JOURNAL OF MATERIALS SCIENCE 30 (1995) 749–757

Low-temperature preparation of nanostructured zirconia and YSZ by sol–gel processing

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Stable zirconia sol, with a particle size sharply monodispersed at 4 nm, was synthesized via hydrolysis of zirconia tetra-*n*-butoxide in 2-propanol. Stable composite sols were prepared via an "interparticle" modification route by introducing yttrium nitrate. Although the nanostructure of the dried gels was insensitive to yttrium addition, the crystallization behaviour was greatly influenced by it. Without yttrium addition the monoclinic zirconia was obtained at 700 K. After "interparticle" modification with yttrium, the cubic phase of yttria-stabilized zirconia was directly obtained at 726 K. The sintering of both the systems was also enhanced at low temperature. As a result of the low-temperature processing, nanostructured zirconia and YSZ with homogeneous grain sizes of a few tens of nanometres have been successfully prepared.

1. Introduction

Nanostructured materials exhibit interesting mechanical, electrical, optical and magnetic properties which are not observed in coarse-grained systems. Enormous ductility in nanostructured ceramics is caused by the enhancement of diffusional creep [1]. This phenomenon has been reported not only on monolithic ceramics but also on their composites [2]. Semiconductor crystallites of ~ 2–10 nm have bulk-like internal lattices, but their optical spectra show partially resolved discrete features [3]. Based on the quantum confinement combined with host/guest chemistry, new promising devices might be developed [4, 5]. Recently, we reported an interesting finding on the densification of nanostructured titania assisted by a phase transformation from anatase to rutile at low temperature [6]. The increased mobility of the atoms during the phase transformation enhanced the sintering, and a densified body was obtained after firing at 600 °C.

Of the processing methods to produce nanostructured ceramics, the sol–gel route is advantageous for its excellent chemical purity and homogeneity. Silica is the most popular product of the processing [7]. Sols and gels of alumina [8–10] and titania [11, 12] were successfully synthesized, and applied to separation membranes [13, 14]. We demonstrated that the surface modification of a colloid particle in a sol was effective in controlling the nanostructure of the gel [15], where the alternative possibility of nanostructure control via the "interparticle" modification route was stressed. In recent years the number of the researches on sol–gel derived zirconia [16–20] and yttria stabilized zirconia (YSZ) [21, 22] has been increasing, because it is not only an important material as far as mechanical property is concerned but is also a hopeful ionic conductor. The characteristic feature of the sol–gel processing of zirconia, compared with the other oxide systems, is the extremely rapid reaction of the alkoxide with water. The control of the processing is, therefore, problematic. In addition, expansion of the simple zirconia system to the mixed oxide of stabilized zirconia is an important step in view of practical usage. In this paper, success in the crystallization and sintering of the sol–gel derived ultrafine zirconia and YSZ at low temperature is reported. In addition, an alternative approach to the mixed oxide system via the "interparticle" modification route is demonstrated.

2. Sample preparation and characterization

YSZ is a solid solution of zirconia and yttria. Our approach to form this mixed oxide is a surface modification of zirconia sol with yttrium. The conceptual illustration is shown in Fig. 1. In other words, homogeneous dispersion of yttrium in a nanostructured grain boundary of zirconia gel is expected. The advantages of this route, compared with the "intraparticle" modification route, are that it is easy to control the nanostructure, and that we can choose the source from a variety of chemicals. In addition, the synthesis of the mixed oxide at relatively low temperature is expected, because the diffusion path of yttrium to form the mixed oxide, zirconia particle size in this case, is very short.

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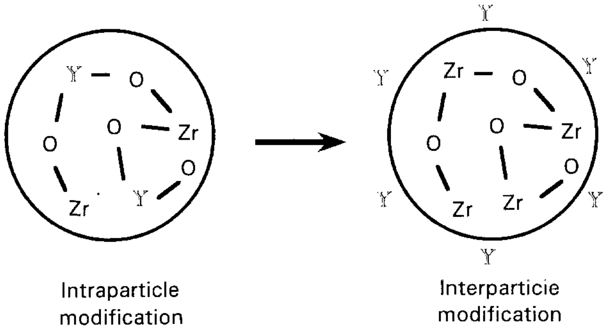

Figure 1 Conceptual illustration of "interparticle" modification.

Many of the works to prepare mixed oxides by the sol–gel route (for example, mullite [23] and barium titanate [24]), reported so far, were carried out via the "intraparticle" modification route. Our approach is an alternative "interparticle" modification, which is not by inserting yttrium into the zirconia particle, but by placing yttrium around it.

