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Phase formation, microstructure and electrical properties of mica glass-ceramics containing Cr_2O_3 produced by heat treatment

Anuson Niyompan[a,*], Sarawut Phumas[a], Rungnapa Tipakontitikul[a], Tawee Tunkasiri[b]

[a]Department of Physics, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand
[b]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract

The mica glass-ceramics containing Cr_2O_3 were produced via heat treatment process from the bulk parent glass specimens. The appropriate treatment temperatures were selected according to the information provided by the DTA measurement. XRD analysis demonstrated that co-existence of the mica and $MgAl_2Si_3O_{10}$ phases were found at the lower treatment temperature while pure mica phase could be formed at a higher temperature. The SEM investigations revealed the effect of Cr_2O_3 addition on mica crystals development. The electrical resistivity of the glass-ceramic samples showed some significant relation with the added ions. With small amount of addition, an increase of the electrical resistivity was observed. The present glass-ceramics could be a promising candidate as advanced insulating materials, as evidenced from the presence of crystalline phases with machinable properties and good mechanical strength coupled with its high resistivity.

Keywords: C. Electrical properties; D. Glass ceramics; E. Substrates

1. Introduction

Glass-ceramics materials are well-known to exhibit combination properties owning in the glassy matrix and in its embedded crystalline phase and they are readily employed in varieties of applications. In particular of electronics and related fields, glass-ceramics excellent in both mechanical and electrical properties have been used as substrate materials. In the early decade, three major glass-ceramic systems, e.g. Li_2O–Al_2O_3–SiO_3, ZnO–Al_2O_3–SiO_2 and MgO–Al_2O_3–SiO_2, were studied intensively [1]. Later, the composite between mica contained glass-ceramic with machinability properties and cordierite with high strength were also proposed for integrated circuit board and semiconductors packaging [2]. The same strategic experiments have been also attempted for other composites [3]. The studies have been also extended to joint between glass-ceramics substrates and the metal electrodes which is now known as low temperature co-fired ceramic (LTCC) substrates [4].

Glass-ceramic substrates sometime are needed to show transparency if being used in optical applications [5]. Fortunately, this can be achieved by controlling the size of crystal of the precipitated phase to be much smaller than the wavelength of light or by obtaining small difference in the refractive index of glass matrix and crystal phase [6].There are some transparent glass-ceramics that have been successfully prepared [7,8].

Using glass-ceramic materials as a substrate requires a novel property of their crystalline phases. Sometimes, two or more crystalline phases are devitrified simultaneously as to obtain a material with higher mechanical strength, higher electrical resistivity, higher thermal shock resistance and transparency. However, many glass-ceramics substrates are difficult to be machined as they always contain high toughness crystals.

The aim of this work is to prepare the transparent glass-ceramic that contains mica crystals that posseses machinable properties. The study will be extended to investigate coloration in the transparent mica glass-ceramic by introducing colored ions, in this case, Cr^{3+} is employed. The effects of ion addition on phase formation, microstructure and electrical resistivity are then invesitgated.

*Corresponding author. Tel.: +66 4528381; fax: +66 45288381.
E-mail address: anuson@rockertmail.com (A. Niyompan).

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2. Experiments

2.1. Preparation

The glasses in the chemical composition $10Li_2O$–$20MgO$–$5Al_2O_3$–$55SiO_2$–$10MgF_2+xCr_2O_3$, where $x=0.1-0.5$ mol%, were prepared using high purity reagent materials by melting a 50 g glass batch in a platinum crucible at 1450 °C for 2 h. The melt was then quenched by pouring onto a steel mold and splashed by another steel plate. The as-prepared glass block was cut into desired dimensions and optically polished for undertaking different experiments and measurements. The selected glass specimens were subjected to heat treatment at the selected temperature for 2 h in the electrical furnace.

2.2. Characterization

The differential thermal analysis (DTA) was emloyed for determination of glass transition and crystallization behavior of the as-quenched samples. The XRD patterns were recorded using an Xpert-Pro diffractometer with CuKα radiation and the scanning were performed at room temperature as to identify the possible forming phases. The crystallinity of the heat-treated glasses was examined by SEM. Electrical resistivity of the samples were determined via ac technique employing the impedance analyzer model HP 4921A that was equipped with a home-made measurement jig.

3. Results and discussion

3.1. Parent glasses

The appearances of the obtained parent glasses were primarily inspected by the necked-eye and the results showed that all as-quenched specimens were transparent with no detection of surface disorder due to surface crystallization. With influence of Cr^{3+} ions, color of the glasses were observed in the light green region and shifted to a darker green region when Cr_2O_3 increased. To study crystallization behavior, grounded parent glasses were subjected to DTA measurements. The results of DTA curves are shown in Fig. 1. Each DTA curves shows well-defined glass transition ranges and two exothermic peaks corresponding to crystallizations of two possible crystalline phases. The locations of main exothermic peaks are in range 700–750 °C. It is clearly seen that the peaks centers (T_c) are shifted toward the higher temperature with the increasing of Cr_2O_3 contents and the extracted T_c values are summarized in Table 1. The additional exothermic peaks are found at temperature level exceeded 800 °C.

