Enhanced Thermal Expansion of Sintered Fluorophlogopite Mica-K₂O-MgO-SrO-B₂O₃-Al₂O₃-SiO₂ Glass Composite

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ABSTRACT

This study demonstrates the enhanced thermal expansion coefficient of mica based glass-ceramic composite synthesized by mixing of alkaline boroaluminosilicate glass, K₂O-MgO-SrO-B₂O₃-Al₂O₃-SiO₂ and fluorophlogopite mica ($KMg_3AlSi_3O_{10}F_2$) glass-ceramic. High glass transition temperature (698 °C) and softening point (733 °C) was experienced by DSC and dilatometry for this alkaline boroaluminosilicate glass. Opaque fluorophlogopite mica glass-ceramic was obtained from SiO_2-MgO-Al_2O_3-B_2O_3-K_2O-F glass by controlled heat-treatment at 1000 °C based on DSC thermograph. Composites were prepared by mixing the high thermal expansion (11.26×10^{-6}/K at 50-800 °C) mica glass-ceramic and alkaline boroaluminosilicate glass (having thermal expansion = 6.03×10^{-6}/K at 50-700 °C) by wet mixing technique in isopropyl alcohol. XRD pattern of the glass/ glass-ceramic composites, heat-treated at 900 °C for 2 h followed by 800 °C for 10 h duration, confirms the presence of predominant fluorophlogopite mica, $KMg_3AlSi_3O_{10}F_2$ phase. Thermal expansion value significantly increased with the content of mica glass-ceramic in the glass/glass-ceramic composite mixture. It is found that the thermal expansion coefficient (50-800 °C) of composite prepared by mixing 90 boroaluminosilicate glass: 10 fluorophlogopite mica (wt. %) is 10.47×10^{-6}/K and increased to 10.87 and 10.91×10^{-6}/K for 80:20 and 70:30 system, respectively. Mica glass-ceramic composites with such higher thermal expansion value ($> 10.5 \times 10^{-6}$/K) can be applicable for SOFC sealing purpose.

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INTRODUCTION

Mica based glass-ceramic is widely used for high temperature application due to its large thermal shock resisting capability and unique crystalline structure. This family of glass-ceramics, consisting of polycrystalline environs 'growing' in residual glass matrix, can be drilled, sawn or turned in a lathe to close tolerances [1-3]. It is a combination of easy cleavage of the mica flakes and deflection blunting mechanism due to random orientation and interlocking of the mica crystals that confer better thermal and mechanical properties to this material. A suitable glass-ceramic based high temperature material needs to suffice several fundamental requirements, such as compatible thermal expansion coefficient, high

temperature sustainability, chemical resistibility, *etc.*, while packing with other components [1-5]. Having such stimulating properties, the mica glass-ceramics find additional applicability in cookware, telescope mirror supports *etc.* SiO_2-MgO-Al_2O_3-K_2O-B_2O_3-F, an alumino-silicate based glass system, is converted to mica glass-ceramic on controlled crystallization. Thus the increase of thermal expansion coefficient of this alumino-silicate glass is a challenging job since last two-three decades [5]. The advantageous of using the mica as the high temperature sealing material include no need of thermal expansion compatibility with adjacent components; only problematical its poor stability and high leak rate at elevated temperature. In the study of mica glass-ceramic for high temperature application, Chou *et al.* [1] reported that the low leak rate could be obtained by mixing glass with mica, *i.e.* the mica/glass hybrid seal. The same authors [1] furthermore optimized the mica/glass hybrid seal as a sandwich structure. The thermal expansion of an aluminosilicate based glass is considerably increased when a composite mixture is prepared by such glasses with some amount of mica glass-ceramic. Higher weight fraction of mica manifests in higher thermal expansion value, which furthermore supports the high temperature applicability [6]. Das and his co-authors [7] demonstrated the synthesis, characterization and ion transport properties of Ag_2O–P_2O_5–(15 %) $LiCl$: xAl_2O_3 glass-ceramic composites. They [7] optimized such glass-ceramic composite materials as promising material for solid state batteries. Similarly, the phosphate glass *i.e.* SrO–ZnO–P_2O_5 glass–Al_2O_3 composites [8], borosilicate glass/alumina composites [9], sodium aluminium phosphate glass–ceramic composites [10] have been studied. Assiri and Desoky [11] synthesized barium titanate based glass-ceramic nanocomposites in the glass system $BaTiO_3V_2O_5Bi_2O_3$; and established that the crystallization temperature increases with increasing $BaTiO_3$ content.

