

Densification and crystallization behaviour of colloidal cordierite-type gels

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Three cordierite-type gels were prepared from an aqueous solution of $\text{Mg}(\text{NO}_3)_2$, a boehmite sol and silica sols of very small particle sizes. The effect of varying the silica particle size on the crystallization and densification behaviour was studied. Phase development was examined by thermal analysis and X-ray diffraction, while the densification behaviour was characterized by measuring the linear shrinkage of pellets. The activation energy of densification by viscous flow was determined using the Franckel model for non-isothermal conditions and a constant heating rate. The results show that spinel crystallizes from the colloidal gels prior to cristobalite, and their reaction gives α -cordierite, which is specific for three-phase gels. Decreasing the silica particles size lowers the cristobalite crystallization temperature and the α -cordierite formation temperature. The activation energy of densification by viscous flow is lower and the densification more efficient, the smaller the silica particles are.

Keywords: cordierite, sol-gel, densification, crystallization, activation energy of densification.

INTRODUCTION

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) as a ceramic material has a wide range of uses and applications stemming from its important properties of low thermal expansion and dielectric constant coupled with high chemical and thermal stability. Preparing dense cordierite ceramics has long been a problem because of the narrow sintering range near the incongruent melting point of the cordierite. Addition of a sintering aid^{1,2} resulted in a decrease of the cordierite crystallization temperature and an increase of the density of the final product. On the other hand, these aids cause an increase in the thermal expansion coefficient and dielectric constant. The preparation of a homogeneous and fine cordierite powder that can be sintered without the addition of a sintering aid is, therefore, considered to be highly desirable.^{3–6}

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The sol-gel procedure has enabled the production of ceramic materials of high purity and with superior properties at lower temperatures than conventional methods.^{7–9} Since alkoxide-derived powders offer potential for remarkable reductions in the crystallization temperatures, alkoxide methods have usually been applied to the preparation of cordierite powders.^{10–19}

However, in multicomponent systems, such as cordierite ceramics, the difference in the hydrolysis rates of each alkoxide causes inhomogeneity in the resultant oxides. Moreover, gel-derived compacts often show the commencement of crystallization before complete densification, leaving large pores unremoved. This problem is most frequently encountered in the densification of multicomponent silica-containing gels that undergo viscous sintering. Since the densification rate is orders of magnitude faster when material transport occurs by viscous flow rather than by atomic diffusion, it is very difficult to remove the remaining pores after the commencement of crystallization. Therefore, in order to obtain dense sinter bodies it is important that the kinetics of viscous sintering are substantially faster than those of crystallization.

Recently, it has been reported that the heterogeneous distribution of the elements in the powders promotes densification in the sintering of some kinds of multicomponent systems. Colloidal processing^{14,15,17,20–22} is considered an effective method for producing such controlled heterogeneity on a nanometer scale. A heterogeneous distribution of each element promotes the sintering of bodies by the genesis of a liquid phase of a lower melting temperature than that of a single phase.

Studies on the sol-gel synthesis of cordierite have confirmed that from colloidal, three-phase gels crystallization of spinel and cristobalite (or quartz) occurred, which react forming γ -cordierite. In this case, there is a wide temperature range in which densification without crystallization of the silica-containing component occurs. This means that full densification without crystallization can be reached by an appropriate choice of temperature and time.

The aims of this work were (1) to examine the crystallization and densification behaviour of colloidal cordierite-type gels, synthesized from an aqueous solution of $\text{Mg}(\text{NO}_3)_2$, a boehmite sol and silica sols of very small particle sizes and (2) to determine the influence of the silica particle size on the densification and crystallization behaviour of these gels.

EXPERIMENTAL

Three colloidal cordierite-type gels were prepared starting from silica sols of different particle size, a boehmite sol and an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The silica sols were obtained by the ion exchange method.²³ The characteristics of the silica sols are given in Table I.

