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M. Ghasemzadeh, A. Nemati, A. Nozad Golikand, Z. Hamnabard, S. Baghshahi

Department of Materials Engineering, Science, and Research Branch, Islamic Azad University, Tehran, I. R., Iran
School of Materials Science and Engineering, Sharif University of Technology, Tehran, I. R., Iran
Ceramic Group, Material Research School, Karaj, I. R., Iran
Faculty of Engineering, Imam Khomeini International University, Qazvin, I. R., Iran

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Utilization of DTA in the Determination of a Crystallization Mechanism in Transparent Glass-Ceramics with a Nanocrystalline Structure

M. Ghasemzadeh,1 A. Nemati,2 A. Nozad Golikand,3 Z. Hamnabard,3 and S. Baghshahi4

1Department of Materials Engineering, Science, and Research Branch, Islamic Azad University, Tehran, I. R. Iran
2School of Materials Science and Engineering, Sharif University of Technology, Tehran, I. R. Iran
3Ceramic Group, Material Research School, Karaj, I. R. Iran
4Faculty of Engineering, Imam Khomeini International University, Qazvin, I. R. Iran

Non-isothermal differential thermal analysis (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to study the nucleation and crystallization behavior of mica glass-ceramics with LiF as nucleating agent. The models enabled establishing the kinetic parameters for crystal growth of individual phases. The activation energies for crystal growth were found to be in the range of 161–301 KJ/mol, 416–424 KJ/mol, and 583–1011 KJ/mol for base glasses, samples with substitution of Li2O or K2O and samples with addition of LiF, respectively. Formation of transparent glass-ceramics from studied glass-samples has been investigated. Transparency is assumed to occur in the samples with nanocrystalline structure.

Keywords activation energies, crystallization kinetics, glass ceramic, microstructure

INTRODUCTION

The properties of glass-ceramic materials are determined by the crystallization phases precipitated from the glasses and their microstructures, which depend on the composition of the parent glass as well as thermal treatment and addition of nucleating agents.[1–3] Mica glass–ceramics are well known typical machinable ceramics.[2–4] Several applications as engineering materials have already been found. However, high thermal expansion coefficient of these glass-ceramics has limited their performances as a structural ceramic.[5] It seems that a product with good machinability and low thermal expansion has high potential for many engineering applications, so precipitation of a low thermal expansion coefficient phase like β-spodumene together with philogopite phase in the microstructure of these glass-ceramics leads to a machinable glass-ceramic with suitable thermal properties.[5] Beta-spodumene is a trapezohedral form of the tetragonal system with a classical formula Li2O.Al2O3.4SiO2, and is a high temperature form of alpha-spodumene. Beta-spodumene results from heating alpha-spodumene to a conversion temperature of 700°C. Beta-spodumene has low expansion coefficient and high hardness. The simultaneous crystallization of beta-spodumene with fluorophlogopit enhances the mechanical properties and the thermal shock resistance through reducing the thermal expansion coefficient.[5] In the ternary system of Li2O—K2O—SiO2, great mobility of lithium ions cause formation of eutectics with low melting points; therefore, Li2O is a suitable oxide that increases rate of melting and facilitates the crystallization, too. Several investigations have been carried on the influence of lithia on the crystallization behavior and type of precipitated phases in the machinable glass-ceramics.[6,7] Henry and Hill have investigated the role of lithia on the crystallization behavior, microstructural development, and mechanical properties in compositions based on 8SiO2.3Al2O3 (6-x MgO. X MgO. BaO).[8] Trauta et al. prepared transparent lithium-mica glass-ceramics and investigated the influence of MgF2 as nucleating agent for crystallization in this system.[9,10]

DTA is a powerful tool in studying the crystallization kinetics of glass.[11–12] Two methods, namely isothermal and non-isothermal methods, are used for the differential thermal analysis of glass samples. JMA equation is generally used for the kinetic analyses of isothermal DTA data.[12] In the JMA method, glass samples are quickly heated and soaked at a temperature above the glass transition temperature. In this case, crystallization occurs at a fixed temperature. Nonetheless, in non-isothermal method, glass samples are heated at a certain heating rate and crystallized during the thermal analysis scan.[12] The non-isothermal method is more simple and quicker than the isothermal method.
Activation energy and crystallization mechanisms are the most important kinetic parameters for the crystallization of glasses. These parameters can be obtained by experimental DTA results using the equations that are proposed to interpret non-isothermal data. However, most of these equations assume that the variation of peak crystallization temperature is directly related to the heating rate. These equations contributed to understanding the nature of the crystallization mechanisms of different glass forming systems.

