicht dotierte Pulver die größten Kristalle auf. Die Kristallitgröße nimmt mit zunehmender Dotierung ab. Die Wirksamkeit der Dotierung hängt auch vom Dotierelement ab. Sie wird auf eine Reduktion der Oberflächenenergie durch die Dotieratome, die mit deren Fähigkeit, die tetragonale und/oder kubische ZrO$_2$-Phase zu stabilisieren, zusammenhängt, sowie die Anreicherung an der Oberfläche der Teilchen und den damit verbundenen 'drag'-Effekt beim Kristallwachstum zurückgeführt.

La calcination d'une poudre de zircone très fine peut conduire à la croissance de cristallites. On a trouvé qu'en plus de la température de calcination et du temps de maintien, la taille des cristallites et leur taux de effect, which is related to their ability to stabilize

poudres non dopées possèdent la taille de cristallites la plus élevée, celle-ci diminuant avec une teneur en dopant croissante, dans des conditions de calcination identiques. L'inhibition de la croissance des cristallites est également dépendante du type de dopant et elle peut être expliquée par la réduction d'énergie de surface lors du dopage. Celle-ci est fonction de l'aptitude des dopants à stabiliser les phases tétragonale et/ou cubique de la zircone et dépend également d'un effet d'enrichissement de la surface et d'attraction du soluté.

1 Introduction

Zirconia powders can be commonly obtained by the alkoxide pyrolysis/hydrolysis method[1–4] and the precipitation/coprecipitation method.[5,6] The hydroxide coprecipitation method for doped zirconia powder is more commonly used for its convenience, low cost and good homogeneity.

To obtain the most active powders, fine particles of the powder are preferred. Particle (crystallite) size of powders is dependent on various factors such as preparation method, composition of the materials, etc. Grain growth generally occurs in dense sintered bodies or porous compacts,[7–9] and also in superfine zirconia powders.[10] This paper investigates the effect of solid solute doping in zirconia powders on the crystallite growth of zirconia.

2 Experimental

Zirconium oxychloride, yttria (99·95%), magnesium chloride (AR) and ceria (AR) were used as the raw materials, and yttria and ceria were dissolved in

117

excess nitric acid before being used in coprecipit-ation. Coprecipitation was performed via the reverse strike method[11] to give a final pH value higher than 9. The coprecipitates were washed with distilled water to remove anions and then with ethyl alcohol to minimize the possible effect of agglomeration.[10] Washed cakes were dried at 100°C and calcined at different temperatures from 420 to 1000°C. Crystal-lite sizes were determined by the X-ray diffraction-line broadening (XRD-LB) method (Rigaku Denki, RAX-10) and the powder morphology was observed

with transmission electron microscopy (JEOL, JEM-200CX).

