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2. P. K. Maiti, Amit Mallik, A. Basumajumdar and Kaberi Das. “Some studies on nucleation, crystallization and microstructural behavior of mica glass-ceramics of the system 0.8BaO-0.2K₂O-4MgO-Al₂O₃-6SiO₂-2MgF₂”, J. Ind. Chem. Soc., 88, pp 1-7, 2011.

Influence of fluorine content on the crystallization and microstructure of barium fluorphlogopite glass-ceramics

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Abstract

The effect of varying the fluorine content on the nucleation and crystallization behavior of barium containing glasses based on the system BaO-4MgO-Al₂O₃-6SiO₂-2MgF₂ was investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Both the crystallization peak temperature (T_p) and activation energies (E) decreased, the Arrhenius exponent (n) and pre-exponential factor (v) increased. The results suggest that fluorine increases the rate of diffusion in the glass and promotes initial crystallization in barium fluorphlogopite glasses.

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Keywords: B. Microstructure-final; D. Glass; D. Glass-ceramics

1. Introduction

Machinable glass-ceramics, wherein two-dimensional mica crystals are nucleated internally and crystallized from fluorine-containing glasses have been developed [1-4] which can be machined to precise tolerances and surface finish with conventional metal working tools. The easy machinability of these glasses result from the unique microstructure of an interlocking plate-like mica crystals forming a 'house-of-cards' structure dispersed throughout a glassy matrix. During machining, fractures follow along the cleavage plane of the mica and glass matrix interfaces, and are repeatedly deflected, branched and blunted leading to a mere microscopic cracks. Existing commercial materials are based on potassium fluorphlogopite including Macor produced by Corning which are having very low strength. But glass-ceramics based on alkaline earth fluorphlogopites [5,7] and in particular barium fluorphlogopites are claimed to have two to three times higher strength than the corresponding potassium fluorphlogopite glass-ceramics [5].

Beall [1] undertook the first studies of the alkali earth fluorphlogopite glass-ceramics. Later on Hoda and Beall [5] investigated different glass compositions containing barium, calcium, and strontium close in composition to the respective fluorphlogopite stoichiometry. Most of the compositions were susceptible to crystallization during casting. Only a few stoichiometric compositions were investigated and despite offering improved mechanical and dielectric strength no further studies exist in the literature where compositional details are given.

Radonjic and Nikolic [6] studied the effect of different sources of fluorine as well as the concentration of it on the system based on MgO-Al₂O₃-SiO₂. They found different phases viz. fluoroborite, norbergite and fluorphlogopite depending at the heat treatment temperature, fluorine source and concentration.

Uno [7] investigated glass-ceramics containing barium-mica in the system Ba₉₅₃Mg₃(Si₃Al)O₁₀F₁₂-Mg₂Al₆Si₁₆O₄₈-Ca₃(PO₄)₂. They found improved fracture toughness and bending strength values. Addition of tricalcium phosphate Ca₃(PO₄)₂ was claimed to improve the stability of the glasses prior to crystallization. But no specific compositional details were given. However, it was stated that the compositions were close to the Ba₉₅₃Mg₃(Si₃Al)O₁₀F₁₂ stoichiometry.

Hu [8] studied the effect of fluorine on the crystallization and microstructure changes in the system Li₂O-Al₂O₃-SiO₂. They found that fluorine promotes initial crystallization and diffusion
in the glass which results in lower crystallization temperature and also lower activation energy for crystallization.

Tian et al. [9] studied the effect of fluorine content on the crystallization of fluorosilicic mica glass and found that only KMg$_2$Si$_2$O$_5$F$_2$ crystallizes in the glass. They concluded that fluorine addition not only improves activation energy of crystal growth by enhancing the degree of irregularity of the interface between glass and crystal, but also increases the frequency factor by lowering the viscosity of glass.

Griggs et al. [10] studied devitrification and microstructural coarsening of a fluoride containing barium aluminosilicate glass. They reported that the fluorine-containing barium aluminosilicate glass crystallized rapidly at low processing temperatures relative to stoichiometric BAS glass.

But the effect of fluorine on the crystallization in barium fluorophlogopite glass-ceramics system has not previously been discussed. The purpose of this study is to characterize the crystallization kinetics and microstructure with the variation of fluorine content in the barium fluorophlogopite glass-ceramics.

2. Experimental

2.1. Glass preparation

For this study, glass batches have weight compositions of BaCO$_3$, SiO$_2$, MgCO$_3$, Al$_2$O$_3$ and MgF$_2$, given in Table 1. These materials were analytical grade reagents of high purity mostly from E. Merck. The three different glass batches were properly mixed in an attrition mill. The batches were melted in a platinum crucible in an electrically heated furnace, melt was kept at the maximum melting temperature of 1500 °C for 2 h for all the batches with occasional stirring with a platinum rod to homogenize the melt. The melts were poured into a hot iron mould to make glass block of about 60 mm x 25 mm x 10 mm dimension. After releasing from the mould, the glass blocks were immediately transferred to an annealing furnace operating at about 650 °C and held for 1 h at the temperature followed by natural cooling to room temperature. Samples from all the above mentioned glass were ground to ~75 μm. XRD experiments were performed by X-ray powder diffractometer (PW 1830, Panalytical) using Ni filtered Cu Ka, X-radiation with a scanning speed of 2° per minute. The diffraction pattern was recorded within Bragg angle range 10° < 2θ < 70°. The phases formed were identified by JCPDS numbers (ICDD – PDF2 data base).

2.2. Characterization techniques

2.2.1. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) was done using Shimadzu DT40 thermal analyzer against α-alumina powder as reference material. The resulting glasses was crushed and finally ground to ~75 μm suitable for DTA analysis. Non-isothermal experiments were performed by heating 17 mg sample, crystallized at different temperatures, at a heating rate of 5, 10, 15 and 20 °C/min. in the temperature range from ambient to 1000 °C. DTA was applied to calculate the activation energy by Kissinger equation and Avrami exponent by Augis-Bennet equation.

2.2.2. X-ray powder diffraction (XRD)

Six heat treatment temperatures for each batch were investigated by X-ray powder diffraction. All samples were heat treated using a heating rate of 10°/min to the nucleation temperature (720 °C), soaked for 2 h at this temperature, heated again at 2°/min to the corresponding crystallization temperature and was kept at the temperature for 5 h followed by natural cooling to room temperature. Samples from all the above mentioned glass were ground to ~75 μm. XRD experiments were performed by X-ray powder diffractometer (PW 1830, Panalytical) using Ni filtered Cu Ka, X-radiation with a scanning speed of 2° per minute. The diffraction pattern was recorded within Bragg angle range 10° < 2θ < 70°. The phases formed were identified by JCPDS numbers (ICDD – PDF2 data base).