In this study, the influence of substitution of Li$_2$O or K$_2$O and LiF as nucleating agent on the crystallization and microstructure development of mica glass-ceramic were investigated. Kissinger, Matusita and Sakka, and Ozawa equations were used to determine the crystallization mechanism and the activation energy values for crystallization.

**EXPERIMENTAL PROCEDURE**

**Preparation of Glass-ceramics**

The chemical composition of three studied glasses are given in Table 1. Standard reagent graded SiO$_2$, Al$_2$O$_3$, MgCO$_3$, Li$_2$CO$_3$, MgF$_2$, K$_2$CO$_3$, TiO$_2$, H$_3$BO$_3$, and LiF were used in the preparation of the glasses. The mixtures melted in alumina crucibles at 1450°C in an electric kiln for 2 h. The glass melt was poured in preheated steel moulds and resulted bulks were annealed at 500°C to eliminate stress. Heat treatment of the glass blocks were done in a tube electrical furnace at the peak crystallization temperatures with a heating rate of 10°C/Min

**Characterization of Obtained Glass**

The glasses produced were characterized by differential thermal analysis (DTA) using DSC-1500 Rheometric Scientific USA. The reference sample for all compositions was α-Al$_2$O$_3$. The crystalline phases formed were detected by X-ray diffractometry. Silicon powder was used as the standard material for semi-quantitative measurements. The microstructure of polished and etched specimens (immersion in 10 wt% HF solution for 20–60s) were observed by scanning electron microscopy Philips XL Seies (XL30). The machinability was evaluated by drilling depth of the glass-ceramics within 30 s, using a 2 mm cermets bit in a drilling force of 50 kN at 500 rpm.

**RESULTS AND DISCUSSION**

The DTA traces of the investigated glasses (Figure 1) showed that the glass transition temperature, $T_g$, is 634°C for base glass K$_0$. This temperature reduces to 562°C after substitution of Li$_2$O for K$_2$O and 530°C due to the addition of 6%wt LiF, as shown in for the sample K$_5$ and K$_0$F$_6$, respectively. Addition of Li$_2$O leads to a decrease of $T_g$ and $T_p$ in comparison with Li$_2$O free batches. These lower temperatures are ascribed to Li$^+$ ions modifying and weakening the network and leading to the reduction of both melting and crystallization onset temperatures. The presence of Li$_2$O and LiF were found to greatly enhance the crystallizability of the glass. This is clear from the DTA curves (Figure 1), where the exothermic crystallization peaks were increased in intensity and, at the same time, displaced to lower temperatures. A study carried by Henry et al. showed that the activation energy of crystallization decreases in the lithia content compositions. They concluded that substitution of lithia for magnesia improved disruption of glass network and lowered the activation energy for crystallization. They explained that the lithia is concentrated in the residual glass phase after crystallization of chondrodite phase, and has possibly a charge-balancing role in the glass network, which has residual alumina, whereas lithium and potassium ion have the same charge.