3 Results

3.1 Crystallite size as a function of dopant level

Yttria-doped zirconia powders with yttria dopant levels of 0, 1·5, 3, 7 and 10 mol% Y_2O_3 (correspond-ing to 0, 3, 6, 13 and 18 mol% $YO_{1.5}$ content, respectively) were selected. The differently doped
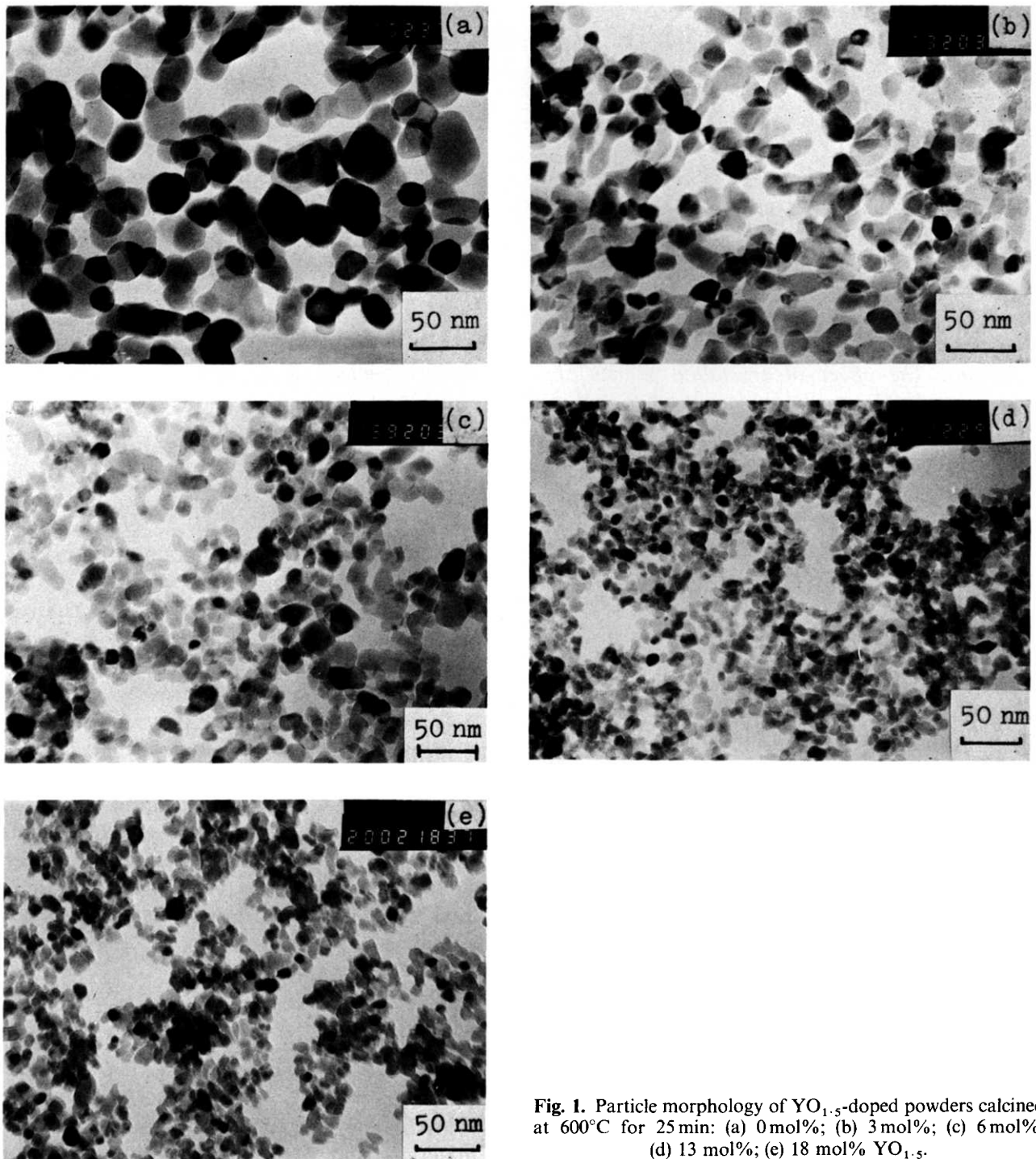

Fig. 1. Particle morphology of $YO_{1.5}$-doped powders calcined at 600°C for 25 min: (a) 0 mol%; (b) 3 mol%; (c) 6 mol%; (d) 13 mol%; (e) 18 mol% $YO_{1.5}$.
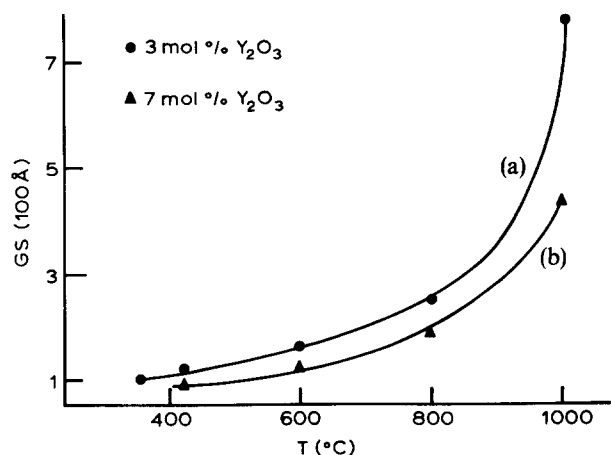
Fig. 2. Crystallite sizes of (a) 6 mol% $YO_{1.5}$ and (b) 13 mol% $YO_{1.5}$ doped zirconia powders versus calcination temperature.