Ghaffari *et al.* [12] studied the sintering behaviour and mechanical properties of mica-diopside glass–ceramic composites where the primary glass–ceramic containing phlogopite and diopside crystals were prepared through sintering of 70 wt. % mica bearing and 30 wt. % wollastonite bearing base glasses. Ghaffari *et al.* [12] demonstrated the improvement of mechanical properties by adding different amounts of partially stabilized zirconia (ZrO_2) particles in the starting composition.

Keeping in view of the significant improvement in case of glass/glass-ceramic composite materials compared to pure glass or glass-ceramic [6-13], we reported the synthesis and thermal properties of boroaluminosilicate glass/mica glass-ceramic composites. The development of mica glass-ceramic by controlled crystallization technique and variation in weight fraction of mica content in different composites to affect the crystallization and thermal expansion is also explored.

E X P E R I M E N T A L

G-1 of composition $39SiO_2$-$24MgO$-$16Al_2O_3$-$6K_2O$-$10B_2O_3$-$10YSZ$-$5SrO$ (Wt. %) and G-2 of composition $39SiO_2$-$12MgO$-$16Al_2O_3$-$10K_2O$-$11B_2O_3$-$10YSZ$-$12MgF_2$ (Wt. %) glasses were synthesized from the highly pure raw materials SiO_2 (Quartz Powder), $Al(OH)_3$ (97 %, Loba Chemie, Mumbai,

India), $Mg(OH)_2$ (97 %, Loba Chemie, Mumbai, India), H_3BO_3 (99.5 %, Loba Chemie, Mumbai, India), K_2CO_3 (98 %, Loba Chemie, Mumbai, India), MgF_2 (99.9 %, Loba Chemie, Mumbai, India) and Yttria Stabilized Zirconia, YSZ (99.9 %, Loba Chemie, Mumbai, India). All the starting raw materials of G-1 and G-2 glasses were weighed, with accuracy to the hundreds after the decimal point, on a digital balance. Homogeneously mixed batches were melted at 1550 °C for 2 h in a platinum crucible in an electrically heated furnace. To remove the residual internal stress in the sudden cooled melt, they were annealed at 630 °C for 2 h and then cooled down slowly to room temperature (about 35 °C).

G-2 glass was then heat-treated at 1000 °C (duration = 4 h) in an electrical furnace for crystallization. G-1 glass and G-2 glass-ceramic were finely powdered by mortar pestle and then two powders (particle size <100 nm) were wet mixed in alcohol (isopropyl alcohol) in an agate mortar to prepare the glass + glass-ceramic composites *i.e.* C-1, C-2 and C-3 as per Table-1. After mixing these two powders, the paste was prepared using poly-vinyl alcohol (PVA) as the binder. Using the composite paste (*i.e.* fully mixed powder paste), the cylinder shaped pellets of length = 25 mm and diameter (Ø) = 6 mm were prepared, by uniaxial hydraulic press providing hand pressure ~10 tons, followed by drying for 2 h. The composites thus obtained were put into a furnace for sintering at 900 °C for 2 h and subsequent isothermal crystallization at 800 °C for 10 h. Glass transition temperature (T_g), Co-efficient of thermal expansion (CTE) and dilatometric softening point (T_d) were evaluated using cylinder shaped glass sample (length ~ 25 mm and diameter ~ 6 mm) by a horizontal dilatometer, NETZSCH DIL 402 PC (NETZSCH-Gerätebau GmbH, Germany) at a heating rate of 5 °C/min with an accuracy of ± 1 % after calibration with a standard Al_2O_3 cylinder. Non-isothermal differential scanning calorimetry (DSC) was carried out using glass powders (particle size < 60 µm) in the temperature range 30-1200 °C at 5, 10, 15 and 20 °C/min heating rate by a NETZSCH instrument (Model STA 449 Jupiter F3, NETZSCH-Gerätebau GmbH, Selb, Germany) to evaluate the activation energy of crystallization (E_c). X-ray diffraction (XRD) of the glass and glass-ceramic samples were performed using an XPERTPRO MPD diffractometer (PANalytical, Almelo, Netherlands) operating with Ni-filtered CuK_α (λ = 1.5406 Å) radiation as the X-ray source, scan range 5-90° with a step size of 0.05°, irradiated at 40 kV and 40 mA.