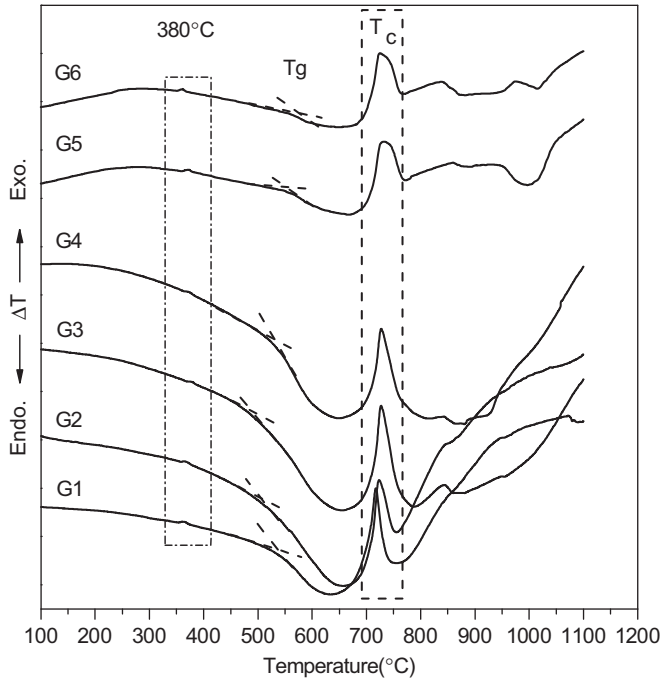

Fig. 1. DTA curves of as-quenched samples (detail of sample assigned names, T_g and T_c see text).

Table 1
Sample assigned names, compositions, glass transition (T_g), crystallization temperatures (T_c) and bulk densities.

Sample	Cr_2O_3 (mol%)	T_g (°C)	T_c (°C)	Density (g/cm^3)
G1	0.0	530	716	2.63
G2	0.1	500	723	2.56
G3	0.2	580	727	2.53
G4	0.3	520	727	2.55
G5	0.4	550	733	2.55
G6	0.5	570	723	2.54

3.2. Phase formation in glass–ceramics

Devitrification process in the glass gave the transparent glass-ceramic specimens. The results of phase formations in the treated samples are shown in Fig. 2. Phase developments in the samples with different Cr_2O_3 contents are similar. Magnesium aluminosilicate ($MgAl_2Si_3O_{10}$, JCPDS no. 73-2337) is identified as the main crystalline phase. Formation of the Li-mica ($LiMg_3(AlSi_3O_{10})F_2$, JCPDS no. 25-1388) was also found though the diffraction peaks in the XRD pattern were very small. It has to be noted that participation of Cr^{3+} ions in the glass compositions did not affect phase types but it induced change of the relative intensities ratio of these two phases. This may be indicated that crystallization rate of the Li-mica was suppressed by the involvement of Cr_2O_3.

Formation of magnesium aluminosilicate phase in the glass-ceramics has been believed to be the intermediate phase for the formation of codierite and idialite if the treatment proceeded to further higher temperature [9]. While formation of Li-mica is more complicate as it was sensitive to glass compositions and phase equilibrium during devitrification process. It structural arrangements as the building blocks of the aluminosilicate layers is also

responsible for its complex crystallization. Frequently, mica can be formed through mechanism of precipitation of several intermediate phases depending on phase relation and treatment conditions as described by Ref. [7].

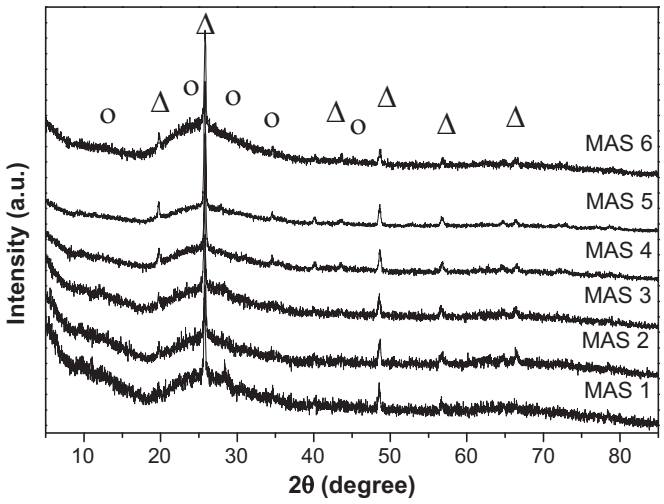

Fig. 2. XRD patterns of glass-ceramics, two crystalline phases are identified, o: Li-mica and D: magnesium alumino silicate ($MgAl_2Si_3O_{10}$).

