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Preparation of cordierite ceramics by sol–gel technique

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Xerogel with cordierite composition $Mg_2Al_3[AlSi_5O_{18}]$ from aluminium and magnesium 2-ethoxyethoxides and tetraethylortosilicate have been prepared, the latter being not previously partially hydrolized. Conditions to obtain not only homogeneous but also sinterable gel have been determined. All the powders derived were characterized by DTA, TG, BET and X-ray diffraction. Bulk α-cordierite material of 97% from theoretical density have been obtained by sintering.

1. Introduction

Numerous attempts intended to produce bulk cordierite are brought about by high attractiveness in various industrial applications. They are related to some favourable properties of cordierite ceramics such as low thermal expansion coefficient, dielectric constant and sufficiently high refractoriness. Nevertheless extremely narrow sintering intervals (about 25 °C), limited by incongruent melting of the ceramics, makes it almost impossible to obtain dense material without special equipment (for instance HIP) and sintering aids, which, in turn, deteriorate the desirable characteristics. The sol–gel technique is a well-known means of preparing fine powders possessing an extensive surface area, high intrinsic energy and consequently high sinterability [1, 2], hence allowing a broadening of the sintering interval. Obviously, for this reason a number of investigators have taken up the sol–gel preparation route for its advantages [3, 4, 5].

The main difficulty, however, appeared to be the appreciable differences in the rates of hydrolysis of tetraethylorthosilicate (TEOS), which is always used as a source of silicon, and of other necessary alkoxides. Because of this obstacle the direct hydrolysis of the alkoxide mixture yields inhomogeneity in the resultant xero-gel and requires successive high temperature treatment to equalize the distribution of ions by diffusion [6, 7]. The problem was approached by partial hydrolysis of TEOS prior to being mixed with other alkoxides [3, 4, 5]. However, it should be mentioned that the matter of determination of the conditions and the extent of partial hydrolysis is sufficiently involved and requires additional experimental research in every particular case.

Therefore, the current paper deals with the synthesis of cordierite powder as well as bulk material by the sol–gel procedure. Results obtained without using partial TEOS hydrolysis or with it under conditions not repeatedly determined are presented.

2. Experimental procedure

TEOS, as well as aluminium and magnesium 2-ethoxyethoxide, are used for gel preparation, the former being synthesized in the course of the reaction between silicontetrachloride and ethanol [8] and the latter by the interaction between ethylglycol (EG) and the proper metal [9].

Two gel preparation routes have been applied:

1. Stoichiometry—with a view to cordierite formation mixture of all the three alkoxides as a concentrated solution in EG—was refluxed and after considerable cooling diluted by the same solvent. 90% of the water necessary to carry out a complete hydrolysis was slowly added and the reaction mixture was subjected to refluxing for 4 h. Then the residual 10% of water was added. The mixture was then heated up for gel formation.

2. The mixture of TEOS and $Al(OC_2H_4O\ C_2H_5)_3$, taken in the amount necessary to build 6-membered rings of cordierite structure [10], were prepared and after a short time reflux, half of the water quantity needed for the rings hydrolysis was slowly added. The solution was refluxed, cooled and then the other alkoxides required for the cordierite structure formation was poured in. Finally, an additional part of water taken in three-fold excess with respect to the stoichiometrical equation was added together with EG. This sequence was followed by heating in the course of which a gel was formed after removal of the solvent. The gel was dried at 150 °C under evacuation.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) was carried out in air or flowing argon. Crystalline phases were identified by X-ray diffraction using CuK_α radiation. Specific surface areas of powders were measured by the BET method using nitrogen as the absorption gas. For sintering, the powders were uniaxially pressed at 200 MPa with

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PVA forming cylindrical pellets of 10 mm diameter and 8 mm height. The density of the samples sintered in an electrical furnace was measured hydrostatically using CCl_4 as a reference liquid.

3. Results and discussion

The preparation route I results mainly from the ideas contained in the papers of Bradley and Yoldas [11, 12]. We have selected aluminium and magnesium 2-ethoxyethoxides with a view reducing their hydrolysis rates in comparison with alkoxides possessing shorter and less branched hydrocarbon chains. In such a way one could hope to equalize the hydrolysis rates of TEOS and other relevant compounds. The additional advantage of using 2-ethoxyethoxides is the possibility of applying a sufficiently high temperature to run the hydrolysis process owing to the comparatively high boiling point of EG (128–138 °C) used as a solvent. The high reaction temperature in turn makes it possible to considerably diminish the difference in exponential factors in the Arrhenius equation whatever the mechanism of the reaction could be.