TABLE-1
COMPOSITION (wt %) OF COMPOSITES, HEAT-TREATMENT AND THEIR PHYSICAL NATURE

Composite	G-1 glass	G-2 glass-ceramic	Heat-treatment	Physical nature (after heat-treatment)
C-1	90	10	900 °C for 2 h and 800 °C for 10 h	White opaque
C-2	80	20		White opaque
C-3	70	30		White opaque

R E S U L T S   A N D   D I S C U S S I O N

Fluorophlogopite mica glass-ceramic shows high thermal resistivity and compressibility, whereas G-1 glass has a high

coefficient of thermal expansion as well as thermal and chemical stability. With the intention of addressing the difference in thermal properties of G-1 and G-2 glasses, the dilatometry and differential scanning calorimetric study were performed with the two as prepared glass samples. Fig. 1a presents the thermal expansion trend as a function of temperature for G-1 glass sample. The coefficient of thermal expansion (CTE) values is calculated from the elongation data and the used formula as:

$$CTE = \frac{\Delta L}{Lo} \times \frac{1}{\Delta T}$$

where L is the sample length and ΔT is temperature difference. The transparent view of this alkaline boroaluminosilicate glass, G-1, is clearly made out in the inset of Fig. 1a.

At temperature 50-300 °C, coefficient of thermal expansion (CTE) of G-1 glass evaluated is 6.08×10^{-6}/K. It is increased when sample experienced more temperature. At 50-500 and 50-600 °C, the CTE value of this K_2O-MgO-SrO-B_2O_3-Al_2O_3-SiO_2 glass is estimated 6.50 and 6.40×10^{-6}/K, respectively. Here, the alkali and alkaline earth metal ion content is 35 wt % ($24MgO$-$5SrO$-$6K_2O$) which is not so higher as the content of silica (39 wt. %). This case is obviously explaining that the thermal expansion is controlled by Si-O-Si phase, as well as a large number of non-bridging oxygen (Si-O^-). At the temperature range 600-700 °C, an alteration in CTE trend is appeared; and its onset point correspond to glass transition temperature (T_g), 697 °C. As presented in Fig. 1a, a considerable alteration in the CTE value is observed before and after T_g. At temperature 50-700 °C, coefficient of thermal expansion of G-1 glass is evaluated 6.03×10^{-6}/K. The peak developed after glass transition region, in Fig. 1a, corresponds to the softening point which is estimated as 733 °C for G-1 glass. The dilatometric T_g is confirmed from DSC study. Fig. 1b exhibits the DSC thermogram of K_2O-MgO-SrO-B_2O_3-Al_2O_3-SiO_2 glass (G-1); and here the first endothermic minimum corresponds to T_g. The close similarity in the dilatometric T_g (=697 °C) and DSC estimated T_g (=699 °C) for G-1 glass proofs the exactness of the evaluation.

The first exothermic peak, corresponding to crystallization of G-1 glass, is appeared at about 825 °C and the glass phase is thermally stable in between the temperature range of T_g and onset of the crystallization peak. From Fig. 1b the thermal stability of G-1 glass phase can be noted as almost 100 °C.

From the inset of Fig. 1b, the amorphous nature of G-1 glass is confirmed. Here, the broad hump appeared at (2θ) 15-35° signifies the amorphous character (short range order) of G-1 glass sample. In the present study, glass/glass-ceramic composite with the weight fraction of crystallized G-2, *i.e.* mica from 10 to 30 % have been examined.