2.2.3. Scanning electron microscopy (SEM)

Samples from all the crystallization temperature (heating schedule as mentioned earlier) were studied to investigate the microstructural development with back scattered electron imaging (BEI) mode in a scanning electron microscope, Hitachi, S3400N, Japan. Before analysis, surfaces were polished with 1 and 0.5 μm diamond pastes. The samples were etched chemically by HF solution for 15 s.

2.2.4. Density

The densities of all the samples, ceramised at different temperatures, were measured by water displacement method, following Archimedes principle.

3. Result and discussion

3.1. Results of differential thermal analysis

DTA curves for the three glass samples at a heating rate of 10 °C/min are shown in Fig. 1. Only one exothermic peak was observed in Batch-MA0. But with the increase in fluorine concentration, one additional peak is visible in MA10. The appearance of the additional peak might be due to the early crystallization of a phase rich in fluorine, probably MgF$_2$ in this case. This observation is similar to that of Hoda and Beall [5] in the high fluorine content alkaline earth mica glass-ceramics. We are considering the second peak for calculating activation energy and Avrami exponent for the Batch-MA10. The glass transition temperature (Tg) and glass crystallization peak temperature (Tp) shifted to lower temperature as the fluorine content increased. The observation is same as reported in a previous investigation [8].
From the Johnson–Mehl–Avrami (JMA) equation [12,13], non-isothermal crystallization kinetics of glass can be described by the Kissinger expression [14,15]

\[ \ln \frac{T_p^2}{\alpha} = \frac{E}{RT_p} + \ln \frac{E}{Rv} \]

where \( T_p \) is the crystallization peak maximum temperature in DTA curve, \( \alpha \) is the heating rate, \( E \) is the activation energy and \( v \) is the pre-exponential factor. \( T_p \) of samples of three batches at different heating rates are given in Table 2. From Table 2 we can see that \( T_p \) increased with increasing heating rate and decreased with increased fluorine content. Values of \( E \) and \( v \) derived from the plots of \( \ln(T_p^2/\alpha) \) versus \( 1/T_p \) in Fig. 2 are also given in Table 2. \( E \) decreased and \( v \) increased with increasing fluorine.

Using the value of the activation energy, the Avrami exponent (\( n \)) was calculated by the Augis–Bennett equation [16]

\[ n = 2.5 \frac{RT_p^2}{\Delta T E} \]

where \( \Delta T \) is the full width of the exothermic peak at the half-maximum intensity. The value of the Avrami exponent (\( n \)) is a parameter that is related to the crystallization mechanism.

According to JMA theory, the value of \( n \) being close to 2 means that surface crystallization dominates overall crystallization, while the value of 3 implies a two-dimensional and the value of 4 indicates a three-dimensional crystal growth for bulk materials [17–19].

From the above equation, the Avrami exponent gradually increased with increasing excess fluorine concentration in three different batches. The value was about 4, in this case indicating that crystallization of the glass-ceramics was large homogenous and assuming a three-dimensional pattern character.

<table>
<thead>
<tr>
<th>Crystal phase JCPDS reference</th>
<th>00-019-0117</th>
<th>00-026-0137</th>
<th>00-019-0768</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium fluorphlogopite (BaMgAl_2Si_2O_8F) – BF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium aluminium silicate (BaAl_2Si_2O_8) – B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium silicate (Enstatite) (MgSiO_3) – E</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Batch</th>
<th>( T_p ) (K), ( E ) and ( v ) of the samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 (K min(^{-1}))</td>
</tr>
<tr>
<td>MA0</td>
<td>890 ± 2</td>
</tr>
<tr>
<td>MA5</td>
<td>883 ± 2</td>
</tr>
<tr>
<td>MA10</td>
<td>877 ± 2</td>
</tr>
</tbody>
</table>
3.2. Results of X-ray diffraction

The JCPDS reference files used to identify the various crystal phases formed are presented in Table 3. In all the heat treated samples of any particular batch, barium fluorphlogopite is observed as a major phase at lower heat treatment temperatures. This observation is similar to that of Beall [1] and Henry [11]. At 850 °C, peaks of enstatite and barium aluminium silicate appeared as new phase along with barium fluorphlogopite (BF). From 850 to 1000 °C there is no change in the intensity of the peaks and new phases appeared, but a new peak of BF at 18° (2θ) appeared beyond 1000 °C which is visible only in the batches MA5 and MA10 (Figs. 3–5). But at 1100 and 1150 °C the sharpness of the peaks of both barium aluminium silicate and enstatite have been increased. It has also been observed that with increase in
ceramic temperature, the formation of barium aluminium silicate increases for any particular batch. With increase in fluorine content, the peaks at 11.31°, 22.5° and 30.09° (2θ), which is supposed to correspond to barium aluminium silicate have been reduced drastically. This may indicate that the excess fluorine reduces the chances of decomposition of BF into barium aluminium silicate.

3.3. Results of scanning electron microscopy

The microstructure of the three different batches of glass, having different fluorine content, ceramised at 1100 °C for 5 h are shown in Fig. 6a-c. Fig. 6a exhibited very fine microstructures consisting of small acicular barium fluorphlogopite crystals. Fig. 6b and c consists of large crystals of barium fluorphlogopite that are electron dense and appeared white in the backscattered electron images. It has also been observed that the sizes of the crystals increased with the increase in fluorine content. Some cracks have been observed at higher temperatures as well as with higher fluorine content. These findings suggest that fluorine promotes crystallization and growth.

3.4. Physical properties

Densities of as-prepared glasses were about 3.08–3.09 gm/cm³. The density changes of the glass-ceramic heat treated at 780–1150 °C for 5 h are shown in Fig. 7 for three different batches. For Batch-MA0, density increases with increasing heat treatment temperature. But Batch-MA5 and Batch-MA10, density achieves the maximum value at 1100 °C, beyond this the density decreased with increasing heat treatment temperature. The decrease in density may be attributed to the decomposition of fluorphlogopite and propagation of cracks into interlocking mica crystals accompanied by crystal growth. This has been corroborated by the SEM observations. This observation suggests the ease of formation of BF at lower temperatures with increasing amount of fluorine. The findings are similar to the observations made by Radonjic [6].

4. Conclusions

The glass transition temperature (Tg) and glass crystallization peak temperature (Tc) shifted to lower temperatures as the fluorine content increased. The peak crystallization temperature was shown to correspond to the crystallization of barium fluorphlogopite. No other crystal phases were found prior or after the formation of barium fluorphlogopite, although the other phases viz. enstatite and BAS present in X-ray diffraction pattern seems to be very minor in the ceramised samples. From the calculation of Avrami exponent, these results indicated that crystallization of the glass was largely homogeneous. All these findings indicate that fluorine promotes initial crystallization.