With this in mind one can easily come to the conclusion that the task consists in the following:

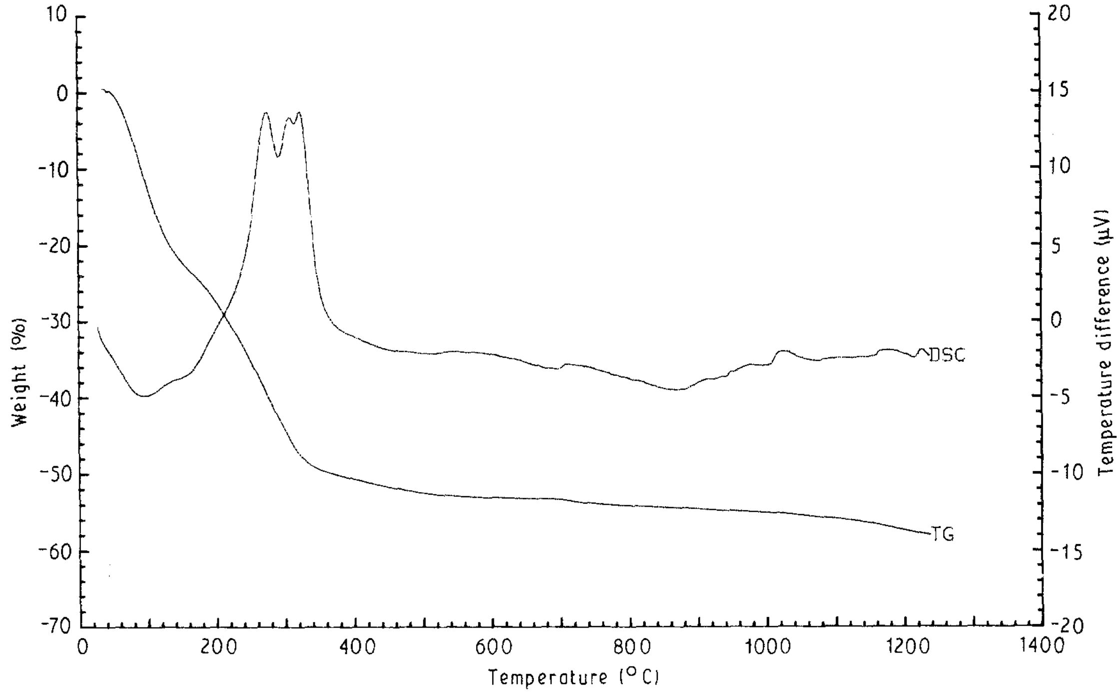

Figure 1 DTA and TG traces of gel prepared by preparation route I and dried in air at 5 K min^{-1}