First, zirconia sol was prepared. We could not obtain a stable sol via the postdispersion of the precipitate, which was successfully applied to alumina [8–10] and titania [6]. This might be caused by the extremely rapid reaction of zirconium alkoxide with water. The reaction product of the alkoxide and water was very sensitive to the kind and concentration of acid, as well as the amount of water. The best conditions employed here were as follows. Zirconium tetra-*n*-butoxide (TBZR, Nippon Soda Co. Ltd) was dissolved in 2-propanol ($>99.9\%$, Wako Chemicals Co.,) and 1 N nitric acid diluted with the solvent was added. The final alkoxide concentration was 0.05 M and the water to alkoxide ratio was fixed at 3. The hydrolysis and condensation was carried out at room temperature under stirring for a few days, and at least one day. Water was effective as a dispersion medium because its greater surface tension produces a dense packing at the drying stage [6]. In order to replace the dispersion medium of 2-propanol with water, excess water was added and 2-propanol was removed by evaporation. The removal of 2-propanol was confirmed by the refractive index of the dispersion medium. At the same time, the sol concentration was adjusted. Finally, yttrium nitrate hexahydrate (99.9%, Wako Chemicals Co.,) was added to the sol and stirred. The yttrium concentration is defined by

$$\text{yttrium concentration, } y\text{: } (Y_2O_3)_y(ZrO_2)_{1-y} \quad (1)$$

This value corresponds with the yttria molar concentration in the final product. The yttrium concentration was changed from $y = 0$ to $y = 0.17$. Thus the stable composite sols were prepared. Unsupported gel was obtained by drying the sol in a Petri dish. The gels obtained were dried and fired in air. Each sample was heated at the rate of $100\,\mathrm{K\,h^{-1}}$, and was kept at 573–1373 K for 5 h.

The products were characterized as follows. Dynamic light scattering (Otsuka Electronics, ELS-800) equipped with a 1 mW He–Ne laser was carried out with changing yttrium content, the zirconium concentration being fixed at 0.05 M. The nanostructure of the gels and oxides was observed by field emission-type scanning electron microscopy (FE-SEM, Hitachi, S-900H). Prior to observation, platinum was carefully coated by magnetron sputtering (Hitachi, E-1030) for a few seconds. Thermal analysis (Shinku-riko, TGD 7000 RH) and X-ray diffraction (XRD, Mac Science, MP3) with CuK$_\alpha$ radiation revealed the structure of the product and the crystallization behaviour.

3. Results and discussion

3.1. Nanostructure without yttrium addition

Fig. 2 shows the weight-based distribution of Stokes' diameter of the zirconia particles in the sol without

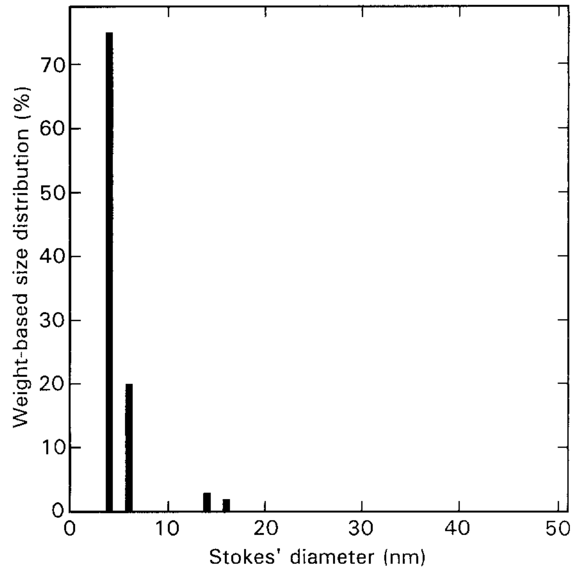

Figure 2 Weight-based distribution of Stokes' diameter in zirconia sol without yttrium.

Figure 3 FE-SEM view of zirconia gel.

yttrium addition. This diameter corresponds with the aggregation size, if formed. The particle diameter was sharply monodispersed at 4 nm, which is much smaller than the value on boehmite (AlOOH) sol [4]. The distribution was similar to that before the replacement of the dispersion medium.

Fig. 3 is an FE–SEM view of the zirconia gel without yttrium addition. The original magnification was ×500 000. The sputtered platinum particles (0.8 nm diameter, white points) are clearly observed. The zirconia particle is 6 nm in diameter. This size is approximately equal to the value determined by dynamic light scattering shown in Fig. 2, suggesting that very small particles are dispersed in a sol without forming an aggregation. The opening pore size is about 5 nm.

3.2. Changes in nanostructure with yttrium addition

The pH of the sol was 5.6 before yttrium nitrate hexahydrate addition, and 5.1–5.2 after that. The changes in the average Stokes' diameter with the amount of yttrium added is illustrated in Fig. 4. As the yttrium content was increased, the aggregation was enhanced, where all the sols were monodispersed, but the sharpness of the distribution was reduced. Replacement of the dispersion medium was effective in suppressing the gelation after introducing yttrium.

The changes in the nanostructure with the amount of yttrium added are shown in Fig. 5a–d. No significant change is observed. Aggregation observed in a sol did not cause the macro pore formation among the aggregates, suggesting that the weak aggregates were broken down during the gelling or drying stage, as in the nickel/alumina system [15].

3.3. Crystallization behaviour

DTA curves for zirconia of $y = 0$ and 0.08, heating rate 10 K min^{-1}, are illustrated in Fig. 6. Around 373 K, broad endothermic peaks due to the desorption of water, are observed. No exothermic peaks with a significant weight decrease due to the combustion of the residual carbon were detected, suggesting hydrolysis was completed before firing. The removal of carbon might be attained by the replacement of the dispersion medium of 2-propanol with water. On the other hand, very sharp exothermic peaks are observed at 700 and 726 K, respectively. At these points no significant weight loss was observed.