For preparing the glass/glass-ceramic composite, in particular, fluorophlogopite mica-boroaluminosilicate glass composite, as prepared G-1 glass was mixed with synthesized G-2 glass-ceramic in different proportions. G-2 glass-ceramic was synthesized from G-2 glass by controlled heat-treatment; and the heating temperature was selected from DSC thermograph. Fig. 2a presents the DSC thermograph of G-2 glass. The inset of Fig. 2a indicates that G-2 glass and corresponding glass-ceramic both are opaque, but the whitish outlook is quite increased after heat-treatment. The first exothermic peak is appeared in the DSC thermograph of G-2 glass at about 690 °C, which correspond to crystallization. And after 1000 °C, the melting signal is indicated for G-2 glass.

In order to synthesize the fluorophlogopite mica crystalline material, in particular, G-2 glass-ceramic, the G-2 glass was heat-treated at 1000 °C for 4 h duration [2]. The glass to glass-ceramic phase transformation is studied by X-ray diffraction pattern. As is evident from Fig. 2b, the amorphous G-2 glass was sufficiently converted into G-2 glass-ceramic after heat-treatment at 1000 °C.

As seen from Fig. 2b, *i.e.* the XRD pattern of G-2 glass-ceramic, the characteristic peaks are appeared at (2θ) 26.91, 28.34, 30.37, 34.25, 36.89, 50.35 and 60.33° due to the phase reflection from (001), (112), (113), (131), (201), (224) and (331) respectively, for the development of single crystalline phase, potassium magnesium aluminium fluoride silicate; fluorophlogopite mica, $KMg_3(AlSi_3O_{10})F_2$; monoclinic system,
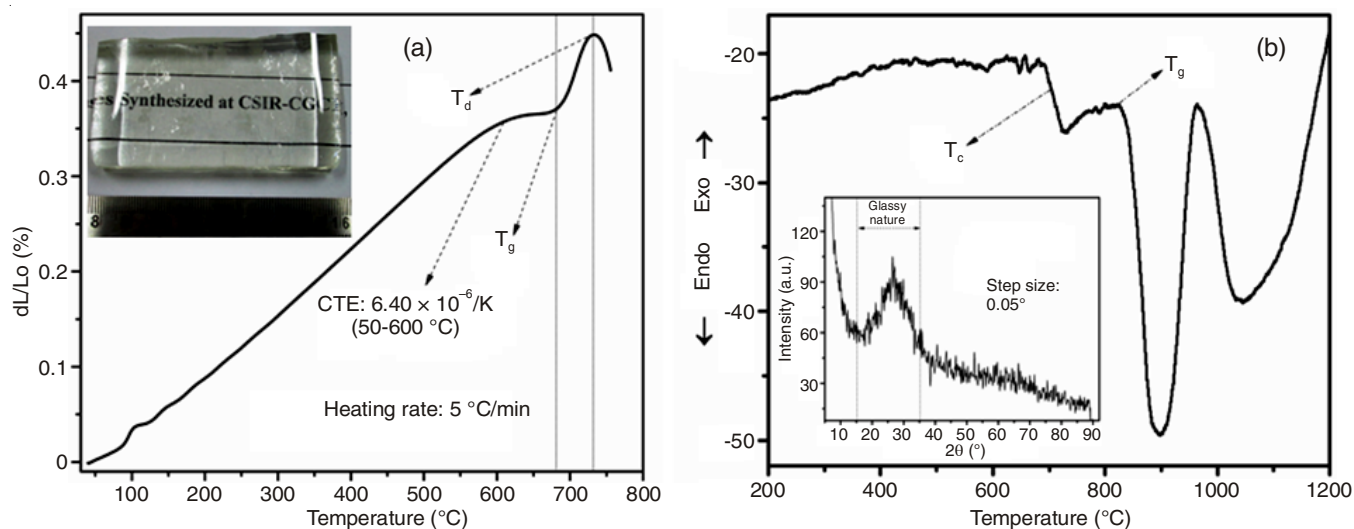