The specific surface area of the solid phase was determined by the potentiometric titration method²⁴ – measuring the amount of OH^- ions adsorbed by the solid phase at pH 4–9. The mean particle diameter was calculated from the value of the specific surface area.

The boehmite sol (AlOOH) was obtained by peptization of freshly prepared $\text{Al}(\text{OH})_3$, with nitric acid, under reflux.²⁵ It contained 2.2 mass % pseudoboehmite particles in an aqueous medium,

stabilized at pH 3.8. The specific surface area of the solid phase, determined by the BET method, was 267 m²/g.

TABLE I. Characteristics of the silica sols

Silica sol	S5.5	S7.5	S9.5
Solid phase content/mass %	4.5	3.3	3.9
pH	9.3	9.8	9.2
$S_p/m^2\text{ g}^{-1}$	490	367	284
d_{av}/nm	5.5	7.5	9.5

All three gels were synthesized in the following way: stoichiometric proportion of the boehmite sol and the silica sol were mixed and stirred for 2 h. Then, an saturated aqueous solution of Mg(NO₃)₂·6H₂O was added and the stirring continued for another two hours. The obtained multicomponent colloidal dispersion was coprecipitated and gelled by the addition of saturated aqueous solution of ammonium carbonate, which increased the pH to 9. The obtained gels were dried at 40 °C for two days and then for 24 h at 110 °C.

The relative linear shrinkage of the gel compacts was measured using a E.LEITZ thermo-microscope, at a heating rate of 10 °C/min, up to 1300 °C. The gels were pressed using a hand press, at about 20 MPa, into a compact with dimensions 3 × 3 × 3 mm.

The phase transformations occurring in the gels during heating were determined by DSC (NETZSCH Model 404) at heating rate of 10 °C/min. The experiments were carried out in an air atmosphere, using Al₂O₃ as a reference. The sample mass was 50 ± 0.5 mg.

The phase composition of powders obtained by gels calcination at 900, 1000, 1100, 1200 and 1250 °C for 2 h were determined using a SIEMENS D500 diffractometer with CuK α radiation in the 2 θ angle range from 5 to 60° or to 80°, with a 0.02 step.

RESULTS AND DISCUSSION

The results of differential scanning calorimetry for the synthesized gels are given in Fig. 1.

Two broad endothermic peaks in the temperature ranges from 20 °C to 220 °C and from 220 °C to 500 °C are noticeable on these curves. The second endothermic peak was formed from three overlapping individual peaks. The first endothermic peak corresponds to the desorption of physically bound water, while the second endothermic peak is ascribed to dehydroxylation, ammonia and CO₂ release, and decomposition of nitrates. At higher temperatures, two exothermic peaks are noticeable: a broad peak in the temperature range of about 900 °C to about 1100 °C and the other, relatively sharp peak, about 1190 °C. As can be seen from Fig. 1, this peak is shifted towards higher temperatures with increasing size of the silica particles in the sol used for the gel synthesis. According to literature data,^{14,15,17,20,21} it can be assumed that the first exothermic peak in the temperature range from 900 °C to 1100 °C, corresponds to the crystallization of either spinel, MgAl₂O₄, or cristobalite, or both. The second exothermic peak, at about 1190 °C, corresponds to the formation of γ -cordierite, resulting from the reaction of spinel with cristobalite. In order to determine the nature of the processes or reactions