<table>
<thead>
<tr>
<th>Wt%</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>F</th>
<th>TiO$_2$</th>
<th>Li$_2$O</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_0$</td>
<td>37.96</td>
<td>15.36</td>
<td>6.32</td>
<td>18.1</td>
<td>7.56</td>
<td>9</td>
<td>5.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K$_5$</td>
<td>37.96</td>
<td>15.36</td>
<td>6.32</td>
<td>18.1</td>
<td>1.89</td>
<td>9</td>
<td>5.6</td>
<td>5.67</td>
<td>0</td>
</tr>
<tr>
<td>K$_0$F$_6$</td>
<td>37.96</td>
<td>15.36</td>
<td>6.32</td>
<td>18.1</td>
<td>7.56</td>
<td>9</td>
<td>5.6</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>
Fluorides may act as network breakers in the glassy anionic structure. The bridging oxygens can be replaced by fluoride ions due to their similarity in radius without causing too great a disturbance in the arrangement of the other ions. Consequently, the replacement of the strong \( \equiv \text{Si-O-Si} \equiv \) linkage by a pair of the weak \( \equiv \text{Si-F} \) can result in the weakening of the glass network structure. This may explain the decrease in the melting temperatures and the increases in fluoride addition. As a result of the decrease of the viscosity, the mobility and diffusion of the different ions and ionic complexes of the glasses during the
crystallization process will be markedly increased, leading to the higher crystallizability.\[10\]

Figure 2 shows the DTA thermogram of $K_0$, $K_5$, and $K_0F_6$ samples at the heating rate of 10, 15, and 20 $^\circ$C/min. It is observed from this figure that peak crystallization temperature increases with heating rate. The overlapping of the crystallization curves for the DTA scan at $\alpha = 15^\circ$C.min$^{-1}$ is shown in Figure 3. Figure 4 shows the fraction, $x$, crystallized at a given temperature, $T$, and is given by $x = A_T/A$, where $A$ is the total area of the exothermic between the temperature, $T_i$, where crystallization just begins and the temperature, $T_f$, where the crystallization is completed, and $A_T$ is the area between $T_i$ and $T_f$.\[11\] The graphical representation of the volume fraction crystallized for the exothermic curve shows the typical sigmoid curve as a function of temperature for different heating rates.
The kinetic parameters of the glass-crystallization transformation were determined under non-isothermal conditions applying three different equations, namely, Kissinger,[14] Matusita and Sakka,[13] and Ozawa.[15] In these equations, assume that the variation of peak crystallization temperature, $T_p$, is directly related to the heating rate, $\alpha$. For example, in the Kissinger method,[14] the crystallization peak temperature is monitored as a function of the heating rate and the following relationship is given:

$$\ln \left( \frac{\alpha}{T_p^2} \right) = \frac{-E_{ck}}{RT_p} + \text{Constant}. \quad [1]$$

Where $E_{ck}$ is the activation energy for crystallization, determined by the Kissinger method. A plot of $\ln \left( \frac{\alpha}{T_p^2} \right) vs. \frac{1}{T_p}$ should be a straight line, from the slope of which $E_{ck}$ can be determined. Matusita and Sakka[13] stated that Eq. (1) is valid only when crystal growth occurs on a fixed number of nuclei. Incorrect values for the activation energy are obtained if a majority of the nuclei are formed during the DTA measurement, due to the number of nuclei continuously varying with $\alpha$. They have proposed a modified form of the Kissinger equation as given below:

$$\ln \left( \frac{\alpha^n}{T_p^2} \right) = \frac{-mE_{c}}{RT_p} + \text{Constant.} \quad [2]$$

Where $E_{c}$ is the correct activation energy for crystallization and $m$ is the numerical factor, which depends on the dimensionality of crystal growth. When surface crystallization predominates, $m = n = 1$ and Eq. (2) essentially reduces to the Kissinger equation $E_{ck}$ equals to $E_{c}$.