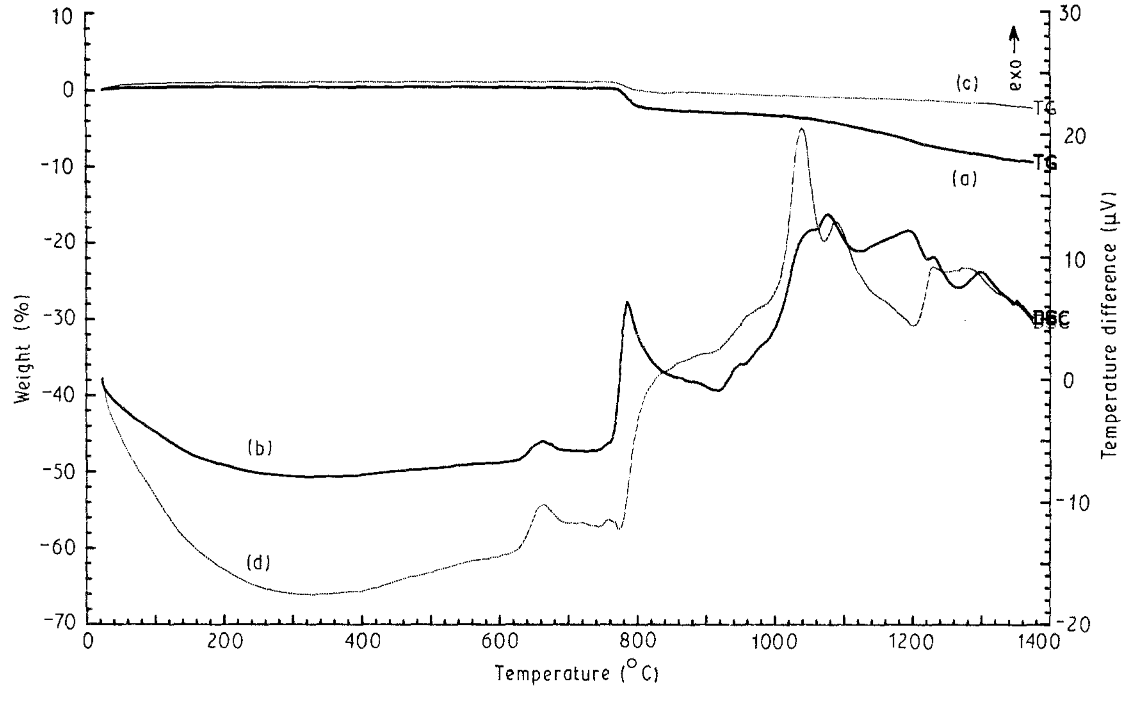

Figure 2 DTA and TG traces of gel prepared by preparation route I and dried at 500 °C (a) and (b) in air at 20 K min^{-1} (c) and (d) in argon at 20 K min^{-1}.

adding in the reaction mixture a necessary amount of water, distributing it homogeneously and heating up the solution to the reflux temperature, trying not to start the hydrolysis before the highest possible temperature is attained. This should be favoured by adding the dilute water solution at a slow rate under the ambient temperature with vigorous stirring. Moreover, with the alkoxide solution being significantly diluted, it was expected to lead to the low probability of Me–O–Me–O–Me linkage formation (when Me is one of the cations used) due to the higher rate of hydrolysis of any alkoxide.

DTA traces of the gel prepared by method I are presented in Figs 1 and 2. Water and solvent evolution is completed up to 400–500 °C. At this temperature the gel acquires black colour and only becomes white at temperatures greater than 1150 °C.

The pronounced alterations in the behaviour of the lines at 760 °C are mainly artificial and connected with the sharp increase of the volume of the powder influencing the recording unit.

It should be mentioned that the surface area after different time exposures within the whole temperature range (150–1100 °C) does not exceed 1–3 $m^2 g^{-1}$ which is very unusual for such gels. It seems that all pores and channels of the gel framework are occupied by the products of pyrolysis of alkoxide residues; part of them are trapped inside and leave on heating, causing a strong dispergation and an increase in the volume occupied by the gel in an explosion-like manner. That this process proceeds in a narrow temperature range indicates a connection with other features of the gel, for instance the beginning of crystallization of some phases. The contamination of the surface by carbon compounds should act as a hindrance in surface and interparticle diffusion, directed to the favoured distribution of various species.

These deductions are supported by X-ray data (Fig. 3). The presence of all possible binary combinations of cations (mullite, spinel, enstatite) shows that the aim to get homogeneous cation distribution in the gel and to equalize the hydrolysis rates have been

