JOURNAL OF MATERIALS SCIENCE **22** (1987) 3556–3560

Lowering crystallization temperature of zircon by nanoheterogeneous sol–gel processing

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The use of deliberate heterogeneity on the nanometre scale via the sol–gel technique was introduced by this laboratory in 1982. In this study the thermal behaviour of different zircon ($ZrSiO_4$)-composition precursors obtained via a sol–gel route and seeded with sols of zircon, rutile or thorite (α-$ThSiO_4$) have been studied. Both compositional diphasicity and isostructural seeding were found to lower the zircon crystallization or formation temperature. As anticipated from the "nucleation and epitaxial growth" mechanism model, rutile seed crystals, with a structure different from that of the equilibrium phase did not show any effect. An unexpected counter-effect was observed when the isostructural thorite seeds were used. These results suggest that crystallization temperatures in zircon can be lowered either by utilizing the heat of reaction in compositionally diphasic gels, or by nucleation and epitaxial growth in structurally diphasic gels.

1. Introduction

The potential of ultrafine-scale diphasic materials (or nanocomposites), first introduced by this laboratory a few years ago, is now well established. Both compositional and structural (crystallographic) diphasicities have been shown to have profound positive effects in ceramic processing [1–11]. So-called "seeding" of ceramic precursor powders with crystalline sols of the final equilibrium phase to catalyse nucleation can be classified as structural diphasicity [8–11]. This process, which consists of introducing crystalline nuclei in a matrix in order to lower the nucleation energy required to form the expected phase, is quite well understood in the case of liquids and glasses and interest in the crystalline ceramics field has been growing for the past few years. Recently it has been shown that isostructural seeding in the Al_2O_3 system controls the formation temperature of corundum [9, 10], and the densification and the microstructure of the sintered pieces [11, 12]. Such a process has been reported to be effective in non-oxide system as well [13].

The application of compositionally diphasic gels in the Al_2O_3–SiO_2 system to enhance densification has also been investigated [14]. In this case the lowering in the sintering temperature was attributed to the additional metastable energy corresponding to the heat of reaction of the two discrete phases.

The purpose of the present study was to extend the work to another oxide system, and more specifically to determine whether crystallographic and compositional diphasicities affect the crystallization temperatures in the ZrO_2–SiO_2 ($ZrSiO_4$) system.

The crystallization behaviour of monophasic, compositionally diphasic, structurally diphasic and both compositionally and structurally diphasic zircon gels upon heat treatment in air was investigated.

2. Experimental procedure

2.1. Preparation of the sols

Two different sols of zirconia were prepared hydrothermally in small Parr bombs (Parr Instruments Company):

(i) One sol was prepared by treating a saturated solution of zirconyl oxynitrate $ZrO(NO_3)_2$, xH_2O in distilled water at 200° C for 24 h. The resulting precipitate was washed and dispersed in distilled water before phase characterization by X-ray diffraction and size determination by transmission electronic microscopy (TEM). The particles forming the stable sol are crystalline (monoclinic zirconia) and approximately 70 nm in size (Fig. 1a).

(ii) The other sol was prepared by treating the mixture of 40 ml 2.2 M zirconium oxychloride solution and 20 ml concentrated ammonium hydroxide at 150° C for 20 h. The stable sol obtained after washing and dispersing the precipitate in distilled water appeared to contain mainly metastable cubic zirconia crystallites, which have a size of about 10 nm (Fig. 1b).

2.2. Preparation of crystalline sols for seeds

Zircon ($ZrSiO_4$), thorite (α-$ThSiO_4$) and rutile (TiO_2) crystalline sols were also prepared hydrothermally in Parr bombs:

(i) A zircon sol was made by treating at 200° C for 48 h in a mixture of the appropriate volumes of a $ZrOCl_2 \cdot 8H_2O$ solution and tetraethylorthosilicate (TEOS) in ethanol. The $ZrSiO_4$ crystallites are lens-shaped, 60 nm thick and 300 nm diameter (Fig. 1c, 1d).