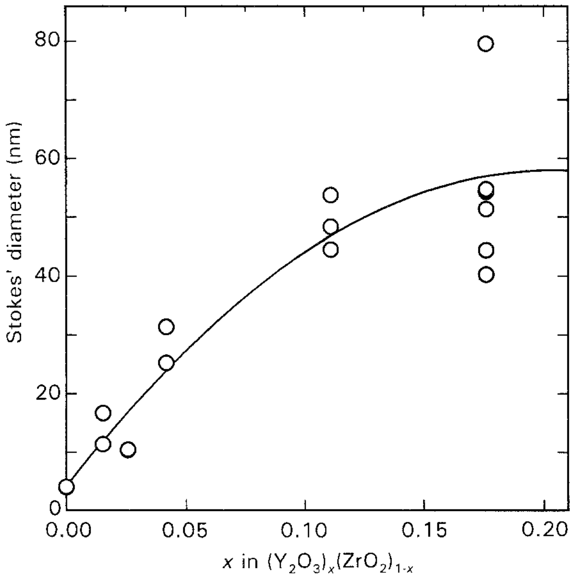

Figure 4 Changes in average Stokes' diameter with yttrium content.

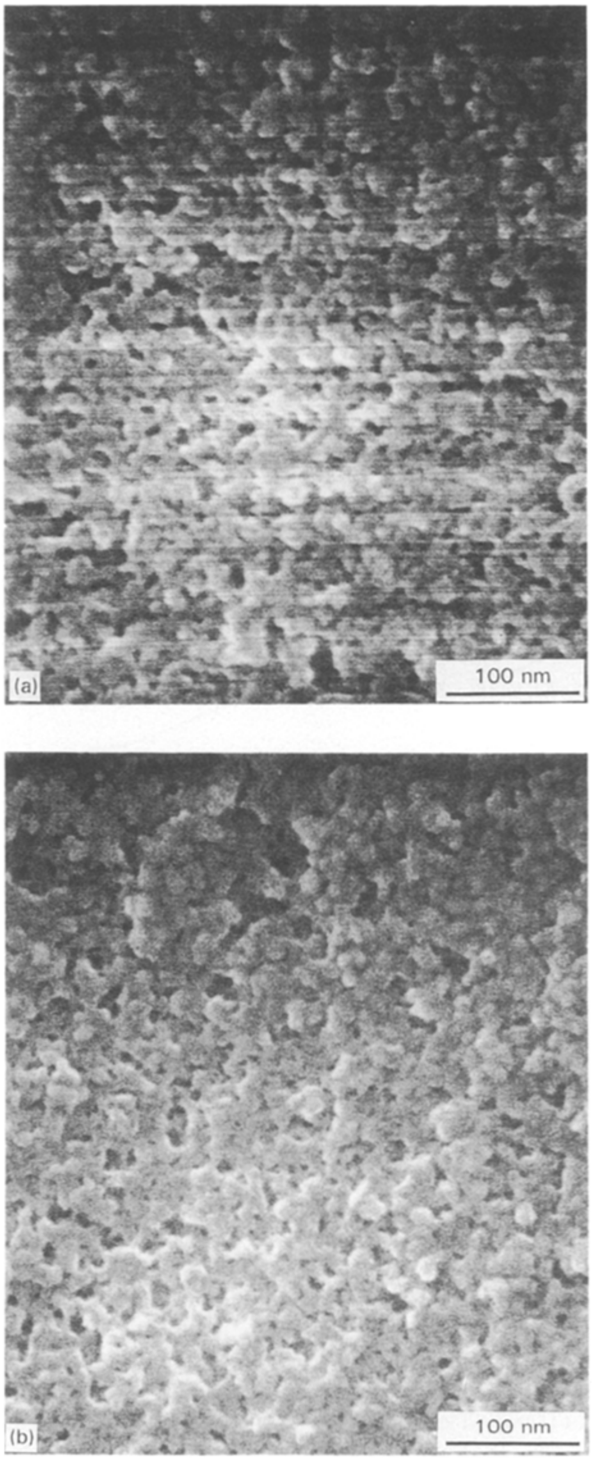

Figure 5 FE-SEM views of zirconia gel including yttrium. (a) ZrO_2 (b) $(Y_2O_3)_{0.015}$ $(ZrO_2)_{0.985}$ (c) $(Y_2O_3)_{0.04}$ $(ZrO_2)_{0.96}$ and (d) $(Y_2O_3)_{0.10}$ $(ZrO_2)_{0.90}$.