Fig. 1. (a) Dilatometric thermograph showing the glass transition region and softening temperature and (b) Differential scanning calorimetric pattern of precursor K_2O-MgO-SrO-B_2O_3-Al_2O_3-SiO_2 glass, G-1 (inset-a depicts the photograph exhibiting transparency of G-1 sample and inset- b presents the XRD pattern *i.e.* the amorphous nature of G-1 glass sample)
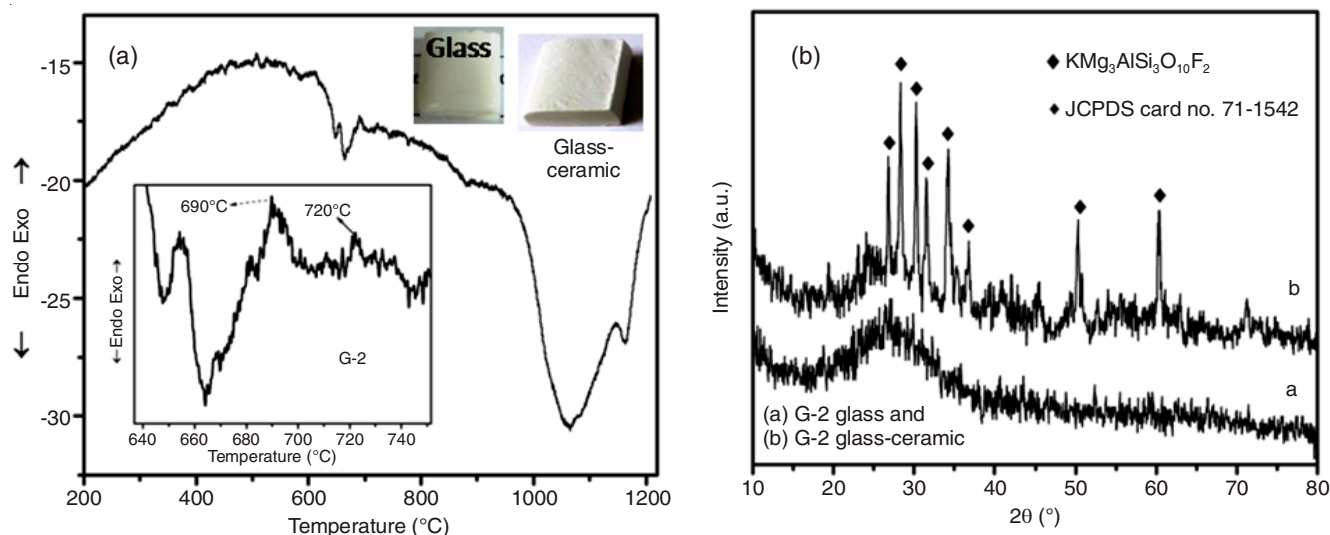
Fig. 2. (a) Differential scanning calorimetry thermograph showing the glass transition region and crystallization temperature of precursor SiO$_2$-MgO-Al$_2$O$_3$-K$_2$O-B$_2$O$_3$-YSZ-F glass, G-2 ; (b) X-ray diffraction pattern of G-2 as prepared glass and heat-treated (at 900 °C) glass-ceramic (inset-a shows the photograph of G-2 glass and G-2 glass-ceramic heat-treated at 1000 °C)

end centered lattice, cell parameter a = 5.308, b = 9.183, c = 10.13; molecular weight = 421.24, JCPDS file number 71-1542 [3]. The ZrO$_2$ content (10 wt % as Yttria Stabilized Zirconia, YSZ) of G-2 glass *i.e.* SiO$_2$-MgO-Al$_2$O$_3$-K$_2$O-B$_2$O$_3$-YSZ-MgF$_2$ supports the crystallization by the formation of heterogeneous crystalline nuclei to develop fluorophlogopite mica phase.

