Crystallization kinetics, sintering, microstructure, and properties of low temperature co-fired magnesium aluminum silicate glass-ceramic

Zhenjun Qing[a],[*], Wenzhan Zhou[a], Wenjie Xia[a], Hao Li[b],[*]

[a] College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China
[b] College of Electrical and Information Engineering, Hunan University, Changsha 410082, China

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ABSTRACT

We investigated the effects of sintering temperature and time on the dielectric and mechanical properties, sintering, microstructure, crystallization, and thermal expansion coefficient of Magnesium aluminum silicate glass-ceramic for the applications of low temperature co-fired ceramics substrates. The glass-ceramic has been prepared by melt quenching route. The crystallization kinetics of glass-ceramic was investigated using non-isothermal methods by differential thermal analysis. The activation energy for crystallization E was found to be 201.92 kJ/mol. $Mg_{0.6}Al_{1.2}Si_{1.8}O_6$ was the first crystalline phase forming in the glass-ceramic. With the increase of sintering temperature, the phases of ZrO_2 and indialite precipitate successively. The coefficient of thermal expansion of glass-ceramic increased with the increase of the sintering temperature and time. With the increase of sintering temperature or holding time, the density, bending strength and dielectric constant of the material all increased first and then decreased. The samples sintered at 900 °C for 2 h showed the best properties: high bulk density (2.695 g/cm^3), low dielectric constant (6.21) and low dielectric loss ($1.2 * 10^{-3}$), good bending strength (163 MPa) and low coefficient of thermal expansion ($6.35 * 10^{-6} K^{-1}$). The results showed that the prepared glass-ceramic can be considered as a potential candidate for the application of low temperature co-fired ceramic substrates.

1. Introduction

Nowadays, with further miniaturization of electronic devices, new materials with high signal propagation speed, high signal density, small power loss, low-manufacturing cost and good reliability are in demand for wireless communication and high frequency applications. Low temperature co-fired ceramic (LTCC) technology has been considered as a useful material which could meet these requirements [1–5]. This is because LTCC materials generally have the following characteristics: low relative permittivity for fast signal transmission, low dielectric loss, high thermal conductivity, suitable coefficient of thermal expansion (CTE) for matching with other materials in integrations and most importantly the sintering temperature should be < 900 °C for co-firing with high electrical conductivity metal pastes like copper, silver and gold [6].

Most of the ceramic substrates used in microelectronic packages are based on beryllia, alumina, magnesia, zirconia, and glass-ceramic. Moreover, glass-ceramic could provide other advantages such as elasticity of design and manufacture in addition to reduce the sintering temperature [7]. Due to its adjustable CTE, good mechanical and

dielectric properties, high hardness according to chemical components, and high relative densities, glass-ceramic has been widely used in producing LTCC substrates [8,9]. Glass-ceramic is a polycrystalline material consisted of one or more crystalline phases buried in the residual glassy matrix obtained by controlling crystallization of certain glasses. In general, the chemical components and microstructure (volume fraction of crystalline and glassy phases, type, shape, and size of the crystals) of glass-ceramic determine its properties [10].

Magnesium aluminum silicate (MAS) glass-ceramics have many advantages, such as good thermal stability, good dielectric properties, high mechanical strength and thermal shock resistance [11,12]. According to the study of A. Gawronski et al. [13], MAS glass-ceramic sintered at 950 °C for 10 h, whose main crystalline phases are quartz solid solution and zirconia, have a higher bending strength (171 MPa) and a lower CTE ($4.7 * 10^{-6} K^{-1}$). Obviously, if we can reduce the sintering temperature of MAS glass-ceramics to 900 °C and keep the excellent mechanical and thermal properties, MAS glass-ceramics have the potential to be applied in the field of LTCC. However, there are few reports about the application of MAS glass-ceramics in the LTCC field. Therefore, in this paper, we add B_2O_3 to MAS glass-ceramic to lower