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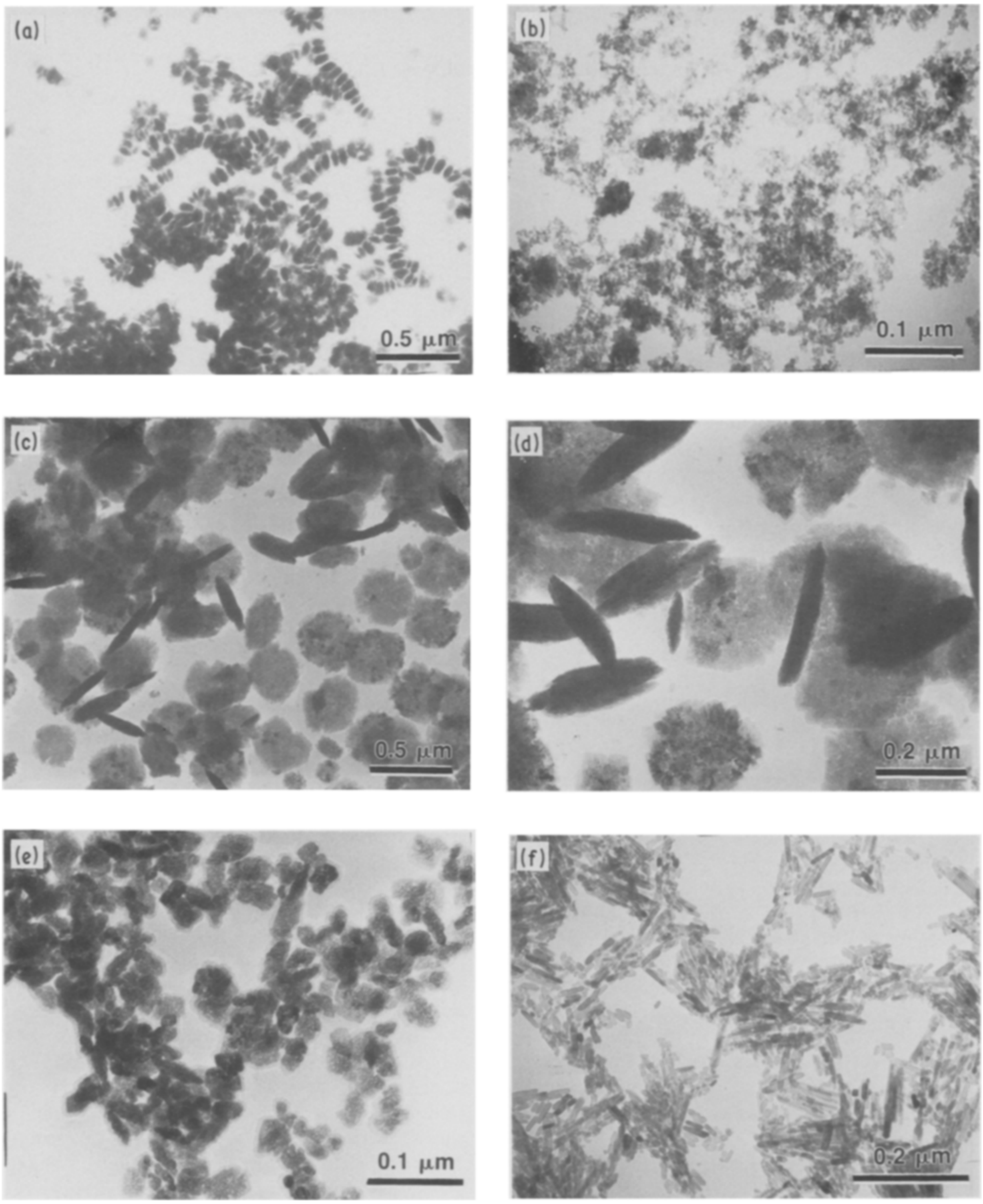

Figure 1 Transmission electron micrographs of hydrothermally produced crystalline sols used in the preparation of diphasic gels: (a) monoclinic zirconia; (b) metastable cubic zirconia; (c) zircon, $ZrSiO_4$; (d) as (c) at a higher magnification; (e) thorite, α-$ThSiO_4$; (f) rutile, TiO_2.

(ii) A thorite (α-$ThSiO_4$) sol was obtained using the same procedure as above, but a $Th(NO_3)_4 \cdot 4H_2O$ solution was used instead of the zirconium oxychloride. The crystalline thorite particles are 30 nm diameter (Fig. 1e).

(iii) A 1 M solution of titanium oxychloride was heated in a Parr bomb at 100° C for 3 days. The resulting sol is a suspension of needle-shaped rutile crystallites, 50 nm long and 10 nm diameter (Fig. 1f).

A Philips 420 transmission electron microscope was used to determine the particle size of the different sols.

