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Preparation of cordierite glass by the sol-gel process

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Cordierite glass was prepared by the sol-gel process from magnesium, $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$. The solution having cordierite-like structure was formed by refluxing the raw materials, followed by gelling and drying to 150° C in the saturated water vapour to hydrolyse completely. On heating the gel, AlO_6 groups transformed into AlO_4 groups, in which aluminium ions were incorporated in SiO_4 tetrahedra units to form a Si-O-Al network structure. The gel was converted into the transparent dense glass by heating above 850° C. The glass transition temperature, 820° C, thermal expansion coefficient, $3.1 \times 10^{-6}\,°C^{-1}$, Vickers hardness, 6.22 GPa and density, $2.59\,g\,cm^{-3}$ were almost the same as those of the conventional glass.

1. Introduction

Cordierite and cordierite-based glass ceramics are promising materials for electric and engineering applications because of their low dielectric loss and low thermal expansion coefficient. Cordierite ceramics are usually produced by sintering the fine powders or crystallizing the glasses [1-4]. However, it is still difficult to consolidate into fully dense and high homogeneous bodies. On the other hand, the sol-gel process enables glasses to be prepared at relatively moderate temperatures. The cordierite crystals precipitate from the glasses [5]. Therefore, one can expect the fully densified cordierite ceramics to be produced from the glass monolith prepared by the sol-gel process.

In the present work, glass of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) composition was prepared by the sol-gel process and the properties of glass were compared with those of glass prepared by the melting method.

2. Experimental procedure

2.1. Sample preparation

Magnesium powders, $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$ were used as the raw materials. $Mg(OC_2H_5)_2$ was not used since it was more moisture sensitive and resulted in crystal precipitations. Magnesium powders (1.66 g), $Al(OC_4H_9)_3$ (33.63 g) and $Si(OC_2H_5)_4$ (35.61 g) were dissolved into 1-propanol (50 g), followed by addition of 1.0 ml CCl_4 as a catalyst, and refluxed at 90° C for 10 h under nitrogen.

The clear solution was poured into the polystylene container and left at room temperature for ~ 5 days to form a stiff gel. The drying of the gel was performed in two different ways. One was gradually heated at a rate of $10°C\,h^{-1}$ to 150° C in air. The other was contained in the glass vessel together with water and tightly sealed with aluminium foil, followed by heating at a rate of $10°C\,h^{-1}$ to 150° C. It was observed that the water remained in the vessel up to 130° C.

Cordierite glass was prepared by melting the gel powders in an alumina crucible for 3 h at 1600° C.

2.2. Measurement of properties

Infrared spectra were recorded with Simadzu IR-440 spectrometer. Liquid samples were dropped onto a KBr plate and solid samples were prepared using the KBr pellet technique. The bulk and apparent densities of the solid samples were determined using mercury and water as the immersing liquids, respectively.

The Vickers hardness of the heated gels was measured with a Simadzu type M microhardness tester. The load was 100 g and loading time was 15 sec. The thermal shrinkage and expansion of samples were measured using a Rigaku Thermal Analysis System TAS 100 with a 5 g load.

3. Results and discussion

3.1. Gel preparation and properties of gel

The solution prepared by refluxing the mixture of raw materials was clear and included no precipitations. However, there is no evidence for the formation of cordierite structure in the solution. Figure 1a shows an infrared spectrum of the solution prepared by refluxing. Absorption bands other than 1020, 850 and $745\,cm^{-1}$ are due to $Si(OC_2H_5)_4$ and alcohols. The band at $1020\,cm^{-1}$ is attributed to the Si-O-Al bond [6], indicating that aluminium ions are incorporated in silica to form Si-O-Al network structure. Further it was observed that the cordierite crystals initially precipitated by heat treatment of gel. From these experimental results, we can conclude that the synthesized solution is not a mixture of raw materials but consists of a cordierite-like structure.

Drying the solution in air leads to a hydrolysis reaction of the alkoxide solution (see Fig. 1b and c).