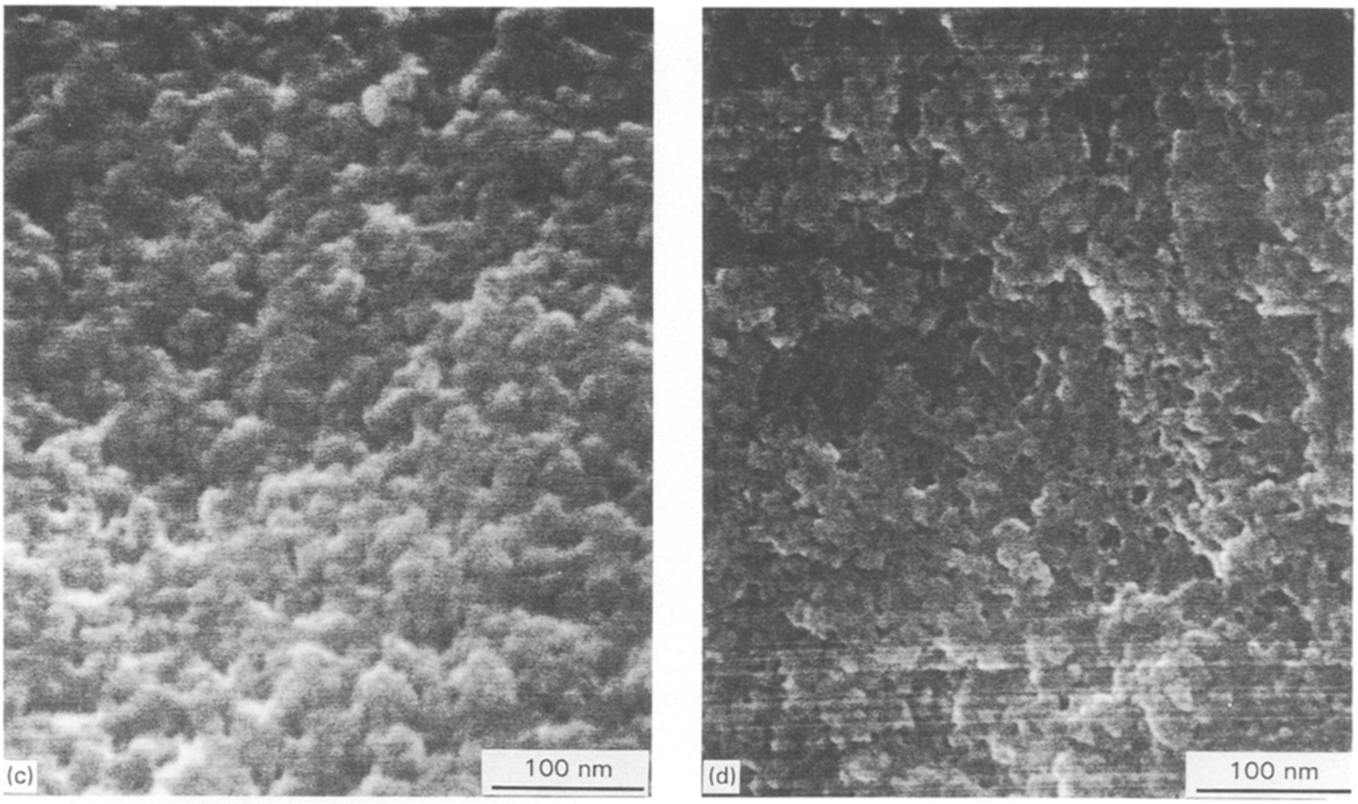

Figure 5 (Continued)

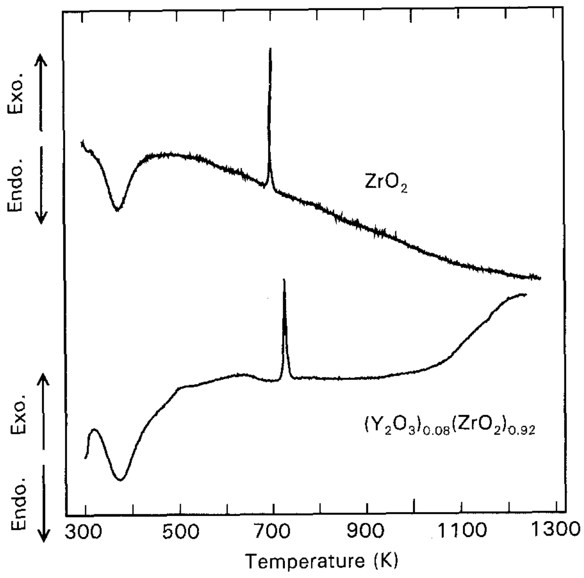

Figure 6 DTA curves of ZrO_2 and $(Y_2O_3)_{0.08}$ $(ZrO_2)_{0.92}$.

Figs 7 and 8 show XRD patterns of zirconia of $y = 0$ and 0.08, respectively. Prior to measurements, the samples were fired at 573, 773, 973 and 1173 K. In Fig. 7, peaks due to a monoclinic single phase are observed for zirconia without yttrium addition above 773 K. Contrary to the work by Ramamurthi *et al.* [18], quasi-stable tetragonal phase was not detected. The detailed mechanism will be discussed elsewhere. On the other hand, peaks due to cubic single phase are observed in Fig. 8 for zirconia of $y = 0.08$ above 773 K. No peaks due to yttrium oxide were detected. These results correspond well with the DTA analysis, showing the crystallization temperatures to monoclinic and cubic phases, that is the synthesis temperatures of monoclinic zirconia and YSZ, are < 773 K. The crystalline formation at lower temperatures would be caused by the size effect of the zirconia particle. The crystallite size determined by Scherrer's formula is summarized in Table I.