Acknowledgements

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References


Some studies on nucleation, crystallization and microstructural behaviour of mica glass-ceramics in the system 0.8BaO.0.2K2O.4MgO.Al2O3.6SiO2.2MgF2

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Abstract : Glass-ceramics containing barium fluorophlogopite as a main crystal phase based on the system 0.8BaO.0.2K2O.4MgO.Al2O3.6SiO2.2MgF2 was investigated with respect to phase separation, nucleation and crystallization by Differential thermal analysis (DTA), X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The glass transition temperature (T_g) and two distinct crystallization peak temperatures were observed in DTA curve. The crystallization kinetics of glass-ceramics was also studied. Avrami exponent and activation energy for the first peak crystallization temperature (T_p1) were 2.7 and 226.3 ± 3 kJ/mol and the corresponding values for second peak crystallization temperature (T_p2) were 3.7 and 322.6 ± 3 kJ/mol.

Keywords : Glass-ceramics, ceramics, X-ray diffraction, scanning electron microscope.

Introduction

The glass-ceramics, a polycrystalline material composed of at least one crystalline phase dispersed in a vitreous matrix, is produced by the controlled crystallization of highly viscous glass-forming melts. The transition occurs from 'vitreous to crystalline' in glass-ceramics via two kinds of transformation-nucleation and crystal growth. The first one is an endothermic process and the second one is an exothermic process. The two dimensional mica crystals are nucleated internally and crystallized from fluoride containing glasses. The most unique feature of mica glass-ceramics is that they can be machined to precise tolerances and surface finish with conventional metal working tools. Mica glass-ceramics, particularly phlogopite system, have excellent machinability due to the layered lattice structure of the sheet silicates arranged in a 'house of cards' microstructures, which causes a perfect basal cleavage along the (001) planes of mica crystals. Besides above, they possess higher strength, fracture toughness, thermal shock resistance, and have excellent dielectric properties.

Glass-ceramics based on alkaline earth fluorophlogopites, particularly barium fluorophlogopite, are claimed to have two to three times higher mechanical strength than the corresponding potassium fluorophlogopite glass-ceramics.

Beall undertook the first study of the alkaline earth fluoromica glass-ceramics, later on Hoda and Beall investigated glasses of different compositions containing barium, calcium and strontium based on fluorophlogopite stoichiometry. Most of the compositions were susceptible to crystallization during casting.

Recently Uno et al. observed glasses from the ternary system Ca3(PO4)-Ba0.5.Mg3(Al.3.Si3.O10)F2-Mg2.Al4.Si5.O18. The detail compositions were not given, however it was stated that the compositions were close to Ba0.5.Mg3(Al.3.Si3.O10)F2 stoichiometry. They clearly indicated the improved strengths and fracture toughness values.

Gregg et al. investigated microstructural development in one composition from the Ca3(PO4)-Ba0.5.Mg3(Al.3.Si3.O10)F2-Mg2.Al4.Si5.O18 system as a part of a US NIH programme towards developing CAD/CAM dental ceramics.

Henry et al. observed nucleation and crystallization...
behavior based on $8\text{Si}_2\text{O}_5\cdot\text{YAl}_2\text{O}_3\cdot4\text{MgO} \cdot 2\text{MgF}_2 \cdot \text{BaO}$ where the varying of aluminum oxide ($Y = 1.5-3.0$). They clearly indicated the reducing the alumina content reduces the glass transition temperature, first peak crystallization temperature and promotes bulk crystal nucleation. The first peak was corresponding to barium fluorophlogopite. High alumina contents favoured the formation of cordierite, mullite and barium aluminum silicate.

Henry et al. observed microstructure, hardness and machinability based on $8\text{Si}_2\text{O}_5\cdot\text{YAl}_2\text{O}_3\cdot4\text{MgO} \cdot 2\text{MgF}_2 \cdot \text{BaO}$ where the varying of aluminum oxide ($Y = 1.5-3.0$). They found hardness and machinability to be highly dependent on the formation of an interconnected house of cards microstructure.

However, to our knowledge, no previous attempt has been made to study the nucleation, crystallization, growth, strength and machinability by partially replacing barium with potassium in barium fluoromica glass-ceramics.

In the present investigation, we have studied the nucleation and crystallization behavior of the glass obtained by substituting 0.1 mole BaO with 0.1 mole K$_2$O in the system BaO.4MgO.6SiO$_2$.2MgF$_2$.

**Experimental**

**Parent glass preparation :**

The glass batches having weight-percentage compositions of BaCO$_3$, K$_2$CO$_3$, SiO$_2$, MgO, Al$_2$O$_3$ and MgF$_2$ were properly mixed in an attrition mill, thereafter melted in a platinum crucible for 4—5 h in an electrically heated furnace operating at 1450—1500 °C. The melt was poured into a hot iron mould to make glass block of about $60 \times 25 \times 10$ mm dimension. After releasing from the mould, the glass block was immediately transferred to an annealing furnace operating at 650 °C and soaked for 1 h followed by natural cooling to room temperature.

After annealing, the block was cut into pieces to about 1-2 mm thickness with the help of a precision low speed cutting machine (Buehler). These cut samples were fired at 710 °C for 2 h for nucleation. This nucleation temperature was determined by DTA study. The samples after nucleation heated to the corresponding crystallization temperature at a rate of 2 °C/min and the samples were kept at the crystallization temperatures for 5 h.

**Characterization techniques :**

**Differential thermal analysis (DTA) :**

Differential thermal analysis (DTA) was done using Shimadzu DT40 thermal analyzer with $\alpha$-alumina powder as a reference material. The glass was crushed and finally ground to $\sim$75 μm suitable for DTA analysis. Non-isothermal experiments were performed by heating $\sim$17 mg glass sample, crystallized at different temperatures, at a heating rate of 5, 10, 15 and 20 °C/min in the temperature range from ambient to 1000 °C. Differential thermal analysis (DTA) procedure was applied to calculate the value of activation energy by Ozawa equation and the corresponding Avrami exponent was calculated by Augis-Bennet equation.

**X-Ray powder diffraction (XRD) :**

X-Ray powder diffraction was carried out for the heat treated samples at different crystallization temperatures. All samples were heat treated using a heating rate of 10 °C/min to the nucleation temperature of 710 °C, soaked for 2 h at this temperature and heated again at 2 °C/min to the corresponding crystallization temperature. The samples were kept at the crystallization temperature for 5 h followed by natural cooling to room temperature. The ceramised glass samples were ground to $\sim$75 μm. XRD experiments were performed using X-ray powder diffractometer (PW 1830, Panalytical) using Ni filtered Cu-$\kappa$$_\alpha$, X-radiation with scanning speed of 2° (2θ) per minute. The diffraction pattern was recorded within Bragg’s angle ranges 5° < 2θ < 70°. The phases were identified by JCPDS numbers (ICDD-PDF2 data base).