The mica based glass-ceramics generally appear with large thermal expansion coefficient (CTE) due to the layered crystalline structure of fluorophlogopite mica [3]. Fig. 3 exhibits the linear increasing thermal expansion trend of G-2 glass-ceramic, composed of fluorophlogopite mica crystalline phases, with increasing temperature.
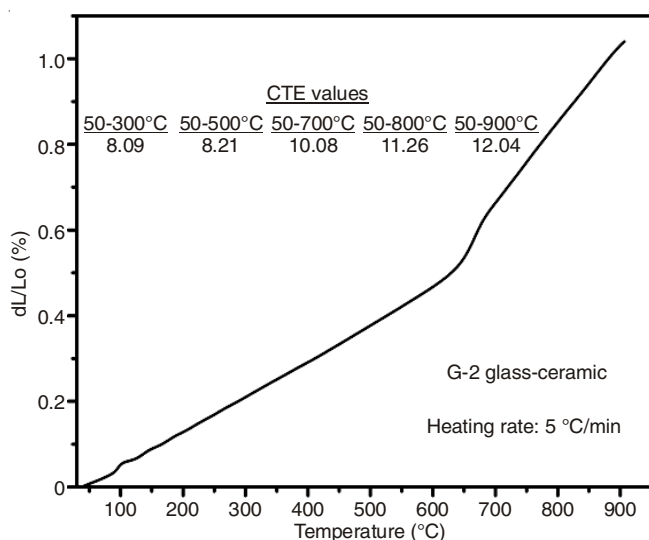

Fig. 3. Variation of thermal expansion as a function of temperature for SiO$_2$-MgO-Al$_2$O$_3$-K$_2$O-B$_2$O$_3$-YSZ-F (G-2) glass-ceramics heat-treated at 1000 °C (inset shows the thermal expansion values at different temperature)

As provided in the inset of Fig. 3, G-2 glass-ceramic possess CTE value 8.09 × 10^{-6}/K in temperature range 50-300 °C. The value is increased to 8.21 and 10.08 × 10^{-6}/K at

temperature 50-500 and 50-700 °C, respectively. For glass-ceramic materials, thermal expansion is largely dependent on the nature and amount of crystalline phases present in glass-ceramic matrix because the CTE value of the remaining glass in the crystallized body decreases when crystalline phases are mostly unconnected by residual glass [4]. In the present case, the G-2 glass is sufficiently crystallized after heating at 1000 °C for 4 h duration to be converted into mica glass-ceramic; so that large CTE value is observed for G-2 glass-ceramic. At the temperature 50-800 and 50-900 °C, the CTE of this glass-ceramic is 11.26 and 12.04 × 10^{-6}/K, respectively. Such an immense CTE value makes a special attention for G-2 glass composition, *i.e.* 39SiO$_2$-12MgO-16Al$_2$O$_3$-10K$_2$O-11B$_2$O$_3$-10YSZ-12MgF$_2$ (Wt. %), that it may be an efficient glass-ceramic based sealing material for high temperature application with metal or electrolyte possessing higher thermal expansion value. Hence, a microcrack, due to the mismatching of CTE can easily be avoided using such composition *i.e.* mica based glass-ceramic [5].

When the G-2 glass-ceramic (crystalline) is mixed with G-1 glass (amorphous) to prepare glass to glass-ceramic composite material, a required thermal expansion for high temperature sealing application can easily be achieved. As shown in Table-1, three different composites (C-1 to C-3) were prepared using G-1 glass and G-2 glass-ceramic in 90:10, 80:20 and 70:30 weight percentage ratio. The composite materials were heat treated as based on the high temperature thermal operation like SOFC (solid oxide fuel cell). Since K$_2$O-MgO-SrO-B$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glass (G-1) is mixed with fluorophlogopite mica glass-ceramic (G-2), the predominant crystalline phase developed is also mica after heating of the composites [12]. As provided in Table-1, C-1, C-2 and C-3 composites were with whitish opaque appearance after heat-treatment at 900 °C for 2 h followed by 800 °C for 10 h duration.

The crystalline phase developed in the composite matrix after heat-treatment, at 900 °C for 2 h followed by 800 °C for 10 h duration, is identified by XRD study (Fig. 4). As is evident from Fig. 4a, *i.e.* XRD pattern of heat-treated C-1 composite,