2.3. Preparation of the zircon precursors

Appropriate volumes of TEOS and a zirconium oxychloride solution were mixed in ethanol and the mixture was heated at 40° C in order to obtain a monophasic zircon gel. The addition of zircon seeds to the same solution prior to gelation led to the structurally diphasic gel. The compositionally diphasic gel was made using a commercial silica sol (Ludox, 1 M in Si, E.I. Dupont de Nemours and Co., Inc., Wilmington, DE) and either the monoclinic zirconia sol or the metastable cubic one, which are both approximately

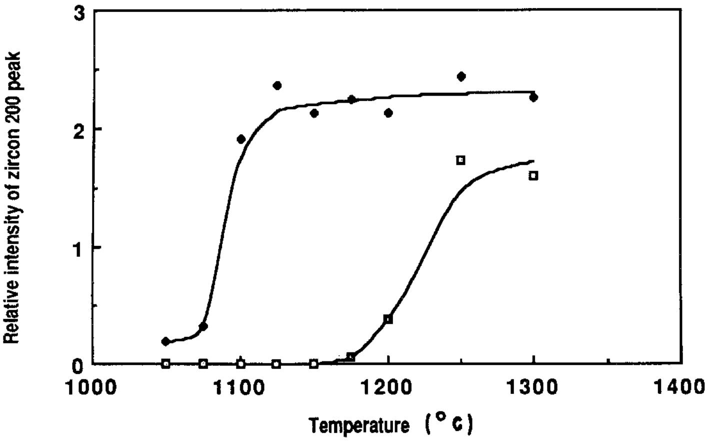

Figure 2 Relative intensity of zircon (2 0 0) peak as a function of the firing temperature for gels prepared with Ludox and the metastable cubic zirconia sol. (□) Unseeded gel, (◆) 2% seeds.

2 M. The sols were mixed in the proportions corresponding to the zircon composition and vigorously stirred. The resulting suspension was gently heated at 70° C to induce the gelation. The gels which are both compositionally and structurally diphasic were prepared by simply mixing the crystalline seed sols with the mixture of silica and zirconia sols and gelling as above. All the precursors were dried at 100° C for a few days and the resulting powders were ground with an agate mortar and pestle.

2.4. Determination of the crystallization temperature of zircon

Because the crystallization of zircon does not exhibit a sharp exotherm by differential thermal analysis, this technique could not be utilized. The following procedure was used instead: the different diphasic xerogel powders were fired at various temperatures for 2 h in platinum crucibles. X-ray powder diffraction analysis was carried out on samples using a Philips diffractometer with nickel filtered Cu*K*α radiation. An internal standard (anatase) was added in the same proportions in each fired sample in order to make semi-quantitative measurements of zircon content. The relative intensity of the (2 0 0) peak for zircon, which can be considered as roughly proportional to the amount of $ZrSiO_4$ formed, was obtained by taking the ratio of the intensity of the (2 0 0) zircon peak to the instensity of the (1 0 1) of anatase. All the mentioned intensities were measured by evaluating the areas of the peaks and are expressed in arbitrary units.

3. Results and discussion

3.1. Seeding of compositionally diphasic zircon gels

The effect of an addition of 2 mol % of crystalline zircon seeds in a gel precursor prepared with the metastable cubic zirconia sol and the commercial silica sol is presented in Fig. 2. It clearly appears that zircon seeding lowers the formation temperature of $ZrSiO_4$ by more than 100° C; the crystallization of zircon seems to be complete after 2 h at 1125° C with a seeded precursor, whereas this result can only be reached after 2 h at 1250° C when an unseeded gel was used. These positive results were confirmed with a slightly different starting gel powder, which was made by mixing monoclinic zirconia sol and Ludox (Fig. 3). The Hedvall effect noticed by Gokhale *et al.* [15] was not seen in these gel-derived materials. One possible explanation is that the phenomenon did not occur because of the relatively low temperature of zircon formation in the case of sol–gel derived samples, compared to powders obtained by a traditional "mixed oxides" technique.