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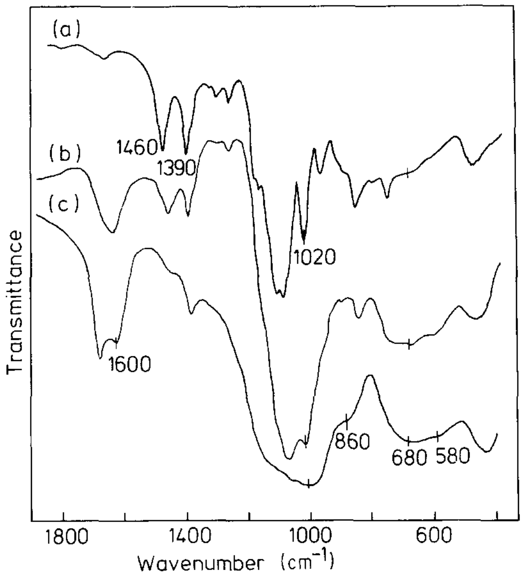

Figure 1 Infrared spectra of solution (a) prepared by reflexing of Mg, $Al(OC_4H_9)_3$ and $Si(OC_2H_5)_4$, solution (b) left for 5 h on KBr plate and gel (c) dries completely on KBr plate.

The bands at 1600 and 860 cm^{-1} are assigned to the bending H–O–H vibration of water and the combination vibration of Si–OH and/or Al–OH groups, respectively. An increase in the absorption at 860 cm^{-1} and a disappearance of the OR groups bands at 1390 and 1460 cm^{-1} indicate the hydrolysis reaction proceeds during gelation;

$$Si(OR) + H_2O \rightarrow SiOH + ROH$$

$$Al(OR) + H_2O \rightarrow AlOH + ROH$$

where R is C_2H_5 or C_4H_9. The absorption bands at ca. 580 and 680 cm^{-1} are attributed to the Al–O bonds in which aluminium ions are in six-fold and four-fold coordinations, respectively [7]. The band of the AlO_4 tetrahedra at 680 cm^{-1} increased simultaneously with the band at 1020 cm^{-1} with an increase in drying time. It is apparent that a number of the aluminium ions replace silicon in the tetrahedra unit to form a Si–O–Al network structure.

The properties of the gels dried at 150° C in air or saturated water vapour are listed in Table I. The apparent density is governed by the relative amount of solid phase and closed pores within the solid phase. The bulk density is that due to the open pores besides these two phases. The Guinier radius is determined from the small-angle X-ray scattering experiment, which is related to the pore size in the gel. There is no significant difference in the apparent density of the two kinds of gels. On the other hand, the bulk density of the gel prepared by water vapour treatment is smaller than that of the gel dried in air. This smaller value for density of gel treated in water vapour indicates that the large amount of open pores are allowed to remain in the gel. The large pore size is confirmed from the large Guinier radius.

TABLE I Properties of gel dried in saturated water vapour (A) or air (B)

Gel	Apparent density ($g\,cm^{-3}$)	Bulk density ($g\,cm^{-3}$)	Porosity	Guinier radius (nm)
A	2.04	1.22	0.54	6.3
B	2.12	1.37	0.48	1.5

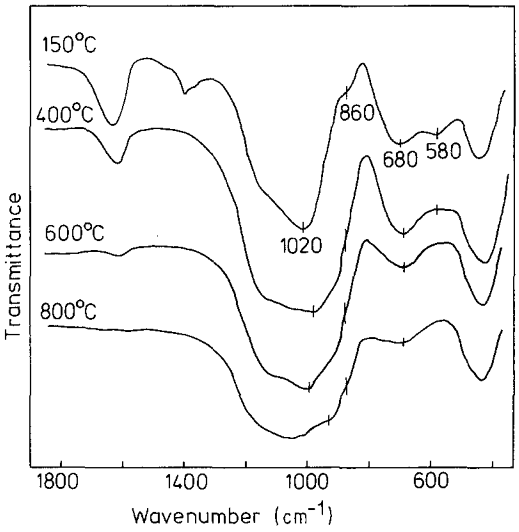

Figure 2 Infrared spectra of gel heated at various temperatures.