powders calcined at 600°C for 25 min had different crystallite sizes, as shown in the TEM micrographs of Fig. 1(a)–(e). It can be seen from the figure that the crystallite size of zirconia powders decreases with the increase of $YO_{1.5}$ content, i.e. crystallite growth of zirconia is depressed by the yttria doping in zirconia. Under the experimental conditions, calcined pure zirconia powder shows the largest crystallite size of about 35 nm, and the crystallite
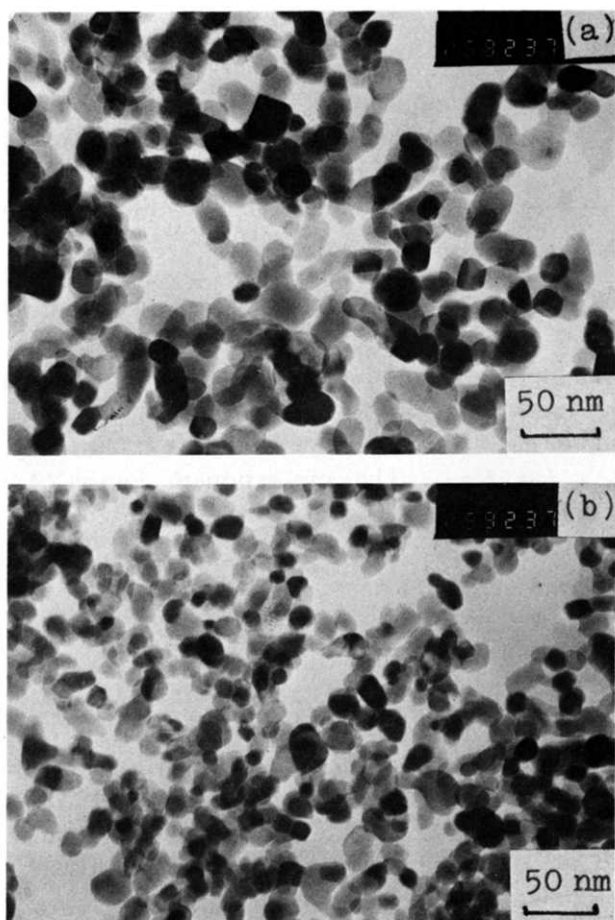

Fig. 3. Particle morphology of CeO_2 doped zirconia powders calcined at 600°C: (a) 6 mol% CeO_2 and (b) 14 mol% CeO_2.
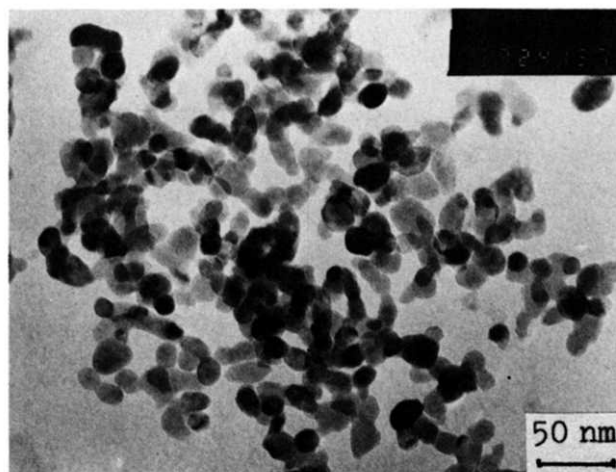

Fig. 4. Particle morphology of 14 mol% MgO doped zirconia powder (calcined at 600°C).

sizes are reduced to about 17 nm and 12 nm when 6 mol% and 13 mol% $YO_{1.5}$, respectively were doped.

Figure 2 shows the relationship between crystallite size and calcination temperature for 6 mol% and 13 mol% $YO_{1.5}$ doped powders. The powder of higher dopant level always shows smaller crystallite size than that of lower dopant level within the temperature range 420–1000°C.