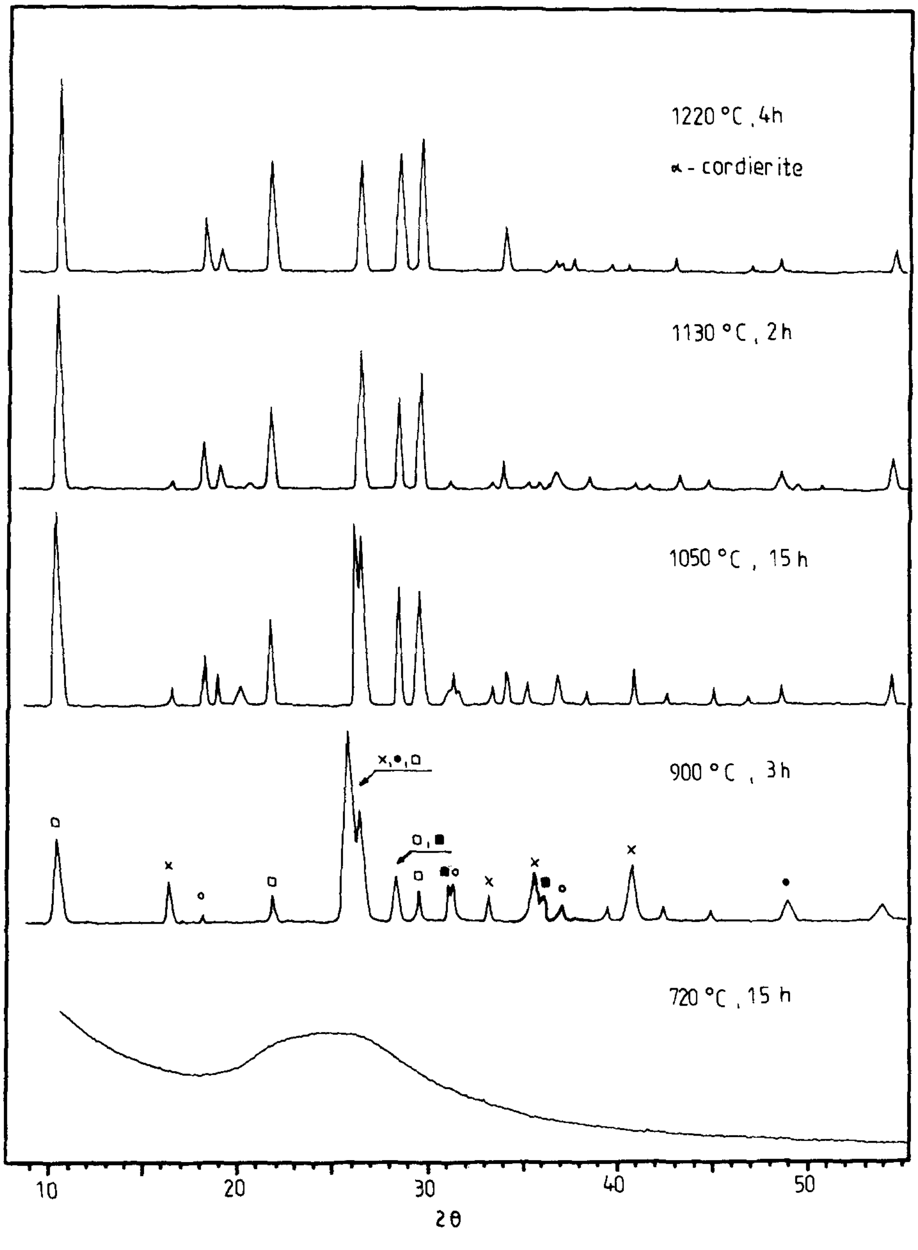

Figure 3 X-ray diagrams of gel prepared by route I after successive thermal treatment. (x) mullite $3Al_2O_3 \cdot 2SiO_2$; (○) spinel $MgAl_2O_4$; (●) μ-cordierite; (■) enstatite $MgSiO_3$; and (□) α-cordierite.

achieved. At the same time the transition from a random cation distribution to that which is fully identical in each gel particle and corresponds to cordierite composition, taking place under the influence of chemical potential, is obviously hindered. Only at the temperatures at which the diffusion-impeding species (presumably carbon) have already been removed (1200 °C) will all the accompanying phases disappear.

One more confirmation is that the prolonged treatment of the gel derived in boiling water with the object increase to the extent of hydrolysis and thus diminish the carbon content, giving rise to a "secondary" gel, which re-establishes its white colour at 750 °C. This gel, at 915 °C for 8 h, crystallizes directly into a metastable cordierite modification (Fig. 4) with a stuffed β-quartz structure referred to as μ-cordierite [13].

The problem of sol–gel preparation, therefore, includes not only the formation of a gel with homogeneously distributed cations but also the creation of the conditions greatly facilitating the diffusion processes.

Taking into account the results previously described we have attempted to create the gel polymeric structure to be not only homogeneous in chemical composition but also, or even rather than, more similiar to the cordierite structure. Simultaneously the process of water addition was changed for the hydrolysis to proceed further.

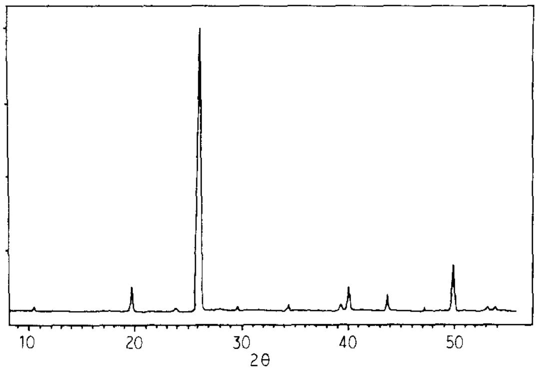

Figure 4 X-ray diagram of gel prepared by route I after the treatment in boiling water and heating at 915 °C for 8 h.

It was the preparation by route II which corresponded to these requirements. This method results in a gel which at 300 °C became light-brown and already at 540 °C re-established a white colour. The specific surface area, after the gel had been heated up to the latter temperature, was equal to 330 m^2 g^{-1}. The part of the DTA and TG pattern of this gel is depicted on Fig. 5. It looks quite like the DTA line in the cordierite gel presented in [3] although the temperature of the first exothermal effect is slightly lower. The peak is a reproducible one and has also been noticed in [4], but its origin remains obscure to us. As to other two effects, our results fully coincide with [3, 4]. The effect at 1015 °C is assigned to crystallization of μ-cordierite and at 1100 °C to μ-α cordierite transformation.