the crystalline peaks appeared at (2θ) 25.83, 27.51, 30.31, 32.55, 35.16, 36.66, 40.02, 50.47, 52.90, 60.18 and 62.98°, due to the phase reflection of (022), (003), (113), (023), (113), (201), (132), (224), (240), (331) and (205), correspond to the crystalline phase fluorophlogopite mica, $KMg_3(AlSi_3O_{10})F_2$, JCPDS file number 71-1542. As seen from Fig. 4b, the fluorophlogopite crystalline peaks remain unchanged in C-2 composite; only one new peak is positioned at (2θ) 22.81° due to the phase reflection of (111) plane, JCPDS file 71-1542. The three highest intense crystalline peaks of $KMg_3(AlSi_3O_{10})F_2$ are positioned at (2θ) 30.31, 50.47 and 27.51° *i.e.* (113), (224) and (003) in XRD pattern of C-1 system (Fig. 4a); whereas, highest intense phase reflections for C-2 system are developed due to (113), (224) and (111) planes (Fig. 4b). On increasing the mica glass-ceramic content in composite mixture, the crystallization pattern prolonged almost same, *i.e.* the case of C-3 system in Fig. 4c. This fact demonstrates that the properties of present glass/glass-ceramic composite mixtures are mainly controlled by mica phase [4].

The coefficient of thermal expansion (CTE) trend of C-1 to C-3 composites, after heat-treatment, at 900 °C for 2 h followed by 800 °C for 10 h duration, is presented in Fig. 4d. The linear increasing trend of CTE for all the composites is seen from Fig. 4c and the values are provided in Table-2. At the temperature 50-300 °C, the CTE of C-1 composite is 7.12 × 10^{-6}/K, which increased to 7.59, 9.55 and 10.47 × 10^{-6}/K at 50-500, 50-700 and 50-800 °C, respectively. This high value of CTE is due to the crystalline phase fluorophlogopite, $KMg_3(AlSi_3O_{10})F_2$[14,15]. Thus, for high temperature vacuum sealing application with metal possessing large CTE, the mica containing composite can be suitable. When weight fraction of mica content is increased in the mixture, *i.e.* glass: mica = 80:20 (C-2) and 70:30 (C-3), the CTE is increased [3]. At the temperature range 50-800 °C, CTE of C-2 and C-3 composites are 10.87 and 10.91 × 10^{-6}/K, respectively (Table-2). Thus, the applicability of present composite system is C-3 > C-2 > C-1, for solid oxide fuel cell sealing purpose.
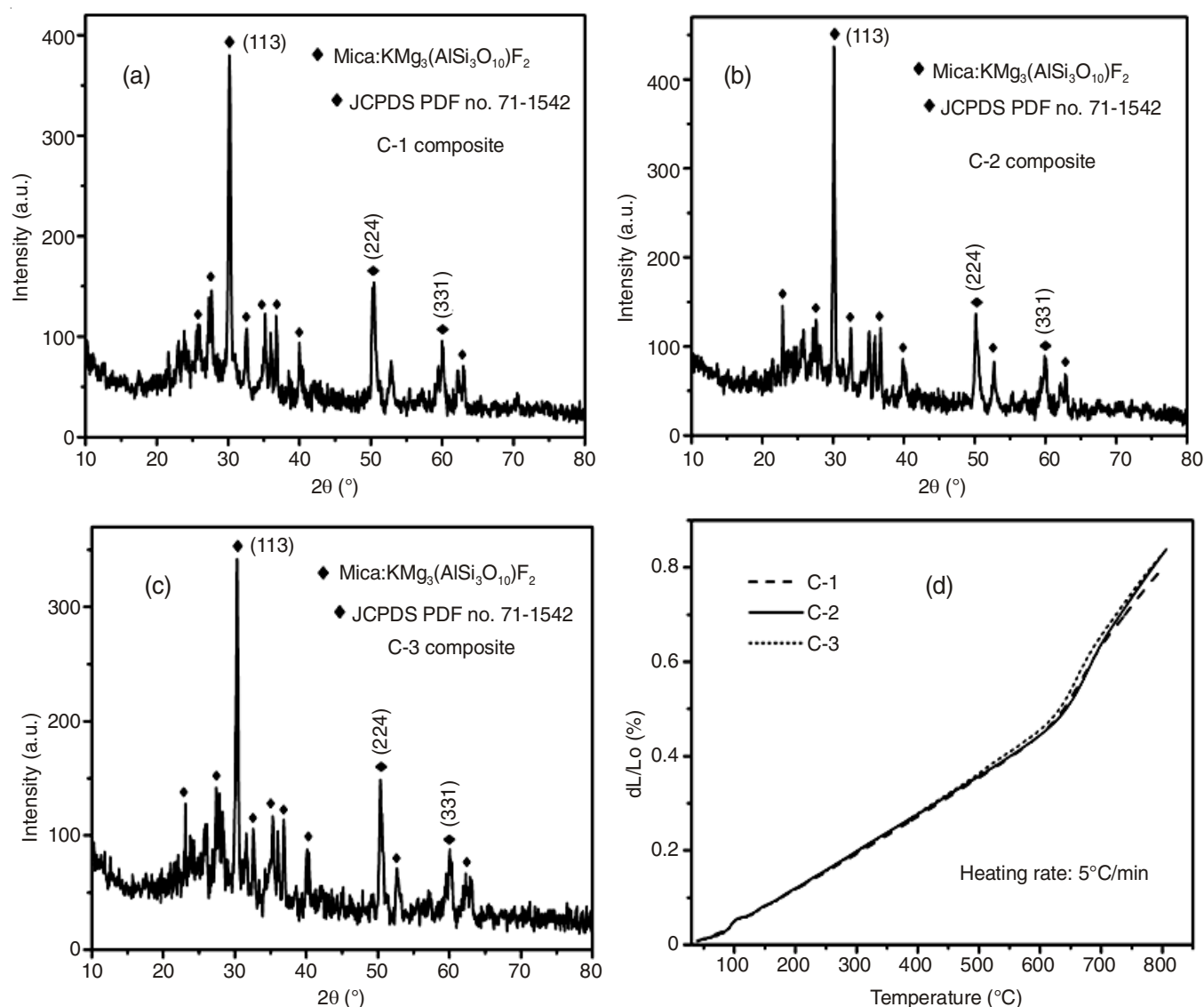