3.2 Effect of dopant types

The crystallite size of zirconia powder can also be decreased by doping with magnesia or ceria, as shown in Figs 3 and 4. Figure 3(a) and (b) are the TEM micrographs of 6 mol% and 14 mol% ceria-doped zirconia powders, respectively. It can be seen that the doping of ceria decreases the crystallite size, but the size-reducing effect is not as strong as for $YO_{1.5}$ at the same doping level. Doping of 14 mol% magnesia has a similar size-reduction effect as ceria, as shown in Fig. 4.
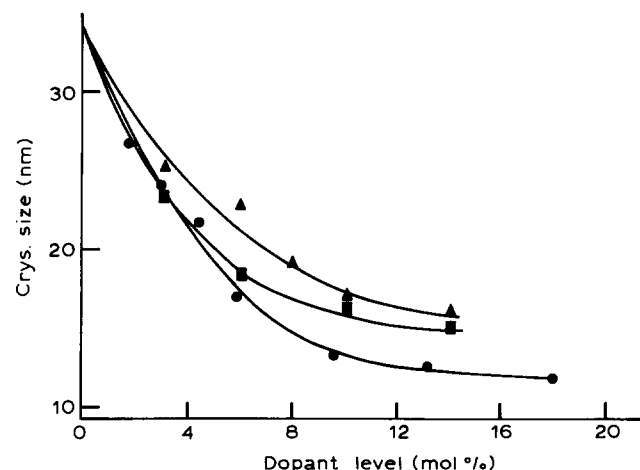

Fig. 5. Crystallite sizes of zirconia powders doped with (▲) MgO, (●) $YO_{1.5}$ and (■) CeO_2 versus doping level by X-ray diffraction-line broadening technique (calcined at 600°C).

The results of crystallite size determination by XRD-LB for different types of dopants and doping level are illustrated in Fig. 5, corresponding to the micro-morphology observation in Figs 1, 3 and 4. It can also be seen from Fig. 5 that the crystallite size reduction is more effective at a lower doping level than at a higher level. $YO_{1.5}$ is the most effective dopant amongst the dopants studied on the crystallite size reduction when the dopant levels are above 6 mol%, and the effect of ceria and magnesia is about similar.

4 Discussion

4.1 Relation between phase stabilization and crystallite size reduction

The main effect of doping in zirconia is to stabilize the tetragonal or cubic phase at room temperature, and the mechanism of the phase stabilization is thought to be the lattice distortion of tetragonal or cubic phase by introduction of dopants into the zirconia lattice, thus making the tetragonal or cubic phase stable at room temperature. Figure 6 shows the change of total content of tetragonal and cubic phases with dopant level of ytrria, magnesia and ceria when calcined at 600°C. Higher dopant level favors the stabilization of tetragonal and cubic phases more effectively.

It is known that the tetragonal phase of zirconia has a lower surface energy than that of the monoclinic phase,[12,13] so when the zirconia particles are less than the critical size, the tetragonal phase can be stable at room temperature.[14,15] The critical size is about 30 nm when elastic energy is also considered and 10 nm when the elastic energy is not considered.[16] There is also evidence that the cubic

Fig. 6. Total amount of tetragonal and cubic phases of zirconia versus doping level for (▲) MgO, (●) $YO_{1.5}$ and (■) CeO_2 doped powders (calcined at 600°C).

phase of zirconia can exist at room temperature after a low temperature of calcination or after a treatment resulting in a smaller crystallite size than that which produces the tetragonal phase.[3,17,18] As the less symmetric phase—monoclinic zirconia—is generally the more stable phase at room temperature, it should have a lower chemical free energy. However, by decreasing the particle size, both tetragonal and cubic phase can be stabilized. So, as analyzed by Garvie,[14] it is proposed that the zirconia phase with higher symmetry would possess a lower surface energy than that with lower symmetry. This means that the following relation is true at room temperature (where γ is surface energy):

$$\gamma_{cubic} < \gamma_{tetragonal} < \gamma_{monoclinic}$$

Dopants of yttria, ceria and magnesia can stabilize tetragonal and cubic phases, and according to Fig. 6, higher content of dopants can stabilize more effectively the tetragonal and cubic phases. It is also clear that the cubic phase is stable at higher dopant levels than the tetragonal one, as suggested by phase diagrams. Thus it is inferred that in addition to any bulk chemical free energy changes, higher dopant levels lower the surface energy of zirconia particles.

Based on the thermodynamic point of view, particles with lower surface energy could exist with smaller sizes than ones with higher surface energy. Kinetically, the surface energy could affect the crystallite growth rate. The crystallite growth process can generally be described by the following:

$$r^n - r_0^n = A \exp(-E/RT)(t - t_0) \qquad (n = 2\text{--}4)$$

where A is the pre-exponent factor, n is a constant ($n = 2$ for dense materials and $n = 3\text{--}4$ for porous compacts), r is the crystallite radius, E is the activation energy for crystallite growth, and T and t are the absolute temperature and time, respectively, r is r_0 at $t = t_0$. The pre-exponent factor A is proportional[7] to the surface (or interface) tension (or surface energy):

$$A \propto \gamma$$

Doping of solid solute of yttria, ceria and magnesia in zirconia crystallites reduces the surface energy and so decreases the pre-exponent factor A and the crystallite size, i.e. introduction of solid solute dopants into the zirconia lattice simultaneously stabilizes the tetragonal and cubic phases on the one hand and reduces the growth rate of zirconia crystallites on the other.