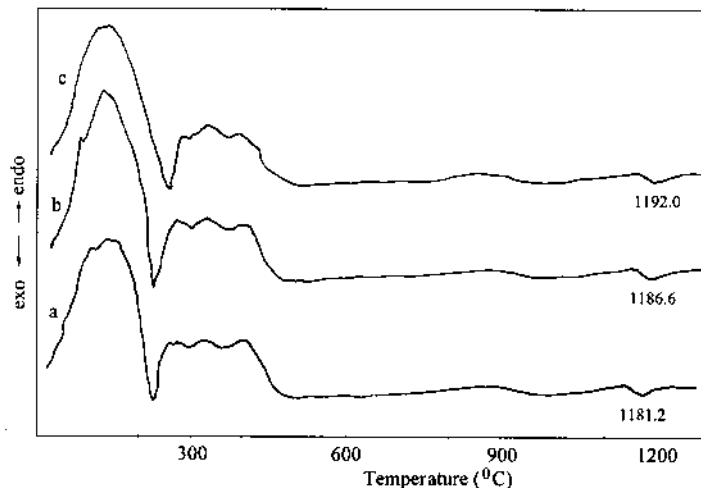


Fig. 1. DSC curves for the G5.5 (a), G7.5 (b) and G9.5 (c) gels (the numbers indicating the size of the SiO₂ particles in the sol used for the synthesis).

corresponding to the mentioned exothermal peaks, the gels were calcined at 900, 1000, 1100, 1200 and 1250 °C, and the phase composition of powders obtained in this way were determined. The diffractograms of the powders obtained by calcination of the G7.5 gel at 900, 1000, 1100, 1200 and 1250 °C are presented in Fig. 2.

In the diffractogram of the powder obtained by gel calcination at 900 °C, weak and diffusive peaks, corresponding to spinel, are noticeable. At 1000 °C, these peaks are slightly sharper and intense. Two other peaks at $d = 0.315$ nm and $d = 0.250$ nm, corresponding to cristobalite, are detectable, although the most intense peak for cristobalite at $d = 0.409$ nm was not detectable on this diffractogram. This peak is visible in the diffractogram of the powder obtained by gel calcination at 1100 °C, together with the above mentioned peaks corresponding to cristobalite. The peaks corresponding to spinel become sharper and more intense. In the diffractogram of the powder obtained by gel calcination at 1200 °C, peaks of low intensity, corresponding to γ -cordierite, are noticeable. The peaks corresponding to cristobalite and spinel are sharp and intense. At 1250 °C, the peaks for spinel and cristobalite are less intense than the ones at 1200 °C, while the peaks of γ -cordierite are sharp and intense. According to these results, it is evident that the first exothermal peak on the DSC gel curves corresponds to crystallization of spinel and cristobalite, while the second peak corresponds to the formation of γ -cordierite by the reaction between spinel and cristobalite. As previous investigations have shown,²⁶ formation of γ -cordierite by the reaction between spinel and cristobalite is a diffusion controlled process, proceeding with a constant number of nuclei and an average activation energy $E_a = 1242 \pm 66$ kJ/mol.

The diffractograms of the powders obtained by calcination of the G5.5 and G9.5 gels at 900, 1000, 1100, 1200 and 1250 °C differ from the corresponding diffractograms of the powders obtained by calcination for the G7.5 gel only in the intensity of individual

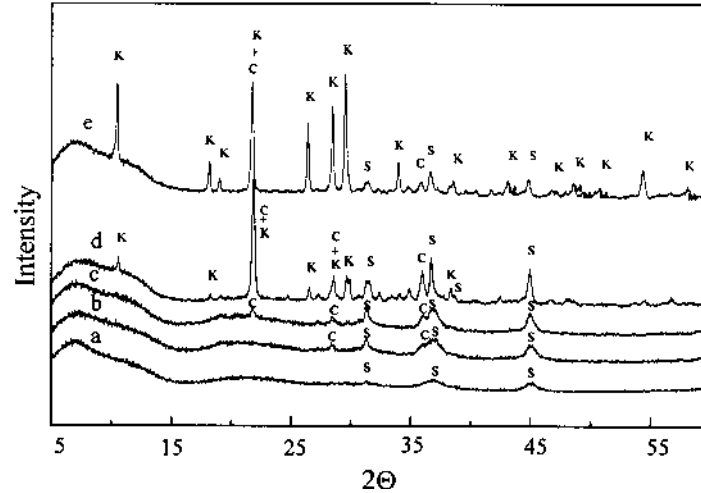


Fig. 2. Diffractograms of the powders obtained by calcination of the G7.5 gel at 900 °C (a), 1000 °C (b), 1100 °C (c), 1200 °C (d) and 1250 °C (e) (S – spinel, C – cristobalite, K – cordierite).

peaks. The diffractograms of the powders obtained by calcination of the G5.5, G7.5 and G9.5 gels at 900 °C and at 1100 °C are presented in Fig. 3 and 4, respectively.