3.4. Changes in nanostructure with firing

Fig. 9a–l shows changes in the nanostructure of unsupported zirconia of $y = 0$ and 0.08 with firing temperature. The original magnification was fixed at ×200000. Fig. 9a and b show the nanostructure before firing. No influence of yttrium addition may be distinguished. In Fig. 9c and d no significant changes were observed after firing at 573 K. In this stage both samples are amorphous. After firing at 773 K where both are crystallized, the growth of the particle is remarkable, as shown in Fig. 9e and f. The constituting particle size is roughly equal to the crystallite size shown in Table I. In this stage, the zirconia size is a little larger than that of YSZ, which also corresponds to the results in Table I. The views after firing at 973 K, Fig. 9g and h, are similar to those at 773 K. After firing at 1173 K, Fig. 9i and j, the residual pores are removed, and nearly densified bodies are obtained for both zirconia and YSZ. At this stage, the grain sizes are around 40 nm for zirconia and 20 nm for YSZ. Wen *et al.* [21] reported that the sintering of sol–gel-derived YSZ was completed at 1693 K, where the DTA curve was broad. The sharpness in the DTA curve shown in Fig. 6 corresponds with the excellent homogeneity in the nanostructure. A dense packing in the gelling or

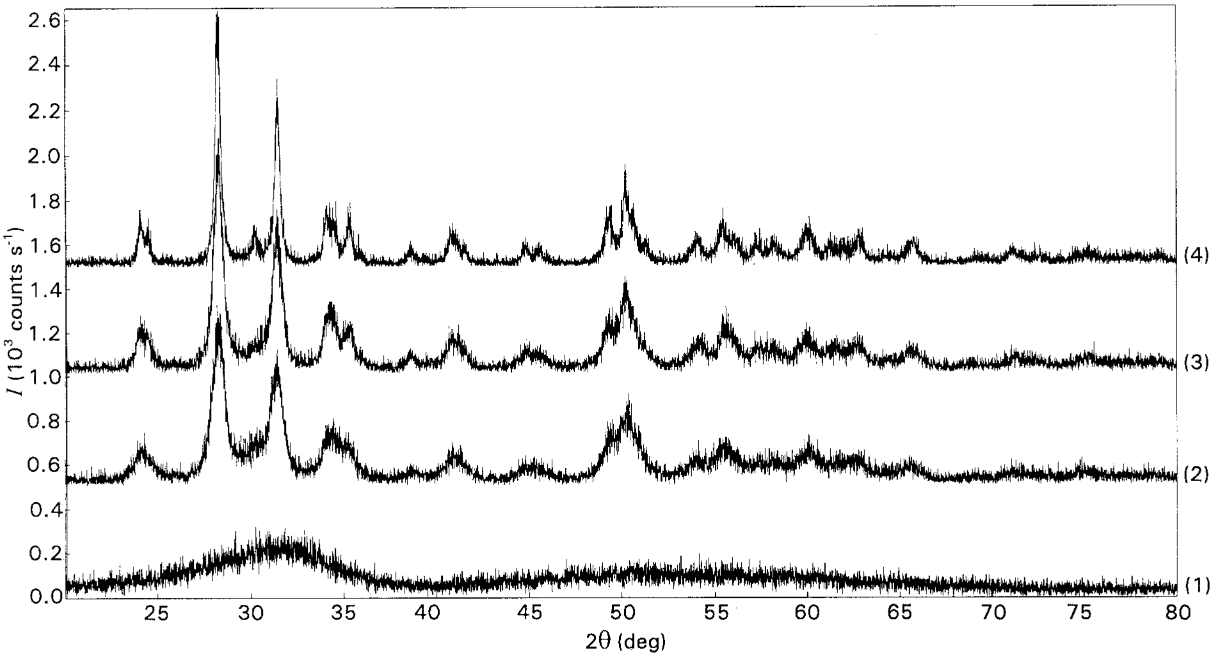

Figure 7 XRD pattern of ZrO_2 after firing at (1) 573, (2) 773, (3) 973 and (4) 1173 K.