**Scanning electron microscopy (SEM) :**

Different samples from all the crystallization temperature (heating schedule as mentioned earlier) were studied to investigate the micro structural development with back scattered electron imaging (BEI) mode in a Hitachi, S3400N, Japan, scanning electron microscope. Before study, surface of all the samples were polished by following standard procedures and finally with diamond paste.
The polished samples were etched chemically by HF solution for 30 s.

Density:
The densities of all the crystallized samples at different temperatures were measured by water displacement method following Archimedes principle.

Results and discussion
Characterization of DTA peaks:
Two well-defined exothermic peaks are visible in all the DTA thermograms. When the glass sample was heated at 10 °C/min, the 1st peak appeared at 793 °C and the 2nd peak appeared at 894 °C (Fig. 1). To characterize the peaks, the powdered sample (grading same as that used for DTA analysis) was heated separately to the corresponding peak temperatures at a rate of 10 °C/min (same as that of DTA) in an electrically heated furnace and the samples then air-quenched at the room temperature supposing complete arrest of any further phase changes during quenching. XRD study was done to identify the different phases formed in the heat treated samples under consideration. It is clear from the study that the first exothermic peak temperature corresponds to the formation of K-fluorophlogopite and the second one corresponds to the formation of Ba-fluorophlogopite (Fig. 2).

Kinetics of crystallization:
DTA curves for glass samples at a heating rate of 5, 10, 15 and 20 °C/min are shown in Fig. 1. Two well-defined crystallization peaks are visible in all the DTA thermograms. Moreover, it is clear from these curves that the two distinct crystallization peak temperatures shifted towards right with increasing heating rate. The nucleation and crystallization temperature were determined from DTA analysis of the glass sample.

The kinetics of glass crystallization is studied on the basis of the Jonshon-Mehl-Avrami (JMA) equation:

\[ X = 1 - \exp \left[ -(kt)^n \right] \] (1)

where \( X \) is the fraction crystallized at a given temperature; \( k \) is the reaction rate constant and \( n \) is the Avrami exponent, which is a dimensionless factor depending on the nucleation process and growth morphology.

From Jonshon-Mehl-Avrami equation, non-isothermal crystallization kinetics of glass can be described by the Ozawa equation:

Ozawa equation is given below

\[ \ln \beta = \frac{E}{RT_p} + C \] (2)

The activation energy \( (E) \) was obtained from the relation between the heating rate \( (\beta) \) and maximum crystallization peak temperature \( (T_p) \) in the exothermic peak of the DTA curve, where \( \beta \) is the heating rate, \( R \) is the universal gas constant. As shown in Table 2 and Figs. 3 and 4.
Table 2. The values of crystallization peak temperature at different heating rates

<table>
<thead>
<tr>
<th>Heating rate, ( \beta ) (°C)</th>
<th>( T_{p1} ) (°C)</th>
<th>( T_{p2} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>775</td>
<td>882</td>
</tr>
<tr>
<td>10</td>
<td>793</td>
<td>894</td>
</tr>
<tr>
<td>15</td>
<td>801</td>
<td>902</td>
</tr>
<tr>
<td>20</td>
<td>809</td>
<td>907</td>
</tr>
</tbody>
</table>

In Ozawa equation, the slope of the plot of \( \ln \beta \) vs \( 1/T_{p} \) is equal to \(-E/R\).

From Augis-Bennett equation\(^{21}\), the value of Avrami exponent \( (n) \) can be estimated using the value of activation energy.

\[
2.5 = \frac{RT_{p}^{2}}{\Delta T} \times \frac{\Delta T_{p}}{E}
\]

where, \( \Delta T \) is the full width of the exothermic peak at \( t \) half-maximum intensity, \( n \) is the Avrami exponent or crystallization index, i.e. Avrami exponent depends upon \( t \) actual nucleation and growth mechanism.

The activation energy and Avrami exponent were calculated using the above equations and shown in Table:

Table 3. Kinetic parameters of crystallization

<table>
<thead>
<tr>
<th>Crystallization peak temperature (Ozawa) (kJ/mol)</th>
<th>Activation energy (kJ/mol)</th>
<th>Avrami exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{p1} )</td>
<td>226.3 ± 3</td>
<td>2.7</td>
</tr>
<tr>
<td>( T_{p2} )</td>
<td>322.6 ± 3</td>
<td>3.7</td>
</tr>
</tbody>
</table>

From 1st crystallization peak temperature, Avrami exponent was found to be 2.7, which is close to 3; therefore the fact indicates that bulk nucleation and two dimensional growth occurs for the glass-ceramics. From 2nd crystallization peak temperature, Avrami exponent was found to be 3.7, which is close to 4, therefore the fact indicates that it is a case of bulk nucleation and three dimensional crystal growths for the material concerned\(^{22-24}\).

Results of X-ray diffraction:

Various crystal phases were identified by JCPDS reference file presented in Table 4.

Table 4. List of JCPDS files to used to identify the main crystal phase formations observed

<table>
<thead>
<tr>
<th>Crystal phase</th>
<th>JCPDS reference file</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium fluoroephlogopite ([BaMg_5AlSi_3O_{10}F_2])-B</td>
<td>00-019-011</td>
</tr>
<tr>
<td>Potassium fluoroephlogopite ([KMg_5AlSi_3O_{10}F_2])-K</td>
<td>01-076-081</td>
</tr>
<tr>
<td>Alpha-hexacelsian ([Ba_0.8MgAlSi_2O_7])</td>
<td>01-088-050</td>
</tr>
<tr>
<td>Enstatite ([MgSiO_3])-E</td>
<td>00-002-054</td>
</tr>
</tbody>
</table>

At 800 °C, peaks of K-fluoroephlogopite appeared 27° (26) and 34° (26) as a major component whereas Ba-fluoroephlogopite appeared as a minor component (Fi. 5). The formation of Ba-fluoroephlogopite at 800 °C seen to be unusual which is against the observation made during the DTA analysis. But the formation of Ba-fluoroephlogopite might be due to the long duration.
fine submicron microstructures consists of some blocky crystal (Fig. 6a). After increasing heat treatment temperature through 900 °C to 1000 °C for five hours, exhibited a large number of slightly bigger blocky crystals (Figs. 6b and 6c) compared to that of at 800 °C. These blocky crystals are dense and appeared white in the back scattered electron micrographs.