3.3. Microstructure development

SEM photographs of the polished and etched glass – surfaces of the glass-ceramic samples are presented in Fig. 3. Agglomeration of crystals in the glass matrix is clearly observed. Crystals of Li-mica are easily detectable as they appear as plate-like particles distributing randomly in the residual glass. Since the images were taken at the same magnification level, thus comparison of crystallite size can be roughly made. It is seen that the larger crystallite size of about a micron is observed in the glass-ceramic sample derived from the glass MAS1. When Cr_2O_3 was added for the other samples, the smaller Li-mica crystals with sub-micron size are found. These results suggested that presence of Cr_2O_3 has influence on the crystallization rate of the mica. It may also be consistent with that observed by XRD results. Presence of magnesium alumnosilicate crystals is difficult to distinguish because they are observed as small particles scattered randomly in the glass matrix. Thus, they are only seen as the brighter spots compared to the darker region of the residual glass matrix. Effect of ions doping on the crystallization behavior of the mica phase which leads to a change

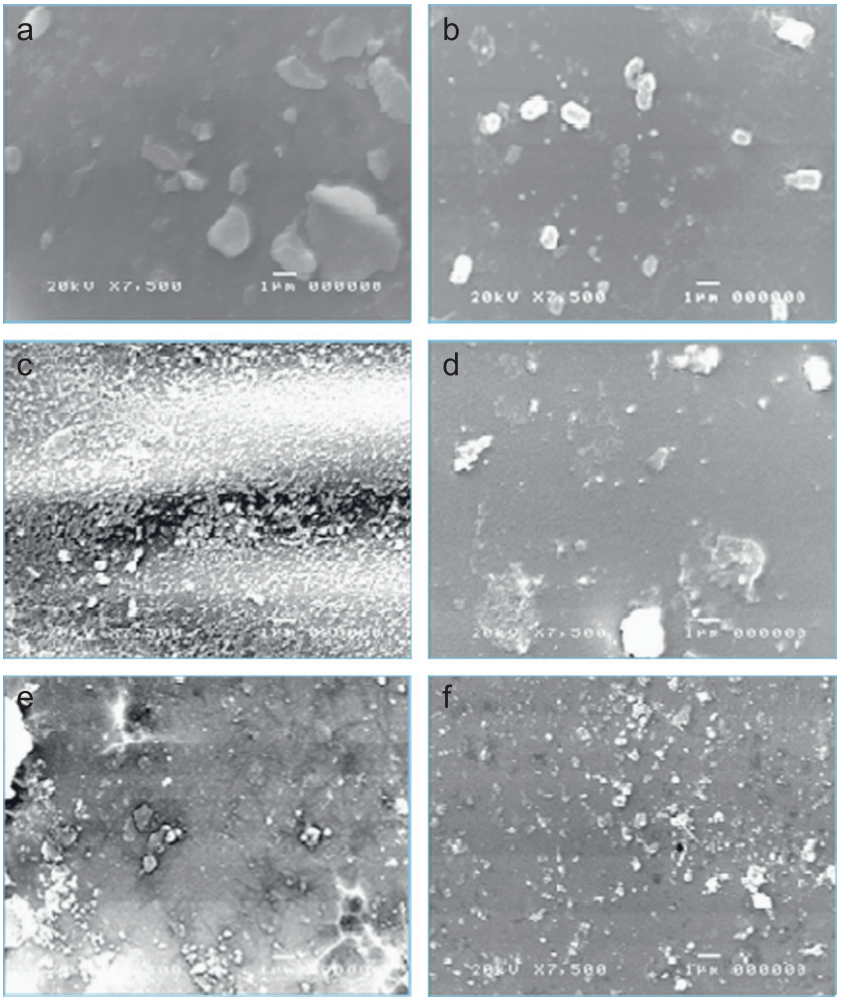

Fig. 3. SEM micrographs of polished and etched surfaces of glass-ceramics with different Cr_2O_3 contents, (a)–(f) are MAS1–MAS6, respectively.