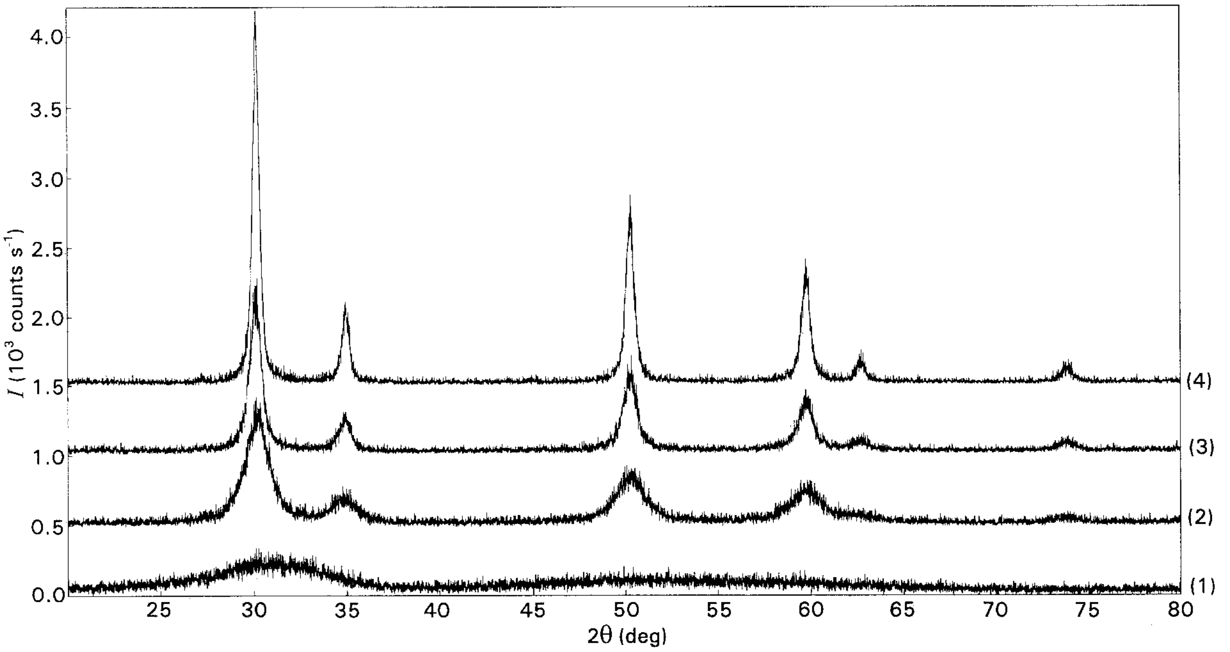

Figure 8 XRD pattern of $(Y_2O_3)_{0.08}$ $(ZrO_2)_{0.92}$ after firing at (1) 573, (2) 773, (3) 973 and (4) 1173 K.

drying stage is effective in the enhancement of densification at lower temperature, as also occurs in titania [6]. Further firing at 1373 K increased the grain size, as shown in Fig. 9k and l.

At this stage the samples are still composed of small pieces. Studies of the densification of the nanostructured thin film formed on a porous support and monolithic ceramics are in progress. Details of the materials will be given elsewhere.

TABLE I Crystallite size determined by Scherrer's formula

Firing temperature (K)	Crystallite size (nm)	
	Zirconia [1 1 1]	YSZ [1 1 1]
773	11	6
973	14	14
1173	24	23