Soaking at this crystallization temperature. At 900 °C, four new peaks of barium aluminum silicate (alpha-hexacelsian) at 11°, 22°, 30° and 54° (29) and one new peak of enstatite 28° (26) appeared along with Ba-fluorophlogopite and K-fluorophlogopite. From 900 °C to 1000 °C there are no changes in the intensity of the peaks except, one new peak of K-fluorophlogopite at 18° (28) appeared. From 1000 °C to 1100 °C there are no changes in the intensity of the peaks but one new peak of enstatite at 63° (28) appeared. At 1100 °C and 1150 °C, the sharpness of the peaks of both barium aluminum silicate (alpha-hexacelsian) and enstatite have been increased. With increasing heat treatment temperature, the sharpness of the barium aluminum silicate (alpha-hexacelsian) is increased. This might be the indication that partial decomposition of Ba-fluorophlogopite into barium aluminum silicate (alpha-hexacelsian) and enstatite. This decomposition is not visible in the DTA scan up to 1000 °C. This decomposition might be co-related to some extent to the changes in Avrami exponent (n) from 3 to 4, where monoclinic crystal structure is converted to hexagonal crystal structure. Even after this, it is needless to mention that Ba-fluorophlogopite and K-fluorophlogopite along with barium aluminum silicate (alpha-hexacelsian) phases are the major phases formed in all the samples crystallized at higher temperature.

**Microstructure analysis**

Samples heated at 800 °C for five hours exhibit very
The appearance of blocky crystals might be due to the formation of mica booklets and in many cases have an aspect ratio of <1. As the temperature further increased, the number of crystal per unit volume decreased and aspect ratio of the crystal increased (Figs. 6a-c). It might be due to the dissolution of crystals with an aspect ratio of <1 and reprecipitation of constituents onto those crystals of higher aspect ratio. This energetically unfavorable configuration might therefore be the driving force towards attaining the long crystal observed after treatment of five hours at 1100 °C and 1150 °C (Figs. 6d and 6e), which is discussed elsewhere.\(^9\)

It is quite clear from the SEM micrographs at 1100 °C and 1150 °C that a few cracks appeared during crystallization. Some cracks are intercrystalline and some are transcrystalline in nature.

**Physical properties:**

Density of as-prepared glass was about 2.98 g/cm\(^3\). The density changes of the glass-ceramic samples heat treated at 800–1150 °C for five hours are shown in Fig. 7. Density achieves the maximum value at 1100 °C, beyond this the density decreased with increasing heat treatment temperature. This decrease in density may be attributed to the partial decomposition of barium fluorophlogopite into barium aluminium silicate (alpha hexacelsian), which may be co-related to the XRD observations. This observation suggests that the stability of barium fluorophlogopite at lower temperatures is better...
than that at higher temperatures. The findings are similar to the observations made by Radonjic26.

Furthermore, the density at higher temperature i.e. at 1150 °C reduced substantially due to the formation of cracks in the crystallized materials, which is also clearly visible from the SEM micrographs.

Conclusions:
(i) The heat treatment conditions for nucleation at 710 °C for two hours and crystallization at different temperatures at 800, 900 and at 1000 °C for five hours can obtain fine structured glass-ceramics. Crystallization for five hours at 1100 °C and 1150 °C can be used to obtain mica crystals of higher aspect ratio and "house of cards" structure.

(ii) The activation energy of 1st peak of crystallization temperature and 2nd peak of crystallization temperature were 226.3 ± 3 and 322.6 ± 3 kJ/mol respectively. The Avrami exponent was determined to be 2.7 for 1st peak of crystallization temperature, which indicate that bulk nucleation and two dimensional growths occur in the glass-ceramics. Similarly, the Avrami exponent was determined to be 3.7 for 2nd peak of crystallization temperature, which indicates that it is a case of bulk nucleation and three dimensional crystal growths for the material concerned.

(iii) From XRD patterns, it can be concluded that at lower temperatures Ba-fluorophlogopite and K-fluorophlogopite are the major phases in the glass-ceramics. With increasing heat treatment temperature, the major phases are partially decomposes to other phases viz. barium aluminum silicate (alpha-hexacelsian) and enstatite.

(iv) It is clear from the findings that when potassium and barium is added in the above mentioned system, both the micas i.e. K-fluorophlogopite and Ba-fluorophlogopite are formed simultaneously.

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References
20. T. Ozawa, Polymer, 1971, 12, 150.
Influence of barium oxide on the crystallization, microstructure and mechanical properties of potassium fluorophlogopite glass-ceramics

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Abstract

The influence of barium oxide, heat treatment time and temperature on the crystallization, microstructure and mechanical behavior of the system $Ba_x K_{1-x} Mg_2 Al_3 Si_3 O_{10} F_2$ (where $x = 0.0, 0.3$ and $0.5$) was investigated in order to develop novel, high strength and machinable glass-ceramics. Three glasses were prepared and characterized by differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscope (SEM) techniques and some mechanical testing methods.

The crystallization kinetics of glass-ceramics was also studied. Activation energy and Avrami exponent calculated for the crystallization peak temperature ($T_p$) of three different glass batches. The Vickers hardness decreased slightly on formation of the potassium fluorophlogopite and barium fluorophlogopite phases, but decreased significantly on formation of an interconnected ‘house of cards’ microstructure.

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1. Introduction

The controlled crystallization of glass produced mica glass-ceramics. Glasses based on the system $K_2O-MgO-Al_2O_3-SiO_2-MgF_2$ crystallize to trisilicic alkaline phlogopite mica ($K Mg_3 Al_2 Si_3 O_{10} F_2$) glass-ceramics. These glass-ceramics have an important feature, which made them machinable to a precise tolerance with traditional metal working tools [1]. The microstructure of this phlogopite mica crystals precipitate in a ‘house of cards’ microstructure, embedded in a glass matrix, facilitates microfracture along the weak mica-glass interface and also through mica basal planes, which resists macroscopic failure during machining.

Beall [2] undertook the first studies of the alkali earth fluoromica glass-ceramics. Later on Hoda and Beall [3] investigated different compositions containing barium, calcium, and strontium glasses close in composition to the respective fluorophlogopite stoichiometry. Most of the compositions were susceptible to crystallization during casting.

Uno et al. [4] investigated glass-ceramics containing barium-mica in the system $Ba_0.5 Mg_3 (Si_3 AlO_10)_2 F_2-Mg_2 Al_2 Si_3 O_{10} F_2-Ca_3 (PO_4)_2$. They found improved fracture toughness and bending strength values. Addition of tricalcium phosphate $Ca_3 (PO_4)_2$ was claimed to improve the stability of the glasses prior to crystallization. But no specific compositional details were given. However it was stated that the compositions were close to the $Ba_0.5 Mg_3 (Al Si_3 O_{10} F_2$ stoichiometry.