As can be seen from Figs. 3 and 4, there is no significant difference in the intensity of the peaks corresponding to spinel, at the same temperature for different powders. The intensity of the peaks corresponding to cristobalite decreases with increasing size of the silica particles in the sol used for the synthesis. This indicates that the temperature of the cristobalite crystallization decreases with decreasing size of the silica particles, but that the silica particle size has no effect on the spinel crystallization temperature. Considering also

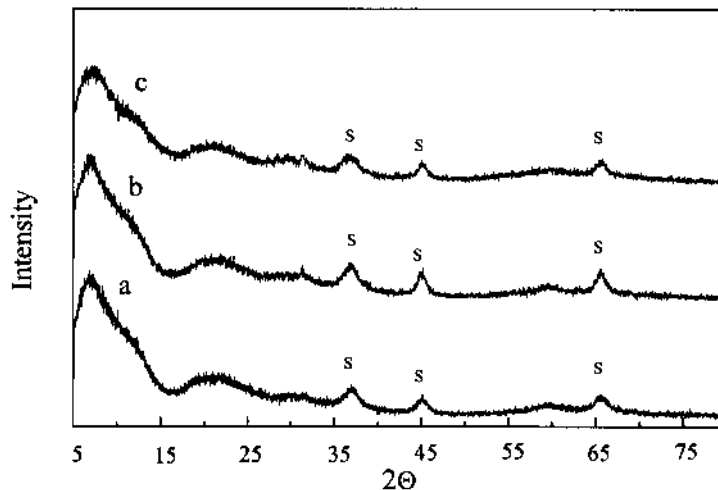


Fig. 3. Diffractograms of the powders obtained by calcination of the G5.5 (a), G7.5 (b) and G9.5 (c) gels at 900 °C.

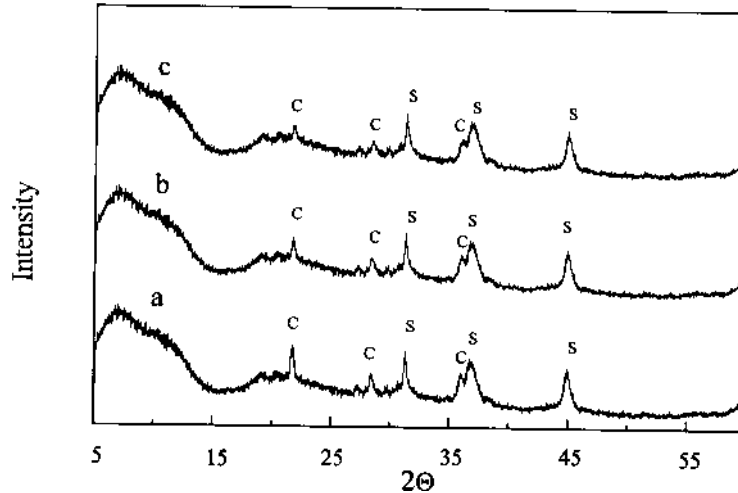


Fig. 4. Diffractograms of the powders obtained by calcination of the G5.5 (a), G7.5 (b) and G9.5 (c) gels at 1100 °C.

the results of differential scanning calorimetry, it can be concluded that decreasing the size of the silica particles leads to a lowering of the cristobalite crystallization temperature, and consequently, a decrease of the α -cordierite formation temperature.