In the presence of bulk crystallization, $E_{ck}$ does not necessarily equal $E_{c}$. Rather, a close inspection of Eqs. (1) and (2) shows that:

$$E_{c} = \frac{(n/m)E_{ck} - 2((n-1)/m)RT_p}{\alpha} \quad [3]$$

For most oxide glass systems, $E_{c} \geq 20RTP_{12}$ and therefore, the elimination of $2((n-1)/m)RT_p \leq 2RT_p$ in Eq(2) will result in an error less than only 10% in the value of $E_{c}$. This error is within the error range of the DTA measurements. Then we obtain the following relation:

$$E_{c} \approx (n/m)E_{ck} \quad [4]$$

For $m = n$, i.e., when crystallization occurs on a fixed number of nuclei, $E_{ck} = E_{c}$. Thus, for predominantly surface crystallization or for crystal growth that occurs on a fixed number of nuclei, the analysis of DTA data by the Kissinger model (Eq. (1)) yields the correct value of $E_{c}$. When the number of nuclei changes during the DTA measurements, either Eq. (2) should be used or $E_{ck}$ determined from Eq. (1) should be multiplied by the term $(n/m)$ to obtain the correct activation energy.

Form the exothermic peak, the Arramı parameter, $n$, can be obtained by using the following modified Ozawa equation:[15]

$$\left| \frac{d(\ln(-\ln(1-x)))}{d\ln(\alpha)} \right|_T = -n \quad [5]$$

where $x$ is the volume fraction crystallized at a fixed temperature $T$ at the heating rate of $\alpha$. Thus, $x$ is the ratio of the partial area at a certain temperature to the total area of a crystallization exotherm. Non-isothermal DTA curves were obtained at different heating rates (10, 15, and 20°C. min⁻¹) for all glass samples (Figure 2). The crystallization peak temperatures, $T_p$, of all glass

### TABLE 2

<table>
<thead>
<tr>
<th>Crystallization mechanism</th>
<th>$n$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk crystallization with a constant number of nuclei (i.e., the number of nuclei is independent of the heating rate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three-dimensional growth of crystals</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Two-dimensional growth of crystals</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>One-dimensional growth of crystals</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Bulk crystallization with an increasing number of nuclei (i.e., the number of nuclei is inversely proportional to the heating rate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three-dimensional growth of crystals</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Two-dimensional growth of crystals</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>One-dimensional growth of crystal</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Surface crystallization</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
samples increased with the increase in heating rates. Matusita and Sakka\cite{13} mentioned that the Kissinger equation is valid only when the number of nuclei is fixed during crystal growth. If most of the nuclei are formed during the DTA measurement, the activation energy values calculated from the Kissinger equation will be incorrect. Assuming that the nucleation and growth processes had occurred simultaneously in as–quenched samples during the DTA measurements, the data for as–quenched glasses were analyzed by Matusita–Sakka model (Eq. (2)) to determine $E_c$. Since Eq. (2) includes the parameters of $n$ and $m$, their values are first determined using Ozawa model (Eq. (5)).

Plots of $\ln (-\ln(1-x))$ vs. $\ln \alpha$ for $K_0$, $K_5$ and $K_0F_6$ samples are shown in Figure 5, and the values of $n$ determined from the slopes of these plots are found 2.34 and 0.89 for the peak corresponding to $\beta$-spodumene ($T_p3$) in $K_0$ and $K_5$, respectively. Value of $n$ is 2.44 for the $T_p3$ (corresponding to $\beta$-spodumene) in $K_0F_6$ sample. These values indicate that surface crystallizations are dominant in $K_5$ and bulk crystallizations in $K_0$ and $K_0F_6$. The $m$ value for the $K_0$ and $K_0F_6$ should be equal to $n-1$ from Table 2. The sample with surface crystallization and the number of internal nuclei formed during the DTA measurement could be neglected. This means that crystal growth for $K_5$ should have occurred on a fixed number of nuclei during the DTA measurements. Therefore, we can assume that $n$ are equal to $m$ for the $K_5$($n = m = 0.89$) and the primary crystallization started from the surface of the samples.

By substituting the appropriate values of $n$, $m$ and $R$ ($R = 8.3144$ J/molK) in Matusita–Sakka equation (Eq. (2)), Figure 6 can be obtained for $K_0$, $K_5$, and $K_0F_6$ samples.

FIG. 6. The Matusita-Sakka plots of the (a) $K_0$ (b) $K_5$ (c) $K_0F_6$. (Figure is provided in color online.)