Henry and Hill [5,6] have shown that reducing the alumina content reduces the glass transition temperature, first peak crystallization temperature and promotes bulk crystal nucleation. The glasses with high alumina contents gave rise to feathery microstructures that did not coarsen readily to give blocky crystals of a high aspect ratio and therefore could not produce the classic ‘house of cards’ microstructure. Hardness and machinability were found to be highly dependent on the formation of an interconnected ‘house of cards’ microstructure.

In the previous work [7], we have studied the kinetics as well as the crystal growth with respect to fluorine content in the barium fluorophlogopite glass-ceramics based on the system $BaO MgO-Al_2 O_3-6SiO_2-2MgF_2$, where it was indicated that the crystallization of the glass was largely homogenous and fluorine promotes initial crystallization.
Greene et al. [8] investigated molar volume (MV), fractional glass compactness (C), microhardness (\(\mu H_v\)), glass transition temperature (\(T_{gmax}\)) and co-efficient thermal expansion (\(\alpha\)) in the (1 – Z)BaO:ZK\(_2\)O: (6 – X)MgO:XMgF\(_2\):(3 – Q)Al\(_2\)O\(_3\):2B\(_2\)O\(_3\):8Si\(_2\)O\(_5\) system (where Z = 0, 0.25, 0.5, 0.75 and 1.0, X = 2, 2.5 and 3.0 and Q = 0, 0.5 and 1). Substitution of barium by potassium results in increases in molar volume and co-efficients of thermal expansion and decreases in fractional glass compactness, microhardness and glass transition temperature values.

But very little or no work has been done on the system containing both potassium and barium to study the crystallization, microstructure and mechanical properties. The aim of this present study was to systematically investigate the effects of substituting barium for potassium in the above-mentioned compositions on their crystallization, microstructure and mechanical properties.

2. Experimental

2.1. Glass synthesis

The glass-forming compositions studied are represented by the following generic formula:

\[
\text{Ba}_x\text{K}_{1-x}\text{Mg}_3(\text{Al}_2\text{Si}_2)\cdot \text{O}_{10}\text{F}_2
\]

where \(x\) varies among 0.0, 0.3 and 0.5 as shown in Table 1. For this study, the glasses were synthesized using the analytical grade reagents, barium carbonate (BaCO\(_3\)), potassium carbonate (K\(_2\)CO\(_3\)), silica (SiO\(_2\)), aluminium (Al\(_2\)O\(_3\)), magnesium carbonate (MgCO\(_3\)), magnesium fluoride (MgF\(_2\)) and boric acid (H\(_3\)BO\(_3\)) powders mostly from E. Merck, mixed thoroughly in an attrition mill. In all the batches, B\(_2\)O\(_3\) as H\(_3\)B\(_2\)O\(_4\) was added purposefully to reduce the viscosity and thereof to increase the rate of diffusion of different ionic species in glass, which may result in the natural tendency towards directional growth of crystals [9]. The different batches were melted in a platinum crucible in an electrically heated furnace, melt was kept at the maximum melting temperature of 1500 °C for 2 h with occasional stirring with a platinum rod to homogenise the melt. The melts were poured in to a hot iron mould to make glass block of about 60 mm × 25 mm × 10 mm dimension. After releasing from the mould, the glass blocks were immediately transferred to an annealing furnace operating at a temperature 50 °C below the midpoint of the glass transition region and held for 1 h at the temperature followed by natural cooling to room temperature.

After annealing, the blocks were cut into pieces to about 2 mm thickness. These plates were fired for nucleation at 670 °C for Ba00, 700 °C for Ba03 and 720 °C for Ba05 batches respectively for 2 h. Subsequently heated to the corresponding crystallization temperature at a rate of 2 °C/min and the samples were kept at the crystallization temperature for 5 h and followed by natural cooling to room temperature.

2.2. Characterization techniques

2.2.1. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) was done using Shimadzu DT40 thermal analyzer against α-alumina powder as reference material. The three different resulting glasses were crushed and finally ground to ~75 μm suitable for DTA. Non-isothermal experiments were performed by heating about 17 mg sample, at a heating rate of 5, 10, 15 and 20 °C/min in the temperature range from ambient to 1000 °C. Differential thermal analysis (DTA) was applied to calculate the value of activation energy by Kissinger equation and to calculate the Avrami exponent by Augis-Bennet equation.

2.2.2. X-ray powder diffraction (XRD)

Five heat treatment temperatures were investigated by X-ray powder diffraction on powder samples. All samples were heat treated using a heating rate of 10 °C/min to the nucleation temperature (above mentioned), soaked for 2 h at this temperature, heated again at 2 °C/min to the corresponding crystallization temperature and was kept at the temperature for 5 h followed by natural cooling to room temperature. XRD experiments were performed using X-ray powder diffractometer (PW 1830, Panalytical) using Ni filter CuK\(_{α1}\) X-radiation with scanning speed of 2° (2θ) per minute. The diffraction pattern was recorded within Bragg angle range 10° < 2θ < 70. The phases identified by JCPDS numbers (ICDD-PDF2 data base).

2.2.3. Scanning electron microscopy (SEM)

Samples from all the crystallization temperature (heating schedule as mentioned earlier) were studied to investigate the microstructural development with back scattered electron imaging (BEI) mode in a scanning electron microscope, Hitachi, S3400N, Japan. Before analysis, surface of all the samples was polished with diamond paste. The samples etched chemically by HF solution for 15 s.

2.2.4. Microindentation hardness and machinability measurement

Micro hardness analyses were carried out on polished glass samples embedded in epoxy resin using LEITZ micro hardness indenter. A load (P) of up to 500 g was used in conjunction with Vickers diamond indenter (face angle 136°) for 15 s. Hardness values were calculated using the following relation [10,11]

\[
H_v = \frac{1.8544 \times P}{D^2}
\]

where \(H_v\) is the Vickers hardness number in kg/mm\(^2\), \(P\) is the normal load in kg, and \(D\) is the length of the diagonal of the
indentation in mm. To convert the $H_v$ into GPa the following relation was used

$$H_v \text{ (GPa)} = \frac{9.81}{1000} \times H_v$$  \hspace{1cm} (2)

The machinability parameter ($m$) can also be used for the effects of various heat treatments as a function of temperature and $H_v$. Machinability can be predicted by the micro hardness data. The following equation indicates the relationship between hardness ($H_v$) and machinability ($m$).

$$m = 0.643 - 0.122H_v$$  \hspace{1cm} (3)

The fracture toughness ($K_{IC}$) is calculated using the following formula:

$$K_{IC} = \frac{0.025P}{c^{\frac{1}{2}}}$$  \hspace{1cm} (4)

where $c$ is the average crack length in mm.