The curves of the relative linear shrinkage during heating of the G5.5, G7.5 and G9.5 gels are shown in Fig. 5. It can be noticed that intense shrinkage occurs in the temperature range of 800–1000 °C, ending at 1050 °C.

Also from Fig. 5, it can be seen that the shrinkage increases with decreasing size of the silica particles, *i.e.*, densification of the gels prepared from sols of the smaller particle size is more efficient.

The activation energy of the sintering by viscous flow can be calculated using the Franckel model for non-isothermal conditions at a constant heating rate:²⁷

$$L/L_0 = (RT/2rA - E) \exp(-E/RT)$$

where: L/L_0 – the relative linear shrinkage, σ – the interfacial energy, T – the temperature, r – the particle size, A – a coefficient, β – the heating rate, E – the activation energy and R – the gas constant. The dependence $\log(L/L_0 T^2)$ on $1/T$ is linear, with a slope equal $-0.43 E/R$.

The dependancies of $\log(L/L_0 T^2)$ on $1/T$ for the G5.5, G7.5 and G9.5 gels compact are shown in Fig. 6. The activation energies of densification by viscous flow were determined from the slope of these plots.

The value of the activation energy for densification by viscous flow decreases with a decreasing in size of the silica particles, which is evident from the following results: for the G9.5 gel – $E = 218 \pm 12$ kJ/mol, for the G7.5 gel – $E = 200 \pm 9$ kJ/mol and for the G5.5 gel – $E = 178 \pm 14$ kJ/mol.

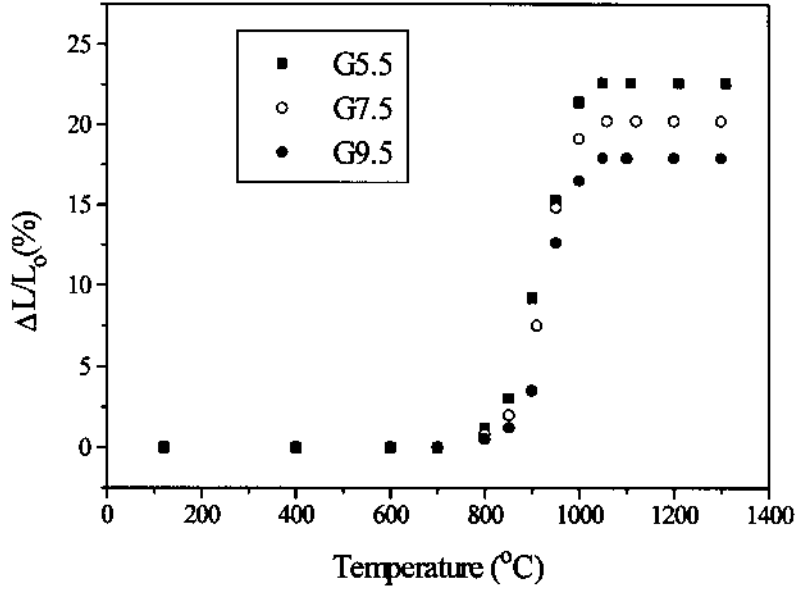


Fig. 5. Relative linear shrinkage during heating of the G5.5, G7.5 and G9.5 gel compacts.

The results of the X-ray analysis show that spinel is the first to crystallize from the three-phase gels at about 900 °C, followed by cristobalite, crystallizing at temperatures between 1000 and 1100 °C. In this temperature range, shrinkage of the compacted gels was completed (Fig. 5). It is evident that densification was not affected by the crystalli-