FIG. 7. The Kissinger plots of the (a) $K_0$ (b) $K_5$ (c) $K_0F_6$. (Figure is provided in color online.)
the slopes of $\ln (\alpha^m/T_p^2)$ vs. $1/T_p$ plots the $E_c$ values are obtained as 301 KJ/mol for $K_0$ and 416 KJ/mol for $K_5$ and 1011 for $K_{0F6}$ glasses. Also using the Kissinger model (Eq. (1)), $E_{ck}$ values of as-quenched glasses can be determined from the slope of the plots $\ln (\alpha/T_p)$ vs. $1/T_p$ (Figure 7). For $K_5$, $E_{ck}$ is equal to 424 KJ/mol, which is close to $E_c$ value determined from the Matusita–Sakka model. For $K_0$ and $K_{0F6}$, $E_{ck}$ value is equal to 161 KJ/mol and 583 KJ/mol, respectively, that is lower than the $E_c$ value determined from the Matusita–Sakka model. For $n = m$, i.e., when crystallization occurs on a fixed number of nuclei, $E_{ck} = E_c$. This case shows that the crystal growth for $K_5$ sample occurred on a fixed number of nuclei during the DTA measurements, so that both Kissinger and Matusita-Sakka equations gave similar results for crystallization activation energy of $K_5$ glass. The activation energy for the peak corresponding to $\beta$-spodumene in $K_5$ sample is lower than the activation energy for that peak in $K_{0F6}$ sample. $T_p$ is known to correspond with the crystallization of $\beta$-spodumene in $K_5$ sample and the glass following crystallization of chondrodite is likely to have a composition close to the $\beta$-spodumene stoichiometry that explains the low activation energy value obtained. The activation energies for crystallization corresponding to $\beta$-spodumene in the LiF containing glasses are considerably higher. The stoichiometry of the glass phase left after crystallization of MgF$_2$ and magnesium fluorid silicate phases, and therefore the crystallization process would be expected to have a high activation energy.

The activation energies for crystallization first peak for $K_0$, $K_5$, and $K_{0F6}$ calculated by Matusita–Sakka model are equal to 205 KJ/mol, 173 KJ/mol, and 538 KJ/mol, respectively. The activation energy corresponding to first peak decrease with addition of Li$_2$O, with substitution of Li$_2$O for K$_2$O would be expected to result in increased disruption of the glass network and a lower activation energy for crystallization. This shows that the barrier towards crystallization is reduced by the addition of lithia, which indicates that these glasses will crystallize more readily. The first peak of $K_{0F6}$ sample corresponding to sellaite indicates an increase in activation energies values with addition of LiF. This shows that the barrier towards crystallization is increased by the addition of LiF. The formation of sellaite may reduce the available amounts of fluorine and magnesium required for formation of the fluorphlogopite phase, and crystallization of the fluorphlogopite phase may be retarded until the sellaite phase has re-dissolved. Addition of LiF will move the glass composition further from the stoichiometry of the fluorphlogopite crystal phase, and this might tend to increase the activation energy.

Figure 8 shows the XRD patterns of different specimens heat-treated at the crystallization peak temperatures. The XRD patterns of all samples, following annealing at the temperature of the DTA exothermic peak, show crystallization of potassium–mica and potassium titanium silicate phases in the $K_0$ sample that heat-treated at 775°C and 830°C (Figure 8a). In Figure 8b, XRD patterns of $K_5$ sample heat-treated at crystallization peak temperatures have been shown. From this figure, it can be seen that chondrodite and $\beta$-spodumene phases have been formed in 670°C. With increasing of temperature up to 725°C, the relative intensity of these two phases have been increased. At 830°C, the relative intensity of chondrodite phase decreased and on the contrary, $\beta$-spodumene phase content have been increased. The XRD pattern of $K_{0F6}$ sample shows crystallization of potassium-mica, lithium magnesium aluminum fluoride silicate, and chondrodite phases in the sample heat treated at 643°C. In the $K_{0F6}$ sample heat treated in 671°C for 2 h, potassium–mica, chondrodite phases were crystallized, whereas in the case of $K_{0F6}$ sample heat-treated in 730°C.
**FIG. 9.** Microstructure of (a) K₀ after heat treatment at 830°C for 2 h (b) K₅ after heat treatment at 725°C (c) K₀F₆ after heat treatment at 643°C for 2 h (d) K₀F₆ after heat treatment at 671°C (e) K₀F₆ after heat treatment at 730°C.