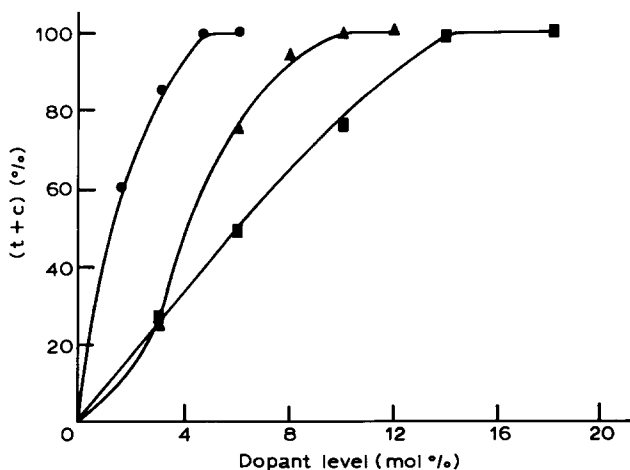Figure 6 has shown that $YO_{1.5}$ is the most effective phase stabilization dopant among the

dopants used, so $YO_{1.5}$-doped zirconia powder has the smallest particle size compared to magnesia- or ceria-doped zirconia powders (Fig. 2) at the same dopant level.

4.2 Effect of doping types on the suppression of crystallite growth

There are ways to create lattice distortion for the phase stabilization: by introducing oxygen vacancies with cations of different valencies than Zr^{4+} or by substituting host ions Zr^{4+} with isovalent cations of different radii. Tables 1 and 2 show the vacancy concentrations introduced into zirconia by dopants (per mol) and the ion radii as well as the radius differences between dopant ions and zirconium ion. Ce^{4+} does not introduce oxygen vacancies in the zirconia lattice as compared to Y^{3+} and Mg^{2+}, so ceria-doped zirconia powder contains the highest content of monoclinic phase at the same dopant level among the dopants used. Although Mg^{2+} can introduce a doubled amount of oxygen vacancies if compared with Y^{3+}, the radius difference between Y^{3+} and Zr^{4+} is much larger than that between Mg^{2+} and Zr^{4+}. As a result, Y^{3+} is more effective than Mg^{2+}, and also than Ce^{4+}, in phase stabilization and crystallite growth reduction. In addition, although Ce^{4+} does not create oxygen vacancies in zirconia, the radius difference between Ce^{4+} and Zr^{4+} is larger than that between Mg^{2+} and Zr^{4+}, so Ce^{4+} is believed to create lattice distortion by the radius difference. As a result, ceria and magnesia have a similar effect on phase stabilization and crystallite growth reduction as well.

In addition to the reasons discussed, dopant segregation to the particle surface may also be important.[19-22] Because of the dopant segregation, the surface charging state and the surface tension may be altered.[19] Such an effect has been observed and discussed by several authors[20-22] for segregation at grain boundaries in zirconia ceramics. According to the argument by Chen,[21] larger cations

with lower valencies ($<4+$) are more effective in decreasing grain boundary mobility and therefore suppressing grain growth in ceramics than smaller cations with higher valencies ($>4+$), based on the consideration of solute dragging and the space charge cloud-forming effect.[22] Since these principles may, at least, be generally true for the suppression of crystallite growth in doped zirconia powders, the more effective crystallite growth-suppressing effect of Y^{3+} as compared to Ce^{4+} can be understood, and as Mg^{2+} is smaller but less positively charged than Ce^{4+}, the similar effect of Mg^{2+} and Ce^{4+} can also be reasoned.