the sintering temperature of glass. In addition, the effects of sintering temperature and holding time on dielectric and mechanical properties, the crystal phase composition, microstructure, densification, sintering, and thermal expansion coefficient of MAS glass-ceramic were investigated. MAS glass-ceramic with excellent properties, which can be used to prepare LTCC substrates, was prepared. Moreover, it is necessary to confirm the kinetics parameters of crystallization for MAS glass-ceramic so as to control the heat treatment system to obtain optimal performance. Accordingly, the crystallization kinetics of MAS glass-ceramic was studied by differential thermal analysis.

2. Material and methods

Analytical reagent $Mg(OH)_2$, $Al(OH)_3$, H_3SiO_3, $Zr(OH)_2$, H_3BO_3 were chosen as the raw materials in this study. A MAS glass with the wt % composition $12MgO-32Al_2O_3-43SiO_2-10ZrO_2-3B_2O_3$ was melted in a platinum crucible at 1600 °C for 2 h. The melt was quenched into water, and then planetary ball-milled in a mill for higher homogeneity ($D_{50} \leqq 2\,\mu m$). The dried powders were granulated by mixing with 5 wt% acrylic acid solution, and then pressed under a pressure of 30 MPa into bars ($65*6*4\,mm^3$) and disks ($\Phi 24*2\,mm^2$), respectively. Subsequently, the pressed samples were sintered at 450 °C for 3 h to burn out the binder, and then further heating to the maximum temperature (800–950 °C) for different holding time ($1-3\,h$) at a heating rate of 3 °C/min.

Differential thermal analysis (DTA) was made by a differential thermal analyzer (Netzsch STA449C, Germany) in the temperature range of 25 to 1300 °C in air. The 20 mg raw material powders of MAS glass-ceramic were fired at rates of 5, 10, 15 and 20 °C/min, respectively. X-ray diffraction (XRD) measurements were performed on a PANalytical X'Pert Pro MPD diffractometer with Cu-Kα radiation in the 2θ range of 10°–80° in steps of 0.017°. Dilatometry was performed using a NETZSCH DIL 402 PC dilatometer. Archimedes principle was used to measure the bulk density. Three-point bending strength tests were made using a MTS CMT6104 electro mechanical universal testing machine. The dielectric properties were studied by an Agilent 4824A high precision LCR meter (1 MHz). A HITACHI S-3400 N scanning electron microscopy (SEM) was used to investigate the structure and morphology of the glass-ceramic. In order to obtain the test errors, three samples were used for each performance test of glass-ceramics.

3. Results and discussions

X-ray diffraction patterns of MAS samples fired for 2 h at 800, 825, 850, 875, 900, 950 °C are shown in Fig. 1. The samples sintered at 800 and 825 °C was amorphous. After the heat treatment at 850 °C, the first

crystalline phase, $Mg_{0.6}Al_{1.2}Si_{1.8}O_6$ (JCPDS PDF no: 075-1568) was observed in the glass-ceramic. As the sintering temperature rose to 875 °C, in addition to the major $Mg_{0.6}Al_{1.2}Si_{1.8}O_6$ phase, a few low intensity XRD peaks for ZrO_2 (JCPDS PDF no: 080-0784) were detected. At 950 °C, a couple of minor XRD peaks for $Mg_2Al_4Si_5O_{18}$ (Indialite, JCPDS PDF no: 012-0235) were also detected.

The effects of sintering temperature and time on the bulk density and linear shrinkage of samples are shown in Fig. 2(a) and (b), respectively.