β-spodumene, MgF₂ and potassium titanium silicate phases were crystallized and mica and chondrodite phases can’t be seen (Figure 8c). β-spodumene crystallizes close to Tₑ₃ after crystallization of the MgF₂ and humite phases. This suggests that the Lithia is concentrated in the residual glass phase after crystallization of the humite phase and is possibly a charge balancing cation for the excess alumina remaining in the glass network.

Figure 9 shows the microstructure of different investigated samples. In the K₀ specimen, low fraction plate-like mica crystals with the grain size of about 3 µm precipitated in the glass matrix and the lowest degree of connectivity occurred between mica crystals; the great amount of residual glass phase in this sample leads to a strong structure preventing plastic deformation by mica crystals that affects the machinability of this sample. In the K₅ sample, a spatial orientation in the arrangement of crystals were observed. This microstructure is generally observed in samples having a low nucleation density.[16,17] On the other hand, low machinability of the investigated samples is affected by a small amount of machinable mica phase, no interlocked structure and resultant more content of glass phase. The machinability of K₀ sample were lower than K₅. It seems that addition of Li₂O to the base glass weakens its structure. SEM of optically transparent K₀F₆ samples heat-treated for 2 h at 643°C and 671°C show the quasi-spherical grain with nano size were precipitated uniformly. The size of crystal grain increased with increasing temperature and transparency is lost after heat-treated at 730°C.

Figure 10 reveals visual appearance of K₀F₆ sample. It appears that optical transparency is maintained in samples heat-treated at 643°C and 671°C for 2 h. Transparency in these glass-ceramics is assumed to occur due to the presence of nano size crystallites. The size of crystal grain increased with increasing temperature and transparency is lost after heat-treated at 730°C, probably due to the increase of the volume fraction.
of crystal phase. Growth of the crystallites at this temperature into larger crystallites results in increased scattering of light.\cite{18} Transparency in K₀ and K₅ does not occur, giving rise in those samples to non-uniform microstructures.

It is generally accepted\cite{18} that fluorides, in large amounts, are immiscible in silicate melts leading to glass-in glass phase separation; numerous droplets of one glass dispersed in another are formed. This phase separation decreases the energy barriers necessary for crystallization.\cite{18} However, phase separation alone may not be sufficient to induce volume crystallization in the glass and cases are known where glasses having a tendency for phase separation exhibit opalescence during heat-treatment, and do not show volume crystallization.\cite{18} The addition of F⁻ in the form of LiF instead of O⁻ in K₀F₆ is observed to have large effect on the transparency of the heat-treated glass sample.

CONCLUSION

Crystallization kinetics of fluorphlogopite glass-ceramic has been studied by DTA, XRD, and SEM. DTA scans exhibited on well defined crystallization exotherm, which was formed by the overlapping of two exothermic crystallization curves. The activation energy of crystallization for the formation of second crystalline phase and Avrami parameter, n was calculated to be 301 KJ/mol and 2.34, respectively. These Avrami parameters correspond to the bulk crystallizations. Substitution of Li₂O for K₂O in the glasses studied caused changes in temperatures and sharpness of the crystallization peak. Activation energies for crystallization of second crystalline phase in sample with substitution of Li₂O for K₂O was calculated to be 424 KJ/mol. Avrami parameter, n was 0.89 corresponding to the surface crystallizations. Activation energies for crystallization of β-spodumene phase in sample with LiF was calculated to be 1011 KJ/mol. Avrami parameter, n, was 2.44, corresponding to the bulk crystallization. It is obvious that the samples with nanocrystalline structure were transparent.

REFERENCES