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Short communication

Sintering and crystallisation behaviour of chemically prepared cordierite for application in electronic packaging

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Abstract

Synthesis and sintering of dense cordierite ceramics, prepared from magnesium and aluminium ions precipitated in dispersed silica have been reported and phase evolution at 1200 °C been studied by XRD. Densification of compacted precursor powder at 1200 °C has been substantiated by SEM and it was found that the dielectric properties of cordierite ceramics prepared by this route are good enough for substrate application.

Keywords: A. Sintering; D. Cordierite; Crystallisation

1. Introduction

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) a very important compound with low thermal expansion co-efficient and low dielectric constant can be prepared by sol–gel synthesis, liquid phase sintering, glass-ceramic route and solid state reaction [1–5]. However, all these techniques have certain drawbacks. In order to overcome these a semi-chemical route was designed by co-precipitation of Mg and Al nitrates in presence of dispersed silica to produce dense cordierite at low temperature. Density and water absorption, EDX, XRD and SEM were studied to emphasise the densification and crystallisation behaviour of the material. Dielectric constant and losses were determined to substantiate the feasibility of this route for preparation of cordierite ceramics for electronic packaging application.

2. Experimental

Magnesium and aluminium nitrate (>98% pure, S.D. Fine Chem. Ltd.) were dissolved in distilled water (in 1:1 mole ratio) and added dropwise to appropriate amount of precipitated silica ($d_{50} \sim 0.6\,\mu m$, >99.5% pure, ACC India Ltd.) dispersed in a beaker containing ammonium hydroxide solution by vigorous mechanical agitation. The characteristics of the powder at this stage were studied by EDX, XRD as shown in Figs. 1 and 2, respectively. The precursor powder was pressed uniaxially in a hydraulic press at 60 kN to form pellets of 12.42 cm diameter and 2–3 cm in height and sintered at 1200 °C for 6 h. Density and water absorption were determined by boiling water method, prior to crushing for determination of the phase composition. X-ray diffraction pattern of the crushed specimens were recorded in SEIFERT ID 3000 diffractometer employing Cu Kα radiation. The microstructural features of some fractured samples were done by SEM in LEO S 430i (UK). Finally the dielectric constant and loss of a few fully densified samples were determined in Hewlett Packard 4194 A impedence analyser.

3. Results and discussions

The composition of the precursor powder was found to be similar to commercial cordierite powder [6] as corroborated from EDX pattern that strongly resembled the cordierite composition. XRD patterns of the co-precipitated mass indicate that the only crystalline phase present in the precursor powder is α-cristobalite, which came from precipitated silica. The remaining consisting of a magnesium–aluminiun

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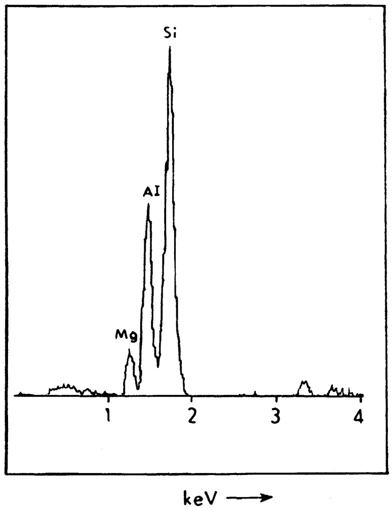

Fig. 1. EDX analysis of the precursor powder.

hydroxide was in a finely divided amorphous state, which do not show regular XRD lines (Fig. 2).

The XRD pattern (Fig. 3) of a crushed pellet sintered at 1200 °C for 6 h was properly indexed using standard JCPDS files. α-Cordierite and magnesium aluminate spinel were the major phases with decreasing content. At around 1175 °C (Fig. 4), the formation of a silicate phase may help in densification of the material and α-cordierite started crystallising at 1200 °C after a brief induction period as also reported by Dupon et al. [7]. It appears from the sequence of events that the formation of cordierite is a liquid phase enhanced reaction where the spinel phase dissolves in the silicate liquid to gradually allow crystallisation of cordierite, probably by the reaction mechanism:

$$2(\mathrm{MgO} \cdot \mathrm{Al_2O_3}) + 5\mathrm{SiO_2} \rightarrow 2\mathrm{MgO} \cdot 2\mathrm{Al_2O_3} \cdot 5\mathrm{SiO_2}$$

Fig. 5 shows that water absorption in these materials sintered at different temperature is consistent with the shrinkage results. It decreased rapidly from 1050 °C and attained almost 0% water absorption at around 1175–1200 °C. The compacts reached a final density of 2.56–2.6 gm/cc.