In spite of the fact that the commencement of amorphous-crystalline transition according to DTA begins at 980 °C one should bear in mind that this temperature has seemingly kinetical rather than thermodynamic reasons. We expect that under isothermal conditions this crystallization may take place at a lower temperature. Indeed this appeared to be the case and 850 °C was quite sufficient for the total transformation into the μ-cordierite phase over 50 h. Powders obtained at that temperature are still sufficiently reactive and may be used for sintering of porous cordierite ceramics with reasonable strength. Such materials are being applied as a catalyst carrier.

As far as the preparation of dense ceramics is concerned one should preferably start from an amorphous gel [14]. Therefore the pellets were pressed from the gel obtained by route II after its thermal

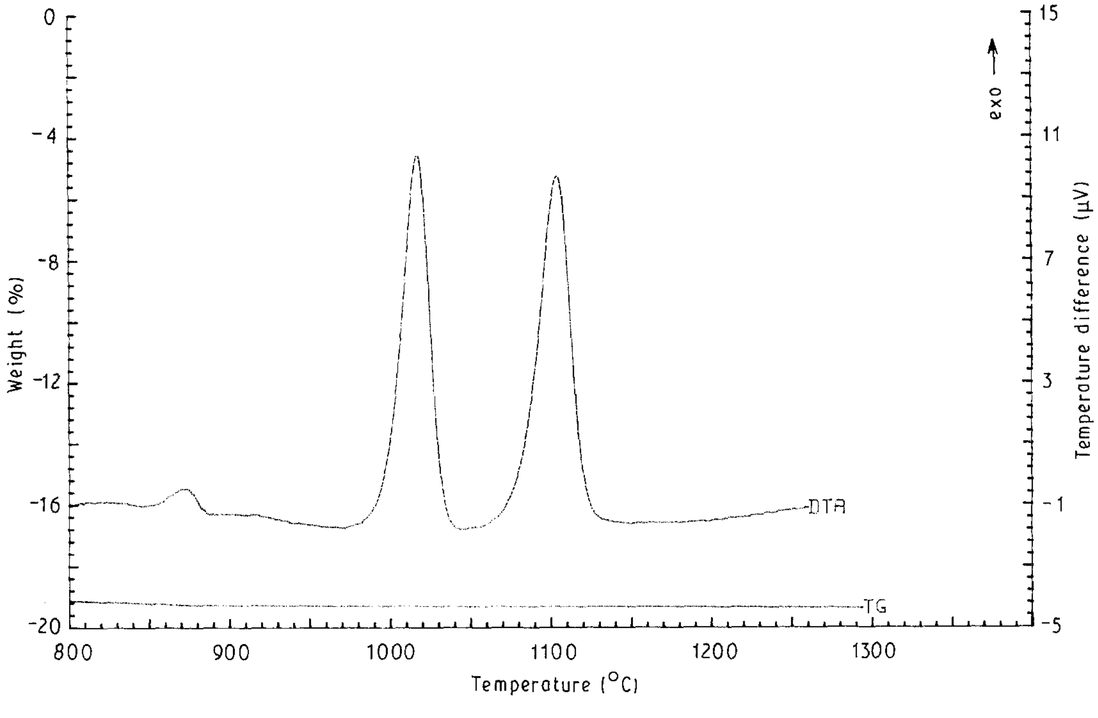

Figure 5 Part of DTA diagram of gel prepared by route II and dried in air at 10 K min^{-1}.

treatment at 540 °C. They were heated with a rate of temperature growth of 1.5 grad per min up to 1120 °C. The slow heating rate was chosen to enable sintering of the gel before crystallization of μ-cordierite takes place and to carefully run the μ-α cordierite transformation without destroying the material. Although the sintering schedule was definitely not optimal, the final density attained was only 97% from its theoretical value (2.512 $\mathrm{g\,cm^{-3}}$) for α-cordierite, the only phase observed.

4. Conclusion

Preparation of the chemically homogeneous polimeric gel of cordierite composition can be approached without preceding TEOS partial hydrolysis. It can be done under high hydrolysis temperatures and considerable dilution of the starting alkoxides if the rates of hydrolysis are previously adjusted by using different alkoxide species for different metal cations. Some peculiarities in carrying out the hydrolysis reaction appear when a gel with high sinterability is desired. This problem can be easily solved by a slight modification of the gel preparation route. Sintered materials achieve the density value close to the theoretical one.

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