3. Results and discussion

3.1. Kinetics of crystallization

DTA curves for three different glass samples at a heating rate of 5, 10, 15 and 20 °C/min are shown in Fig. 1a–c respectively. Only one exothermic peak was observed in both Ba00 and Ba05 batches. The exothermic peak corresponds to potassium fluorophlogopite and barium fluorophlogopite in Ba00 and Ba05 respectively. But two exothermic peaks are visible in Ba03. The first one is for potassium fluorophlogopite and second one is for barium fluorophlogopite [12]. The precipitation of crystal phases depends upon the ionic mobility of cations. The crystallization peak for K-fluorophlogopite appeared first in the DTA thermogram of the batch Ba03 because the ionic mobility of $K^+$ is higher compared to that of $Ba^{2+}$, due to smaller cationic size of the former. In the DTA thermograms, heating rate at 10 °C/min, the 1st exothermic peak of Ba03, which is supposed to be for K-fluorophlogopite, is shifted towards higher temperature approximately by 55 °C compared to the exothermic peak of Ba00 (Fig. 1a and b; Table 2). But the 2nd exothermic peak of Ba03, which is identified as Ba-fluorophlogopite, is shifted towards higher temperature approximately by 4 °C compared to that of Ba05 (Fig. 1b and c; Table 2). The first cause of shifting of peaks might be due to the higher viscosity of the glass imposed by the presence of barium. The 2nd cause, though insignificant, might be due to the hindrance encountered by the counter ions, i.e. $Ba^{2+}$ and $K^+$ during the formation of their corresponding crystal phases. In case of 2nd peak, the shifting is only by 4 °C compared to that of 1st peak, which might be due to the significant lowering of viscosity at higher temperature.

The activation energy for the crystal growth of the samples Ba00 and Ba05 was estimated to be 209.1 kJ mol$^{-1}$ and 304.9 kJ mol$^{-1}$, which is lower than the value obtained by Bagdassarov [13] (245 kJ mol$^{-1}$) and Henry and Hill [12] (307 kJ mol$^{-1}$). The discrepancy in these values might be arising from the different chemical compositions [14].

From these curves, it is visible that the glass transition temperature ($T_g$) and crystallization peak temperature ($T_p$) shifted towards right with increasing heating rate.

The activation energy ($E$) of crystallization was calculated using the following modified form of Kissinger equation established by Matusita and Saka [15].

$$\frac{\ln \frac{T_p^2}{\beta}}{\beta} = \frac{E}{RT_p} + C$$  \hspace{1cm} (5)

where $\beta$ is the heating rate, $R$ is the universal gas constant. The Avrami exponent ($n$) was calculated using the value activation energy ($E$) by the Augis–Bennett equation [16].

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E}$$  \hspace{1cm} (6)
Table 2
Values of activation energy (Kissinger (EJ) and Avrami exponent.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Heating rate (β) (°C/min)</th>
<th>1st crystallization peak temperature (T1) (K)</th>
<th>Activation energy (kJ mol⁻¹)</th>
<th>Avrami exponent (n)</th>
<th>2nd crystallization peak temperature (T2) (K)</th>
<th>Activation energy (kJ mol⁻¹)</th>
<th>Avrami exponent (n)</th>
</tr>
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<tr>
<td>Ba00</td>
<td>5</td>
<td>713 ± 2</td>
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<td>2.83</td>
<td>20918 ± 2</td>
<td>4.00</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>723 ± 2</td>
<td>2.93</td>
<td>0</td>
<td>796 ± 2</td>
<td>2.93</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>732 ± 2</td>
<td>3.03</td>
<td>0</td>
<td>796 ± 2</td>
<td>3.03</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>740 ± 2</td>
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<td>0</td>
<td>796 ± 2</td>
<td>3.13</td>
<td>0.0</td>
</tr>
<tr>
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<td>5</td>
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<td>197.2 ± 3</td>
<td>2.63</td>
<td>886 ± 2</td>
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<td>796 ± 2</td>
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<td>0</td>
<td>921 ± 2</td>
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<tr>
<td>Ba05</td>
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<td>304.9 ± 3</td>
<td>3.43</td>
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<td>901 ± 2</td>
<td>3.63</td>
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<td>1091 ± 2</td>
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</tr>
<tr>
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<td>912 ± 2</td>
<td>3.83</td>
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<td>1091 ± 2</td>
<td>4.00</td>
<td>0.0</td>
</tr>
</tbody>
</table>

where n is the Avrami exponent or crystallization index and ΔT is the full width of the exothermic peak at the half-maximum intensity. The crystallization index (n) depends upon the actual nucleation and growth mechanism. According to JMA theory, crystallization index (n) is also related to crystallization manner, n = 2 means that the surface crystallization dominates overall crystallization, n = 3 means that the two dimensional crystallization or volumetric crystallization, n = 4 means that the three dimensional crystallization for bulk materials [17–19]. The Avrami exponent and activation energy were calculated using the above equations and shown in Table 2. In Ba00 and Ba03, for the 1st crystallization peak temperature (T1), Avrami exponent was 2.93 and 2.90 respectively, which are close to 3, therefore the fact indicates that bulk nucleation and two dimensional growth occurs for the glass-ceramics.

From 2nd crystallization peak temperature, Avrami exponent was found to be 3.94 and 3.72 for Ba03 and Ba05 respectively, which are close to 4, therefore the fact indicates that it is a case of bulk nucleation and three dimensional crystal growths for the material concerned.

3.2. Results of X-ray diffraction

In Ba00, at 800 °C, peaks of K-fluorophlogopite (KMg₃Al₂(Si₉O₂₅)₂F₂) (JCPDS reference-00-019-0117) appeared as a major phase. The amount of this phase increases with increasing heat treatment temperature as shown in Fig. 2a. At 900 °C, several peaks of K-fluorophlogopite at 19.5°, 23.2°, 32.6°, 35.8°, 36.7°, and 45.4° and one peak of enstatite (JCPDS reference-00-002-0546) at 63° appeared along with K-fluorophlogopite. At 1000 °C, peaks of K-fluorophlogopite at 17.7°, 26°, 27.4°, 30.8°, 31.6°, 41.9° and 55.2° and one peak of mullite (JCPDS reference-00-026-0137) at 54° as shown in Fig. 2b. At 900 °C, two peaks of alpha-hexacelsian appeared at 22.7° and 30.0° along with Ba-fluorophlogopite, K-fluorophlogopite and barium aluminium silicate. At 1000 °C, two fresh peaks of Ba-fluorophlogopite at 17.4° and 36.7°, one peak of K-fluorophlogopite at 25.8°, one peak of alpha-hexacelsian (JCPDS reference-01-088-1050) at 54° and two peaks of enstatite at 35.8° and 34.4° appeared along with Ba-fluorophlogopite and K-fluorophlogopite but a peak of barium aluminium silicate at 11.4° disappeared. From 1000 °C to 1100 °C, there are no changes in the intensity of the peaks but one peak of K-fluorophlogopite at 41.9° and a peak of enstatite at 63° appeared. From 1100 °C to 1150 °C, there are no changes in the intensity of the peaks but the sharpness of the peaks has been increased.