Drying the gel in air was not adequate for the complete hydrolysis of the alkoxide, which retained a small number of alkoxy groups. Because of the residual alkoxy groups, the gel changed colour to black and was broken into pieces by heat treatment. On the other hand, when the gel is treated in saturated water vapour in the sealed vessel, the water easily enters into the gel structure to completely hydrolyse the alkoxide. The high pressure in the sealed vessel also hinders the contraction of the gel. This water vapour treatment is valuable for the formation of completely hydrolysed gel with large sized pores. This gel behaviour might be similar to that of gels dried under hypercritical conditions of alcohol using an autoclave.

3.2. Gel to glass conversion

Figure 2 shows the infrared spectra of gels heated at various temperatures. The band of SiOH and/or AlOH groups at 860 cm^{-1} diminishes with increasing temperature, indicating the condensation reaction proceeds during heating. The absorption intensity of the band of AlO_4 at 680 cm^{-1} shows an increase corresponding with the vanishing of the band of AlO_6 at 580 cm^{-1} with increasing temperature. It is also observed that the band of Si–O–Al at 1020 cm^{-1} shifts to a lower wavenumber. From these experimental results, it is apparent that AlO_6 groups transform

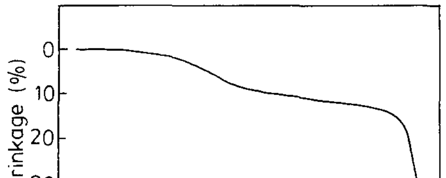

Figure 3 Thermal shrinkage curve of gel heated at the rate of 5° C min^{-1}.

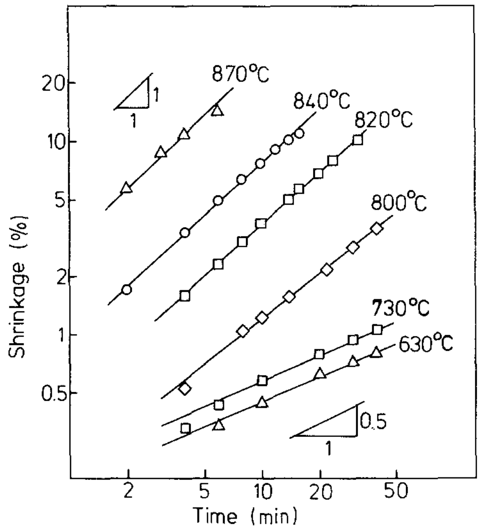

Figure 4 Isothermal shrinkage plots of gel heated at various temperatures around 800° C.

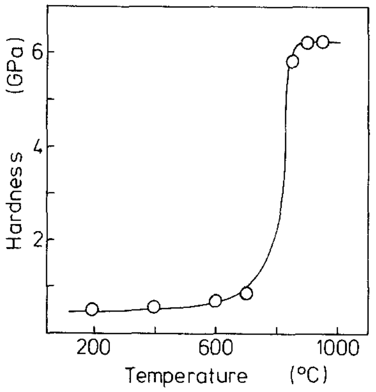

Figure 6 Hardness of gel heated at various temperatures for 1 h.

into AlO_4 groups during heating the gel, in which aluminium ions are incorporated in SiO_4 tetrahedra units to form a Si–O–Al network structure.

Figure 3 shows the thermal shrinkage of the gel during the constant heating rate experiment, which is essentially the same as those for gels of silica [8], ZrO_2 or B_2O_3 containing silicates [9, 10] and others. The gel undergoes a steady contraction on heating from 300° C, followed by serious shrinkage above 800° C. It is known that the shrinkage during the gel to glass conversion mainly occurs by condensation, structure relaxation and viscous sintering [11].

The small shrinkage in the intermediate temperature range can be associated to the condensation reaction $2MOH \rightarrow M\text{–}O\text{–}M + H_2O$ between adjacent hydroxyl groups. This condensation reaction is also confirmed from infrared spectra which shows the removal of water and formation of Si–O–Si or Si–O–Al bonds (Fig. 2).