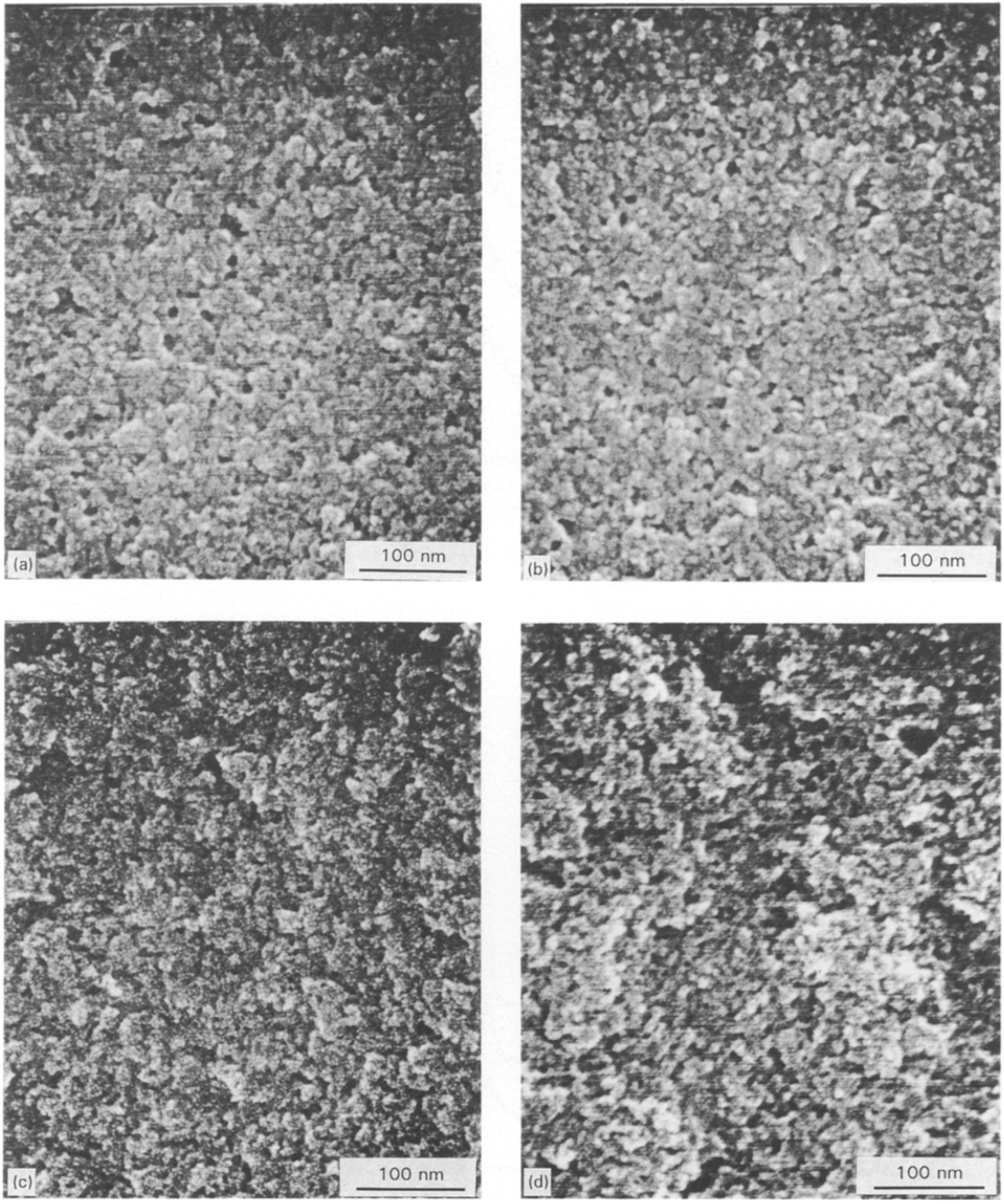

Figure 9 Nanostructure of (a, c, e, g, i, k) unsupported ZrO_2 and (b, d, f, h, j, l) $(Y_2O_3)_{0.08}$ $(ZrO_2)_{0.92}$ surface with firing temperature: (a, b) before firing, and after firing at (c, d) 573 K, (e, f) 773 K, (g, h) 973 K, (i, j) 1173 K, and (k, l) 1373 K.

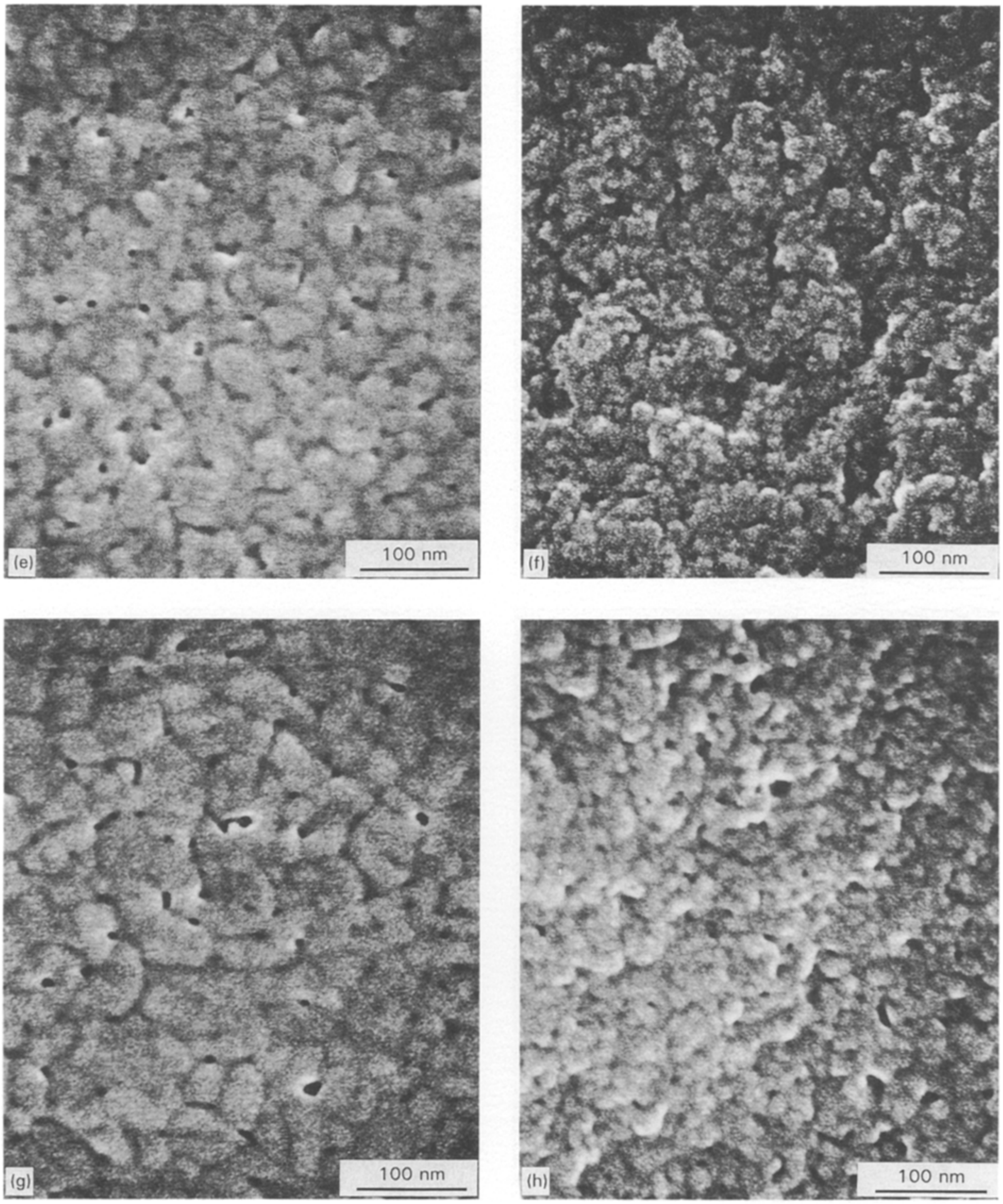

Figure 9 (Continued)