The influence of the concentration of $ZrSiO_4$ seeds on the crystallization of zircon has also been studied and the results are plotted in Fig. 4. In this work the samples derived from the monoclinic zirconia sol and Ludox were all fired for 2 h at 1120° C. The effect of seeding seems to level off at about 3 mol % addition, which corresponds to a nucleation frequency of 3×10^{14} seeds per cm^3 of equimolar mixture of α-cristobalite and zirconia. A possible mechanism for

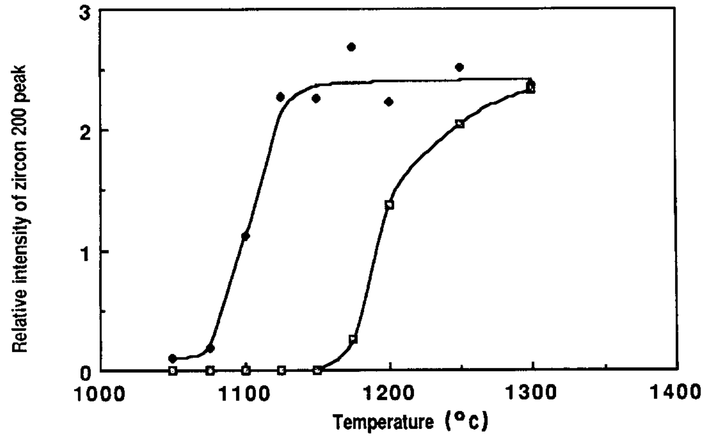

Figure 3 Relative intensity of zircon (2 0 0) peak as a function of the firing temperature for gels prepared with Ludox and the monoclinic zirconia sol. (□) Unseeded gel, (◆) 2% seeds.

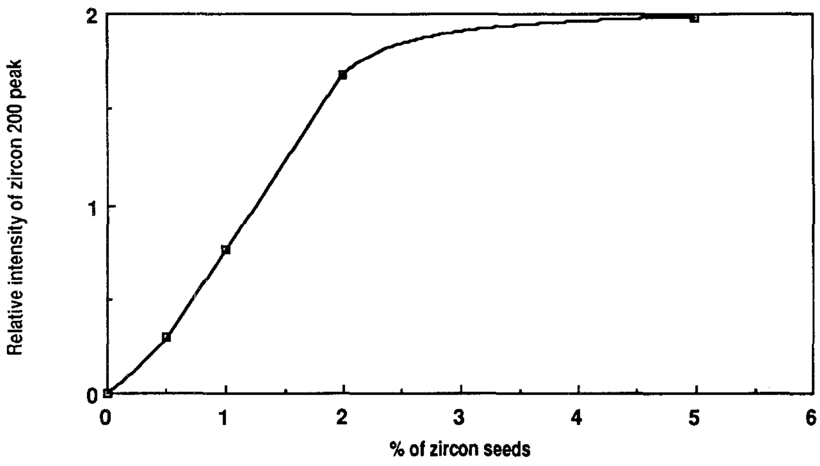

Figure 4 Relative intensity of zircon (2 0 0) peak as affected by varying concentrations of $ZrSiO_4$ seeds.

such a phenomenon may be an heterogeneous or, more precisely, catalysed nucleation: seeds upon which nuclei form, are introduced in the matrix in order to lower the surface free energy of the system. On the other hand, the addition of seeds affects the volume free energy and a strain factor must be taken into account [16]. It is therefore evident that the degree of lattice matching between the seeds and the growing phase is very important, the most favourable case being, of course, to seed with crystallites identical to the expected equilibrium phase.

In order to test the validity of this mechanism (heterogeneous nucleation followed by epitaxial growth) the addition of a selected set of seed crystals was studied. Together with the results corresponding to the unseeded and the zircon seeded precursors, data relating to a rutile seeded and a thorite seeded samples are presented in Fig. 5. As expected, seeding with rutile (TiO_2), which is structurally different from zircon, has no effect at all. Thorite (α-$ThSiO_4$) is a most interesting case; its structure is the same as the zircon, as shown in Table I, but its lattice parameters are substantially larger. Seeding with the isostructural thorite, instead of catalysing, completely inhibits the crystallization of zircon. Instead of the slight lowering or having no effect expected (based on the lattice mismatch) the crystallization temperature is raised. The reason for this counter-effect is not fully understood yet, but it may be due to the decomposition of thorite to SiO_2 and ThO_2, this last phase stabilizing tetragonal (or cubic) zirconia. There is, however, no evidence to prove this hypothesis.

3.2. Compositionally and/or structurally diphasic zircon gels

The lowest temperatures at which zircon formed for the different kinds of gel precursors are reported in Table II. The use of compositionally and/or structurally diphasic zircon gels resulted in a substantial lowering of the zircon crystallization temperature. For example, the single-phase gels crystallized to zircon at approximately 1325° C while the structurally and compositionally diphasic gels crystallized at 1100 and 1175° C, respectively. The data clearly show that isostructural seedings helps to control the thermodynamics of the reaction of formation of zircon, but one can notice that the compositional diphasicity also affects this reaction in the same positive way. As pointed out above and elsewhere, isostructural seeding works via epitaxial growth on the nuclei provided, thereby lowering the crystallization temperature in the structurally diphasic gels. The lowering in compositionally diphasic gels may, at least in part, be attributed to the excess of metastable energy that a diphasic gel stores (Fig. 6) [4]. This additional energy (compared to a single-phase gel) is derived from the exothermic heat of reaction of the two discrete phases, ZrO_2 and SiO_2, to yield the equilibrium phase, $ZrSiO_4$.