To determine the shrinkage mechanism, the shrinkage of gel was measured as a function of time around 800° C, which was shown in Fig. 4. Below 800° C, shrinkage seems to be proportional to the square root of time, suggesting the condensation reaction is controlled by the diffusion of the byproduct, water. On the other hand, above 800° C it is apparent that a linear relationship with the slope of unity holds between shrinkage and time, indicating that the shrinkage is controlled by viscous flow. The viscous sintering has been analysed using the spherical or cylindrical particles model [12], in which viscosity can be calculated from the slope of shrinkage against time plots. The slope includes the terms of surface energy and particle size besides viscosity and it is known the viscosity is influenced by the residual water in the gel [13]. In order to estimate the activation energy for viscous flow, the shrinkage rate was plotted against the reciprocal temperature, which was shown in Fig. 5. The activation energy was calculated to $440\,kJ\,mol^{-1}$, which is lower than the value; $585\,kJ\,mol^{-1}$ determined from the viscosity measurement for the molten glass [14].

Figure 6 shows the hardness of gel heated at various temperatures for 1 h. The temperature dependence of hardness is the same as that of the shrinkage curve. It is apparent that the hardness of gel of which the sintering was completed above 850° C reaches the constant value.

3.3. Properties of glass

The completely sintered sample is transparent and shows no characteristic peaks in the X-ray diffraction pattern. Figure 7 shows the thermal expansion curves of gel heated at 850° C for 1 h, which is essentially the same as that of glass prepared by melting the gel

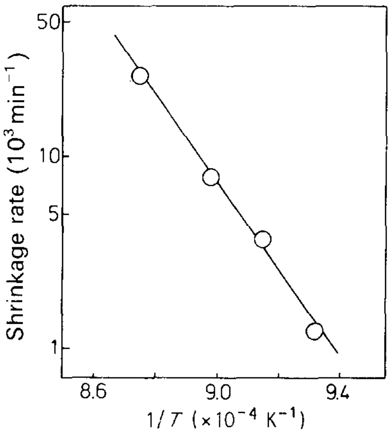

Figure 5 Relation between shrinkage rate and reciprocal temperature. $\Delta E = 440\,kJ\,mol^{-1}$.

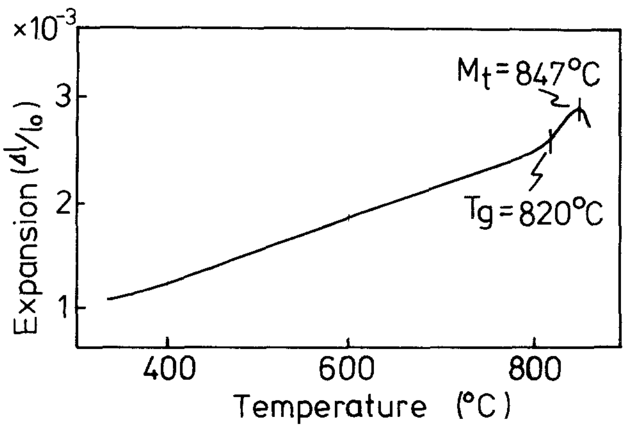

Figure 7 Thermal expansion curve of glass prepared by the sol–gel process.

TABLE II Properties of glass prepared by sol–gel or melting process

Process	Thermal expansion coefficient (° C^{-1})	T_g (° C)	Density (g cm^{-3})	Hardness (GPa)
Sol–gel	3.1×10^{-6}	820	2.59	6.22
Melting	3.6	823	2.64	6.24

powders at 1600° C. It is apparent that the sol–gel process enables the glass to be obtained at a lower temperature, at approximately 750° C lower than the temperature in the melting method. The transition temperature and thermal expansion coefficient of glass are 820° C and 3.1×10^{-6} ° C^{-1}, respectively. Some properties of the glass are listed in Table II together with those of glass prepared by the melting method. No significant difference is observed in the properties of the glasses prepared by the different process.

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