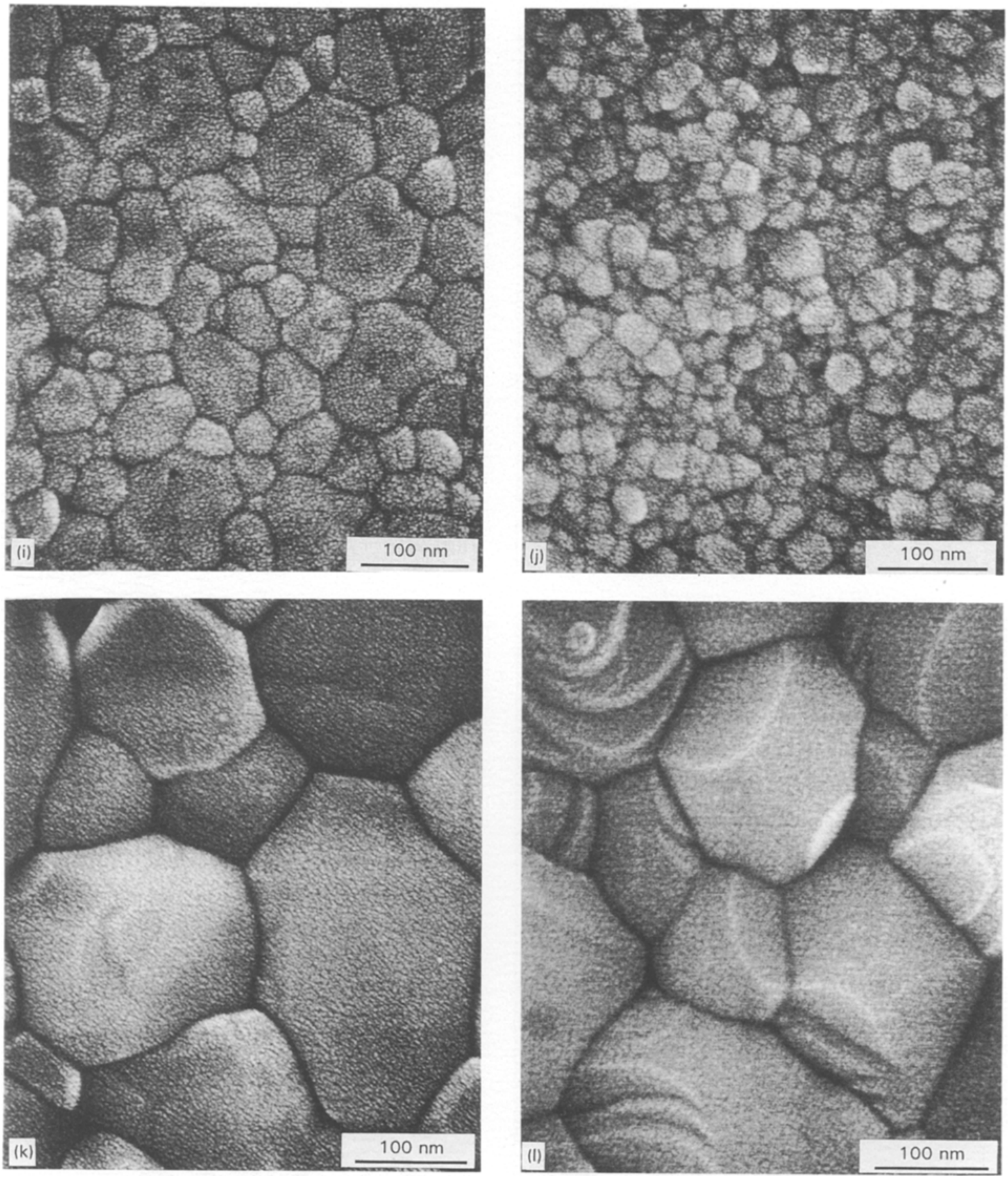

Figure 9 (Continued)

4. Conclusions

Ultrafine amorphous zirconia was crystallized at < 773 K. The surface modification of the zirconia particle with yttrium led to YSZ formation at < 773 K. As a result of the low-temperature processing, nanostructured zirconia and YSZ were obtained.

Acknowledgements

The authors thank Mr S. Yamashita and Tokyo Gas Co., Ltd, for the FE-SEM observation, and Dr M Yamada and Nisshin Flour Milling Co., Ltd, for dynamic light scattering measurement. Mr K. Ono and Dr M. Ishiwatari, Engineering Research Institute, The University of Tokyo, are gratefully acknowledged for their technical assistance in XRD and DTA measurements, respectively. The alkoxide was donated by Nippon Soda Co. Ltd. This work was financially supported in part by The Foundation "Hattori-Hokokai".

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Received 30 September 1993
and accepted 9 June 1994