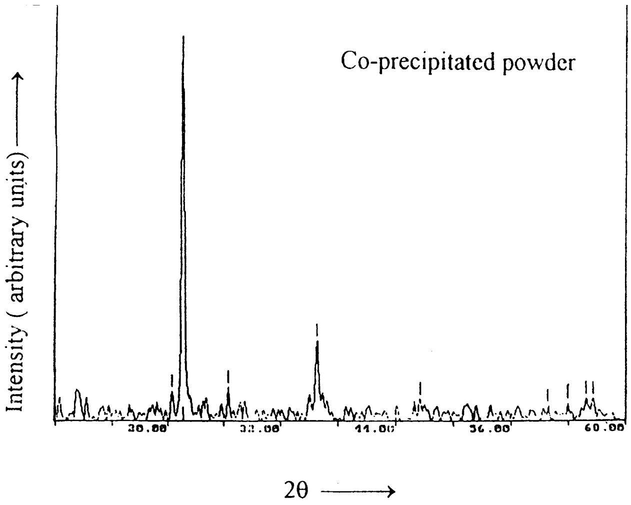

Fig. 2. XRD pattern of co-precipitated powder.

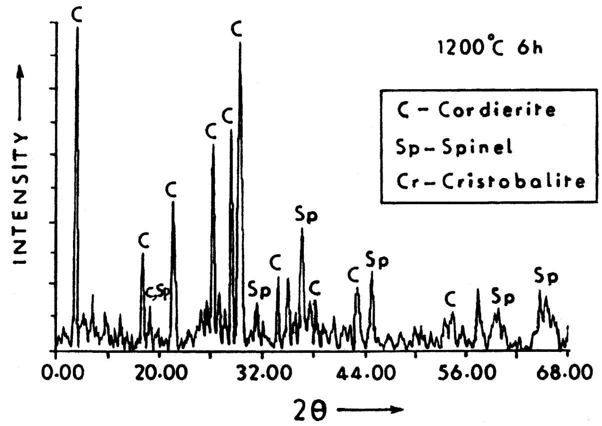

Fig. 3. XRD pattern of precursor powder compacts sintered at 1200 °C for 6 h.

From the results of the sintering studies and phase analysis of the precursor powder prepared by semi-chemical route, we may suggest that there are three distinct phenomena occurring during the firing of the compacts. In the initial stages, crystallisation of spinel occurs from the intimately mixed Al^{3+} and Mg^{2+} ions, then densification occurs by the formation of some viscous liquid within a very short temperature range. Thereafter, crystallisation of cordierite takes place when the compacts are fired for longer duration of time. It should be noted that in order to obtain dense product, sintering of the compacts must precede crystallisation as the reverse would greatly decrease the mobility of the ions and impede sinterability. In this case, crystallisation of cordierite takes place after the compacts have sintered completely.

It is observed that a dense and homogenous microstructure has been developed in this chemical route due possibly to the intimate mixing of the starting ingredients (Fig. 6). Onset of crystallisation is quite prominent at 1200 °C with the coalescence of small pores resulting in sporadically

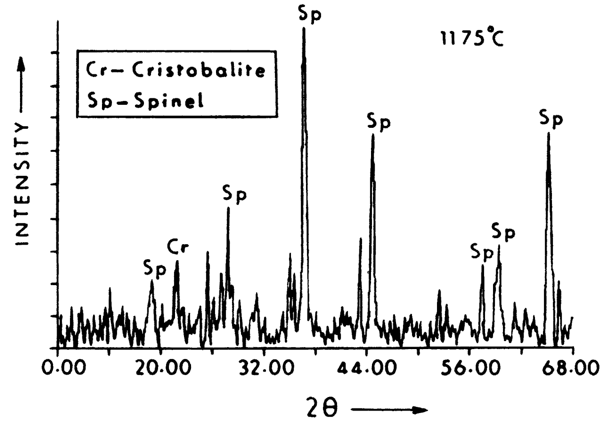

Fig. 4. XRD patterns of precursor powder compacts quenched from 1175 °C.