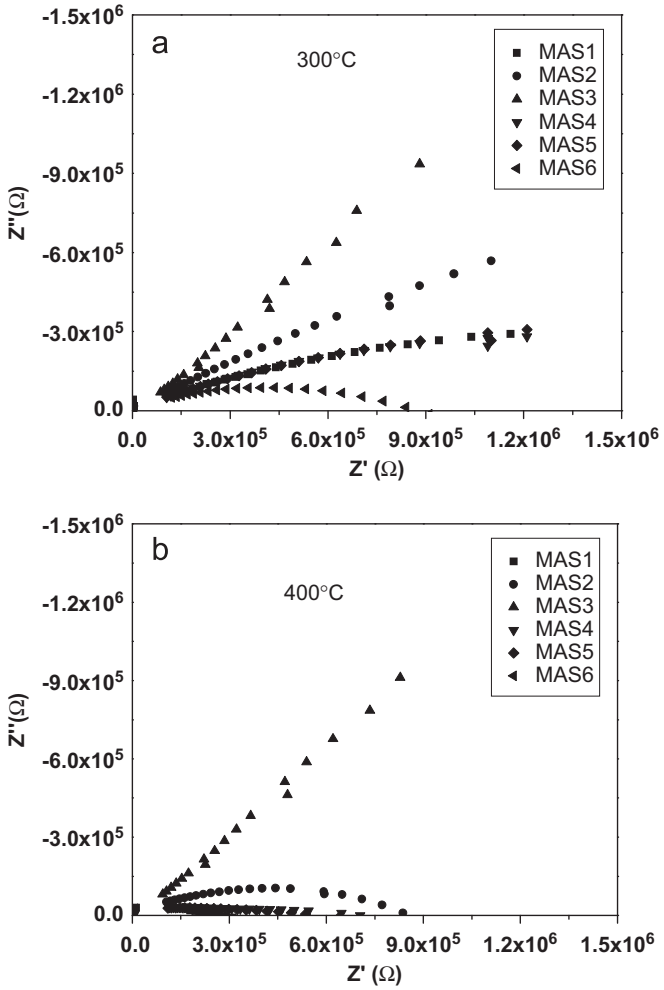

Fig. 4. Complex impedance plots for two different measurement temperatures, (a) 300 °C and (b) 400 °C.

on its morphology has been described by the view of composition adjustment in the separated matrix phases of the glassy samples [10].

3.4. Electrical resistivity

The complex impedance plots were produced covering the frequency range of 100–1000 kHz. A non-linear curve fitting was employed to determine the bulk resistance (R_b) values. Fig. 4 is the represented plots of complex impedance of all samples measured at 300 °C and 400 °C, respectively. Due to complex phase relations and the large resistance of these glass-ceramics, the line shapes of the complex impedance plots are not well-defined as semicircle. However, by carefully optimizing the fitting parameters, the bulk resistivity for each sample can be determined and the reported values are summarized in Table 2.

In Fig. 4, it is seen that there is a steep rising branch in the Z'' versus Z' plots at low frequency side. By comparing these plots with the equivalent circuit model presented elsewhere [11], it can be assigned that the equivalent circuit must contain a high value of blocking electrode capacitance. Thus,

Table 2
Treatment condition, crystalline phase and electrical resistivity of glass-ceramic.

Sample	Treatment (°C), h	Phase	ρ ($\times 10^6$ Ω cm)	
			300 °C	400 °C
MAS1	716, 2	Mic, S	2.44	0.23
MAS2	723, 2	Mic, S	8.89	1.20
MAS3	727, 2	Mic, S	10.76	0.66
MAS4	727, 2	Mic, S	3.10	0.56
MAS5	733, 2	Mic, S	2.51	0.49
MAS6	723, 2	Mic, S	0.91	0.25

Mic = lithium-mica, S = $MgAl_2Si_3O_{10}$.

to ensure the best value of the obtained resistivity through the complex impedance analysis, the impedance spectra were also produced but the results are not included here due to space limitation. The method of analysis in this work was the same as that has been applied for other glass-ceramic materials [12].

The present result has demonstrated that entering of the Cr^{3+} ions into the glass-ceramic compositions induced change of electrical resistivity. Initially, increases of electrical resistivity are clearly seen in MAS2 and MAS3 samples. But, when more Cr^{3+} was presented (in MAS4–MAS6), the electrical resistivity is slightly decreased. This may be due to participation of conduction mechanism from the Cr^{2+}/Cr^{3+} redox equilibria in the samples with larger Cr_2O_3 content.

4. Conclusion

Transparent glass-ceramic containing lithium mica crystals were successfully prepared through the heat treatment process. Adding of Cr^{3+} as the colored ions into the glass-ceramic nominal composition was also performed. This addition did not lead to change of crystalline phase type but it suppressed growth of the mica crystals. Entering of small amount of the Cr^{3+} ions also gave rise to the increasing of electrical resistivity observed at 300 °C and 400 °C. The understudied glass-ceramic material also shows a very large electrical resistivity which required for insulator application.

Acknowledgments

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