In Ba03, at 800 °C, peaks of K-fluorophlogopite appeared at 27° and 34° as a major component whereas, Ba-fluorophlogopite (JCPDS reference-00-019-0117) appeared as a minor component and one peak of barium aluminium silicate (JCPDS reference-00-026-0137) appeared at 11.4° as shown in Fig. 2b. At 900 °C, two peaks of alpha-hexacelsian appeared at 22.7° and 30.0° along with Ba-fluorophlogopite, K-fluorophlogopite and barium aluminium silicate. At 1000 °C, two fresh peaks of Ba-fluorophlogopite at 17.4° and 36.7°, one peak of K-fluorophlogopite at 25.8°, one peak of alpha-hexacelsian (JCPDS reference-01-088-1050) at 54° and two peaks of enstatite at 35.8° and 34.4° appeared along with Ba-fluorophlogopite and K-fluorophlogopite but a peak of barium aluminium silicate at 11.4° disappeared. From 1000 °C to 1100 °C, there are no changes in the intensity of the peaks but one peak of K-fluorophlogopite at 41.9° and a peak of enstatite at 63° appeared. From 1100 °C to 1150 °C, there are no changes in the intensity of the peaks but the sharpness of the peaks has been increased.

In Ba05, the formation of Ba-fluorophlogopite phase is dominant in all heat treatment temperatures, and the amount of this phase increased with increasing heat treatment temperature as shown in Fig. 2c. At 800 °C, peaks of enstatite appeared at 40.9° and barium aluminium silicate appeared at 11.4°, 22.4°, and 29.8° along with barium fluorophlogopite. From 800 °C to 1000 °C there is no change in the intensity of the peaks and no new phases appeared. At 1100 °C, one new peak of barium fluorophlogopite appeared at 26.9° along with remaining other peaks. But at 1100 °C and 1150 °C, the sharpness of the peaks of both barium aluminium silicate and enstatite has been increased.

The formation of K-fluorophlogopite and Ba-fluorophlogopite is major phases in Ba00 and Ba05 respectively. But both the phases viz. K-fluorophlogopite and Ba-fluorophlogopite appeared in Ba03 simultaneously.
3.3. Microstructure analysis

In Ba00, Ba03 and Ba05 samples heated at 800 °C for 5 h exhibit very fine submicron microstructures consists of some blocky crystal (Figs. 3a, 4a and 5a). Samples heated at 900 °C and 1000 °C for 5 h exhibited a large number of slightly big blocky crystals compared to that of at 800 °C (Figs. 3b, 4b and 5b and c). But the sample Ba00 formed large sized long crystals at 1000 °C (Fig. 3c). These crystals are dense as appeared white in the back scattered electron micrographs with more or less low aspect ratio in highly siliceous residual gla with acicular morphology. Samples heated at 1150 °C for 5 h exhibited large sized crystals with high aspect ratio in high siliceous residual glass with acicular morphology (Figs. 3d, e and 5d).

As the temperature increased, the crystal size increase along with the aspect ratio (length/diameter) of the crystals increased (Figs. 3a and b, 4a-c and 5a-c). It might be due to the dissolution of crystals with an aspect ratio of <1 at a reprecipitation of constituents onto these crystals of high aspect ratio. This energetically unfavorable configuration might therefore be the driving force towards attaining the long crystal observed after treatment for 5 h at 1000 °C and 1150 °C for Ba00, and 1150 °C for Ba03 and Ba05 (Figs. 3c and d, 4d and 5d), which is also discussed elsewhere [20].

According to the study, crystal growth or the growth index [21, 22] of mica was 3 and 4, which indicates that the mica crystals grew along two and three dimensions respectively. Therefore, most mica based glass-ceramics possessed 'plaque-like' and 'house of cards' microstructure [4, 23, 24]. The aspect ratios and size of mica crystals were considerably much dependent on the viscosity of melt. As the crystallization temperature increased, the viscosity of melt decreased. The diffusion of ions from glass matrix to crystal was easy; realize, the size of mica crystals increased.

3.4. Hardness and machinability measurement

Generally, it is observed that at 800 °C, the Vickers hardness values reduces to a large extent on formation of the either potassium or barium, or both potassium and barium fluorophlogopite phases compared to that of original glasses. When the temperature is further increased, the Vickers hardness values gradually decreases up to 1100 °C. The hardness values increase slightly beyond this temperature up to 1150 °C (Fig. 6), but the increase is very low and sufficiently lower than that of the original glasses. The large reduction in hardness value correlates with the formation of the interconnected 'house of cards' microstructure [6]. At any particular temperature, the hardness values increases with gradual increase in barium content.

In all the batches for different heat treatment temperatures the machinability parameter (Fig. 6) was calculated from the Vickers hardness ($H_v$) values. It is clear from the results that the higher the hardness values the lower the machinability parameter, whereas, at any particular temperature the machinability decreases with gradual increase in barium content. In all the batches for different heat treatment temperatures, the fracture toughness (Fig. 6) calculated from Vickers hardness ($H_v$) values. It is clear from the results that the higher the hardness values the higher the fracture toughness. At an particular temperature the fracture toughness increases with gradual increase in barium content. Invariably in all the batche
crystallized at 1150 °C, the sudden increase in hardness values might be due to the formation of other crystal phases like insatiate and barium aluminium silicate, etc.

The hardness decreases with increasing aspect ratio of the crystal and the crystallinity of mica, and the machinability also increases. The glass-ceramics showing negative values of $m$ cannot be considered to be machinable, because they need a large threshold cutting force to initiate machining and are difficult to machining to intricate shapes. On the other hand, samples having positive $m$ can be machined precisely by
Fig. 6. Vickers hardness ($h$), machinability (m) and fracture toughness ($K_{IC}$) against different heat treatment temperatures for Ba00, Ba03 and Ba05 samples.

Fig. 5. SEM photograph of polished and etched surface of Ba05 nucleated at 720 °C for 2 h and crystallized at 800 °C (a), 900 °C (b), 1000 °C (c) and 1150 °C (e) for 5 h.

4. Conclusions

(a) Partial substitution of potassium by barium can lead to the formation of K-fluorophlogopite and Ba-fluorophlogopite crystal phases simultaneously, and forms interconnected “house of cards” microstructure.

(b) Fully substituted potassium with barium has the highest hardness, fracture toughness and lowest machinability.

(c) Hardness, machinability and fracture toughness were found to be highly dependent on the formation of an interconnected “house of cards” microstructure and aspect ratio of the formed crystals.

(d) Machinability and strength can be customized by judicious substitution of potassium by barium and also by the time of crystallization.

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References