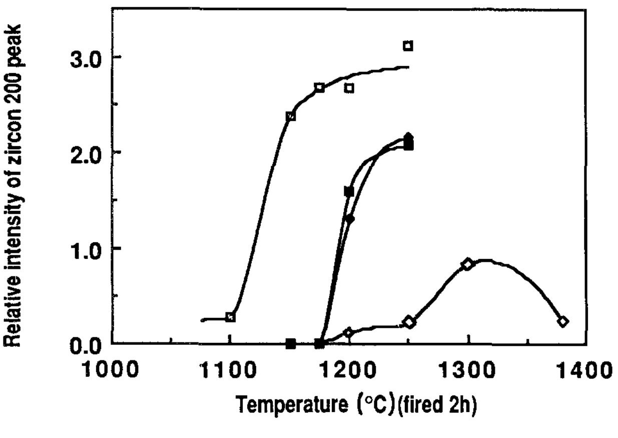

Figure 5 Relative intensity of zircon (2 0 0) peak plotted against firing temperature for (◆) unseeded gels and gels seeded with (□) zircon, (◇) thorite and (■) rutile crystals.

TABLE I Comparison of the lattice parameters of isostructural zircon and thorite

		Zircon	Thorite	Mismatch
Structure		tetragonal	tetragonal	
Lattice	*a*	6.604	7.132	8.0%
parameters:	*b*	5.979	6.322	5.7%

TABLE II Lowest temperature at which zircon formed in different mono- and diphasic precursors

Structural diphasicity	Compositional diphasicity	
	No	Yes
No	1325° C	1175° C
Yes	1100° C	1075°C

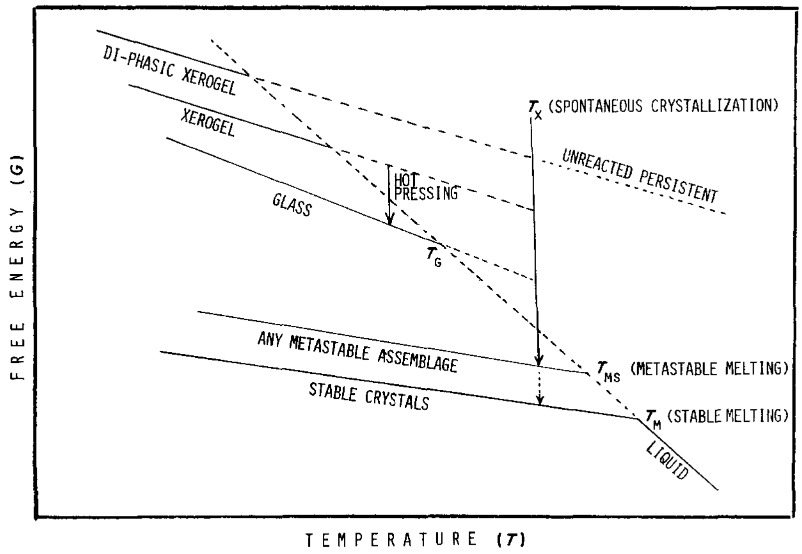

Figure 6 Representation of G–T relations among isoplethal phases.

4. Conclusion

This study has demonstrated that isostructural seeding and/or compositional diphasicity lowers the crystallization temperature of zircon very substantially (> 200° C). The lowering of the crystallization temperature in structurally diphasic gels can be explained by an epitaxial growth mechanism, while in compositionally diphasic gels it is due to the availability of excess metastable energy. There are already a few examples in solid state chemistry in which nanoheterogeneity was found to be useful in lowering crystallization temperature and enhancing densification, and if such results can be generalized, several new applications will be possible in the future.

Acknowledgements

This research was supported by the Ceramics and Electronic Materials Program, Division of Materials Research, National Science Foundation, under Grant No. DMR-8507912. Gabriel Vilmin would like to thank Rhone-Poulenc for its financial support of his tenure at the University.

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Received 30 September 1986
and accepted 16 January 1987