The results show that with the increase of sintering temperature, both of the bulk density and linear shrinkage of the glass-ceramic increase first and then decrease. Similarly, with the increase of sintering time, the bulk density and linear shrinkage of the glass-ceramic also increase first and then decrease. The sintering of MAS glass is a process of liquid phase sintering. The viscous flow of liquid phase can promote the adhesion and polymerization between particles, forcing the gas to be removed along the grain boundaries or to form a closed pore between the grains, and finally to make the sample compact [14]. When the sintering temperature and time are small, the viscosity of the glass is large, which makes the glass difficult to densification. With the increase of sintering temperature and time, the decrease of viscosity will be beneficial to the adhesion, polymerization and removal of pores between particles, and eventually the sample will be gradually densified. As the temperature and time continues to rise, the glass particles begin to crystallize, which will lead to the increase of viscosity and restrain the densification of the sample.

The SEM micrographs taken on the fractured surface of samples heated at 875, 900, 925, 950 °C for 2 h are shown in Fig. 3. Many large pores are distributed in the MAS glassy matrix of the sample sintered at 875 °C, and almost all of them disappear when the temperature rises up to 900 °C. As the sintering temperature continues to improve, the pores reappear in the samples because of overheating. Obviously, the MAS sample sintered at 900 °C exhibits the densest microstructure. This result is in accordance with measurement of bulk density and linear shrinkage. In addition, many grains with size between 0.5 and 1 μm are evenly distributed in the glass matrix, and the increase of sintering temperature does not significantly affect the size and distribution of grains. These grains should be crystalline phases precipitated in the glass matrix.

Fig. 4(a) shows the variations in relative permittivity and loss at 1 MHz with the increasing sintering temperature.

The MAS samples exhibit a low relative permittivity (5.7 to 6.2) and show the same tendency as the bulk density. It is understood that a high density would lead to a high relative permittivity owing to lower porosity. The values of the dielectric loss of the MAS samples are in the low level of $1.2–4.5*10^{-3}$ and show the opposite tendency as the bulk density since the glass-ceramic has high bulk density and low porosity which usually results in low dielectric loss. Fig. 4(b) shows the variations in relative permittivity and loss at 1 MHz with the increasing sintering time. With the increase of sintering time, the relative permittivity of the glass-ceramic increases first and then decreases, while the dielectric loss of the material shows an opposite trend. From the point of view of the dielectric properties such a material fully satisfies the requirements of LTCC technology.

Fig. 5(a) displays the three-point bending strength and CTE of MAS glass-ceramics sintered at 850–950 °C for 2 h. With the increase of sintering temperature, the bending strength of the glass-ceramic increases first and then decreases, which is between 97 and 163 MPa. In fact, it reaches maximum value (163 MPa) at the temperature of 900 °C, which is the optimum sintering temperature of the MAS glass-ceramic. In general, the microstructure, crystalline phases and pores are the main factors to determine the bending strength of glass-ceramics. Moreover, the pores are correlated with the bending strength of the glass-ceramic: a decrease in porosity conduces to an increase in bending strength of the glass-ceramic [15]. Thus, these results may be due to the porosity and the formation of the crystalline phases of MAS samples
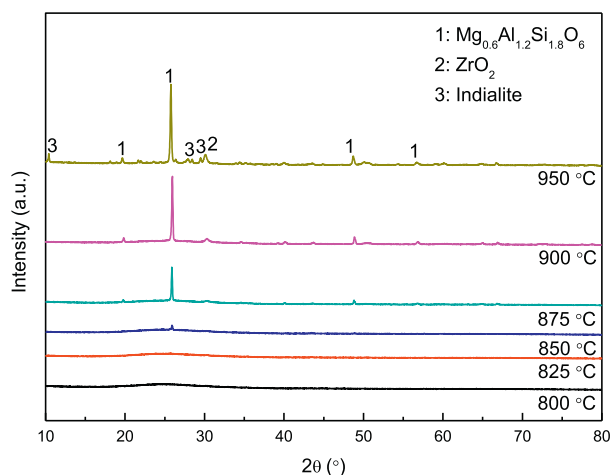

Fig. 1. XRD data of MAS samples fired at 800–950 °C for 2 h.