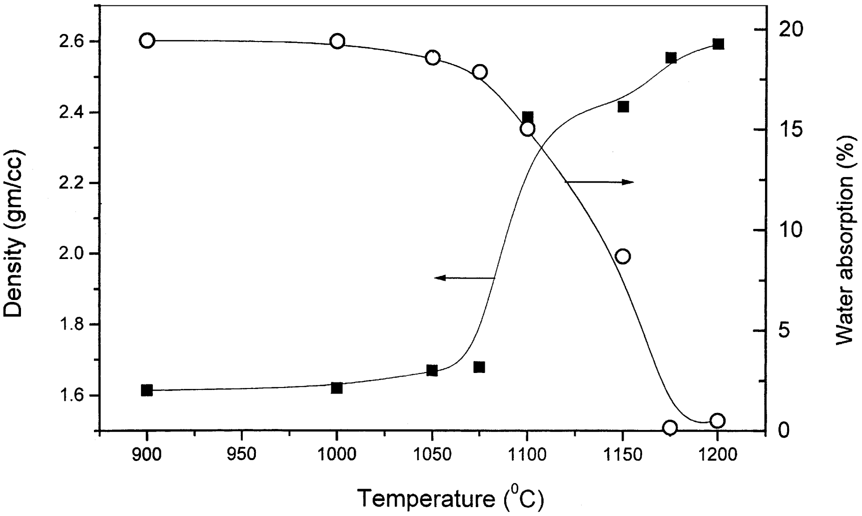

Fig. 5. Change in water absorption and density of precursor powder compacts quenched from different firing temperature.

Fig. 6. SEM photomicrograph of sample fired at 1200 °C for 6 h.

observed larger ones. The micrographs reveal coalescing of the particles and smoothening of the rough edges, which has been similarly reported by other researchers to be due to a viscous flow of silicate liquid [2,8,9].

Fig. 7 shows the dielectric constant and loss of the sample fired at 1200 °C for 6 h. the dielectric constant (<6) and dielectric loss (<0.01) at 1 MHz indicate the suitability for application as packaging material.

4. Conclusions

In this present investigation we have demonstrated a cost effective, semi-chemical route for preparing dense cordierite ceramics at low temperature (1200 °C), suitable

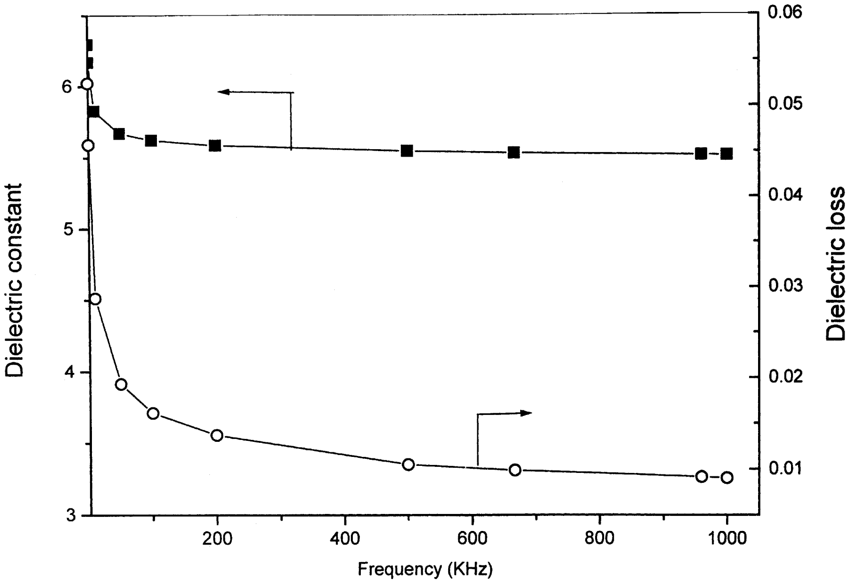

Fig. 7. Dielectric constant and loss of sample sintered at 1200 °C for 6 h.

for electronic applications as packaging materials for semi-conducting circuits. The semi-chemical route provides a method for synthesis of powders having cordierite composition. The powders are highly sinterable, even without the addition of any fluxes. The compacts sinter by a viscous mechanism due to the formation of a viscous liquid. The final densified compacts had α-cordierite as the main phase, the accessories being spinel and vitreous phases.

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