5 Conclusions

Doping proper solid solutes like yttria, ceria and magnesia in zirconia powders prepared by coprecipitation can reduce the crystallite sizes or suppress the crystallite growth of zirconia particles in the temperature range from 420 to 1000°C, which is accompanied by tetragonal and cubic phase stabilization. The crystallite growth-suppressing effect in zirconia powders is attributed to the surface tension reduction of the powder particles by doping, which is believed to be also effective partially in the stabilization of tetragonal and cubic phases in the superfine zirconia powders. The difference of the crystallite growth-suppressing effects between Y^{3+}, Mg^{2+} and Ce^{4+} is related to their different properties (valencies and radii), which affect their segregation on crystallite surfaces and the surface mobility decreasing effect of the dopants.

References

1. Mazdiyasni, K. S., *Ceramics International*, **8** (1982) 42.
2. Ishizawa, H., Sakurai, O. & Kato, M., *Am. Ceram. Soc. Bull.*, **65** (1986) 1399.
3. Mazdiyasni, K. S., Lynch, C. T. & Smith, J. S., *J. Am. Ceram. Soc.*, **50** (1967) 532.
4. Barringer, E. A. & Bowen, H. K., *J. Am. Ceram. Soc.*, **65** (1982) C-199.
5. Haberko, K., *Ceramics International*, **5** (1979) 148.
6. Roosen, A. & Hausner, H., in *Ceramic Powder*, ed. P. Vincenzini. Elsevier, Amsterdam, Oxford, New York, 1983, 773.
7. Brook, R. J., in *Ceramic Fabrication Process*, ed. F. F. Y. Wang. Academic Press, New York, 1976, p. 331.

Table 1. Oxygen vacancy concentration (per mol) in zirconia doped with $YO_{1.5}$, MgO and CeO_2

Dopant	MgO	$YO_{1.5}$	CeO_2
V_0'''	6.02×10^{23}	3.01×10^{23}	0

Table 2. Ionic radii of dopants and the radius differences between dopant ions and host ion (Zr^{4+})

Ions	Zr^{4+}	Mg^{2+}	Y^{3+}	Ce^{4+}	$|\Delta Y^{3+}-Zr^{4+}|$	$|\Delta Mg^{2+}-Zr^{4+}|$	$|\Delta Ce^{4+}-Zr^{4+}|$
Ionic radius	0.87	0.78	1.06	1.02	0.19	0.09	0.15

8. Lay, K. W., In *Sintering and Related Phenomena*, ed. G. C. Kuczynski. Plenum Press, New York, 1973, p. 65.
9. Greskovich, C. & Lay, K. W., *J Am. Ceram. Soc.*, **55** (1972) 142.
10. Shi, J. L., PhD thesis, Shanghai Institute of Ceramics, 1989.
11. Johnson, D. W. & Gallagher, P. K., In *Ceramic Processing before Firing*, ed. G. Y. Onoda, Jr. & L. L. Hench. John Wiley & Sons, New York, 1978, p. 125.
12. Holmes, H., Fuller, Jr., E. & Gammage, R., *J. Phys. Chem.*, **76** (1972) 1497.
13. Livey, D., *J. Am. Ceram. Soc.*, **39** (1956) 363.
14. Garvie, R. C., *J. Phys. Chem.*, **69** (1965) 1238.
15. Garvie, R. C., *J. Phys. Chem.*, **82** (1978) 218.
16. Haberko, K. & Pampuch, R., *Ceramics International*, **9** (1983) 8.
17. Hishinuma, K., Kumaki, T., Nakai, Z., Yoshimura, M. & Somiya, S., In *Advances in Ceramics*, Vol. 24, *Science and Technology of Zirconia III*, ed. S. Sōmiya, N. Yamamoto & H. Yanahida. The American Ceramic Society, Columbus, OH, 1988, p. 201.
18. Nishizawa, H., Yamasaki, N., Matsuoka, K. & Mitsushio, H. *J. Am. Ceram. Soc.*, **65** (1982) 342.
19. Kingery, W. D., Bowen, H. K. & Uhlman, D. R., *Introduction to Ceramics*. John Wiley & Sons, New York, 1976, p. 240.
20. I-Wei Chen & Lian An Xue, *J. Am. Ceram. Soc.*, **73** (1990) 2585.
21. Hwang, S. L. & I-Wei Chen, *J. Am. Ceram. Soc.*, **73** (1990) 3269.
22. Oishi, Y., Ando, K. & Sakka, Y., In *Advances in Ceramics*, Vol. 7, *Characterization of Grain Boundaries*, ed. M. F. Yan & A. H. Heuer. The American Ceramic Society, Columbus, OH, 1983, 208.