Fig. 4. X-ray diffraction pattern of (a) C-1, (b) C-2 and (c) C-3 glass/glass-ceramic composites showing the formation of fluorophlogopite mica as predominant crystalline phase after heating at 900 °C-2 h followed by 800 °C-10 h; (d) thermal expansion trend of heat-treated composites as a function of temperature

TABLE-2
VARIATION OF COEFFICIENT OF THERMAL EXPANSION
(CTE) OF DIFFERENT MICA GLASS-CERAMIC COMPOSITES
HEAT-TREATED AT 900 °C FOR 2 h AND 800 °C FOR 10 h

Sample identity	Coefficient of thermal expansion ($\times 10^{-6}$/K)			
	50-300 °C	50-500 °C	50-700 °C	50-800 °C
C-1	7.12	7.59	9.55	10.47
C-2	7.46	7.68	9.62	10.87
C-3	7.39	7.83	9.92	10.91

Conclusion

Thermal and crystalline properties of the sintered fluorophlogopite mica/K_2O-MgO-SrO-B_2O_3-Al_2O_3-SiO_2 glass composites with weight fraction of mica from 10 to 30 % have been studied. Composites prepared by mixing the high thermal expansion (11.26×10^{-6}/K at 50-800 °C) mica glass-ceramic, obtained from SiO_2-MgO-Al_2O_3-B_2O_3-K_2O-F glass by controlled heat-treatment at 1000 °C and alkaline boroaluminosilicate glass (having thermal expansion = 6.03×10^{-6}/K at 50-700 °C, glass transition temperature = 698 °C and softening point = 733 °C) were whitish opaque in nature. XRD study of glass-ceramic composites heat-treated at 900 °C for 2 h followed by 800 °C for 10 h duration confirms the presence of predominant fluorophlogopite mica, $KMg_3AlSi_3O_{10}F_2$ phase on crystallization. The coefficient of thermal expansion (CTE) significantly increased with the content of mica glass-ceramic in the glass/glass-ceramic composite mixture. The coefficient of thermal expansio of composite system prepared by mixing 90 wt % boroaluminosilicate glass and 10 wt % fluorophlogopite mica (wt %) is 10.47×10^{-6}/K and increased to 10.87 and 10.91×10^{-6}/K for 80:20 and 70:30 system, respectively. Glass/glass-ceramic based composites with such higher thermal expansion value can be applicable for high temperature sealing purpose like solid oxide fuel cell.

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