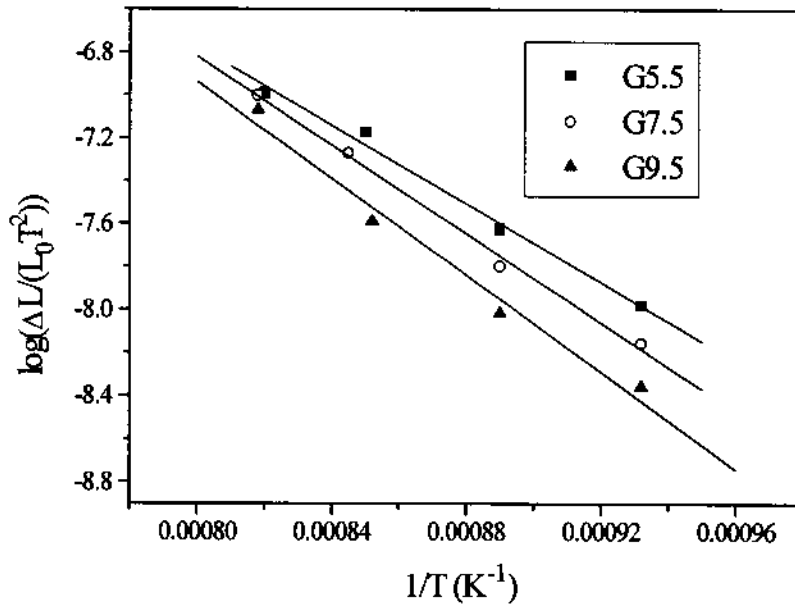


Fig. 6. Dependence $\log(\Delta L/(L_0 T^2))$ on $1/T$ for the G5.5, G7.5 and G9.5 gels.

zation of spinel, *i. e.*, intense shrinkage of the calcinated gel compact continues irrespective of spinel crystallization. In the temperature range 1000–1100 °C, both completion of shrinkage and the onset of cristobalite crystallization occur. The temperature of cristobalite crystallization decreases with decreasing in size of the silica particles. Due to the decrease of the cristobalite crystallization temperature, the temperature of α -cordierite formation by the reaction between spinel and cristobalite also decreases with a decreasing size of the silica particles. The size of the silica particles has a great influence on densification because the activation energy of densification by viscous flow decreases with decreasing particle size.

CONCLUSION

Three colloidal cordierite-type gels were prepared from a boehmite sol, an aqueous solution of $Mg(NO_3)_2$ and silica sols of very small particle size. Despite the fact that the size of the silica particles is very small, spinel and cristobalite crystallizing from the gels react with each other forming α -cordierite, which is specific for three-phase cordierite gels. However, decreasing the size of the silica particles leads to a decrease of the cristobalite crystallization temperature and, consequently, to a decrease of the α -cordierite formation temperature. The size of the silica particles has a great influence on densification because the activation energy of densification by viscous flow decreases with decreasing particle size.

ИЗВОД

ДЕНЗИФИКАЦИЈА И КРИСТАЛИЗАЦИЈА КОЛОИДНИХ ГЕЛОВА КОРДИЈЕРИТНОГ САСТАВА

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Припремљена су три гела кордијеритног састава полазећи од воденог раствора $Mg(NO_3)_2$, бемит сола и солова SiO_2 , веома малих величина честица. Варирана је величина честица сола SiO_2 да би се испитао утицај величине честица сола SiO_2 на дензификацију и кристализацију гелова. Диференцијално скенирајућом калориметријом и рендгенском анализом утврђене су промене које се одигравају при топлотној обради гелова, док је дензификација испитивана мерењем линеарног скупљања компакта гелова. Енергија активације дензификације вискозним током је одређена применом Френкеловог модела за неизотермске услове са константном брзином загревања. Резултати показују да из колоидних гелова кордијеритног састава прво кристалише спинел, затим кристобалит, који реагују и дају α -кордијерит, што је карактеристично за трофазне гелове. Са смањењем величине честица SiO_2 снижава се температура кристализације кристобалита, што доводи до снижења температуре формирања α -кордијерита. Енергија активације дензификације вискозним током је мања, а дензификација ефективнија што су честице SiO_2 мање.

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