Characterization of Fe-doped lithium aluminosilicate glass-ceramic materials by synchrotron radiation techniques

Yu-Han WU,*, Kuo-Chuan HSU** and Chih-Hao LEE*,***,†

*Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan 30013
**Ta Hsiang Containers Ind. Co., Ltd., Hsin Pu, Hsinchu, Taiwan 30543
***National Synchrotron Radiation Research Center, Hsinchu, Taiwan 30013

The effects of doping of Fe ions in lithium aluminosilicate glass-ceramic under varied thermal treatment conditions were studied by synchrotron X-ray powder diffraction, X-ray absorption near edge structure (XANES) and infrared microscopy. When doping concentration is high (> 0.6 wt%), Fe ions tend to migrate into the main crystalline phases; while these ions remain in a disorder environment at low doping level. In high doping samples heated at higher than 800°C, multiple scattering peaks in XANES spectra can be observed in samples, which imply that Fe ions substitute into the Li sites of the main solid solution phase. The diffraction results show that a small amount of Fe oxide (< 0.2 wt%) in a LAS glass-ceramic material decreases the crystallization temperature of β-quartz solid solution by ~50°C. Samples doped with ~0.6–3 wt% of Fe ions results in a raised formation temperature of β-quartz solid solution and a retarded phase transformation of β-quartz solid solution to β-spodumene solid solution.

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1. Introduction

Lithium aluminosilicate (LAS) glass-ceramic materials have been widely studied due to their low or near zero thermal expansion property, high mechanical strength and good chemical durability. Transition metal elements usually act as coloring agents or impurities in a LAS glass-ceramic material. Fe ions are one of the most common coloring agents.1,2) Depending on the redox state, glass containing Fe ions exhibits blue, green, yellow, brown or even black colors. Its structural role is a critical factor for this material in optical applications. The effect of doping with Fe ions on the microstructural evolution is also one of the most interesting issues for the production of LAS glass-ceramic materials. High concentration Fe ions in glass-ceramics with magnetite or hematite as the main crystalline phase for hyperthermia3) or semiconducting electrical device4) are widely studied. In the previous work, Z. J. Wang et al.5) reported that the iron-rich glass-ceramics produced from slags have much lower melting temperature, glass transition temperature, and crystallization temperature, glass transition temperature, and crystallization temperature, which results in a further energy-saving process. For LAS glass-ceramics, recently, H. Yang et al.6) reported that no significant effect was observed on the main crystalline phase formation and phase transformation of mixed coloring agents (0.18% Fe₂O₃ + 0.91 or 0.64% Co₂O₃ + 0.46 or 0.73% Ni₂O₃) and the coloring agents did not change the main crystalline structure, either. However, all the previous works using X-ray diffraction (XRD), Raman scattering, and infrared (IR) spectroscopy methods cannot specify the microstructural information around the doping Fe ions. In this work, X-ray absorption spectroscopy (XAS), which is an element sensitive technique, was adopted to see the local structural change around the doped ions. Since Fe ions exhibit stronger cation field strength than the alkali ions in silicate glass, substantial effects on phase transformation during microstructural evolution will be occurred. It is interesting to see the effect of the doped ion on the nucleation and crystallization behavior and morphology in a wider concentration range. Our experimental results show that doping with Fe ions may help or retard the crystallization and main crystalline phase transformation under different composition ranges. In addition, these ions present in different structural states during devitrification process and the microstructural uniformity becomes irregular at high doping levels. Possible mechanisms of the above phenomena will be proposed in the following.

2. Experimental

The LAS glass-ceramic samples were prepared by the general monolithic method following the process of previous work.7) The composition of the prepared LAS glass-ceramic samples is similar to a commercial product with nominal oxide compositions in wt% as follows: SiO₂ (65.4%), Al₂O₃ (20.3%), Li₂O (5.0%), TiO₂ (2.0%), ZrO₂ (2.0%), ZnO (1.5%), MgO (1.0%), BaO (1.0%), Na₂O (0.5%), K₂O (0.3%), and Sb₂O₃ (1.0%). The additional contents of Fe₂O₃ introduced are from 0.1% to 3.2%. The contents of Fe in a glass-ceramic sample also verified by the edge jump height of the X-ray absorption near edge structure (XANES) spectra measured in the fluorescence mode. Well-mixed industrial or analytical grade raw materials in the form of oxides and carbonates were melted in Pt or alumina crucibles at 1680°C ± 10°C for 3 h. The high temperature glass melts were poured into a metal mold and cooled to ambient temperature. The quantity of samples synthesized was ~50 g or 100 g per batch. The as-quenched bulk glass samples were annealed at 650°C for 1 h to release residual stresses, and then were heat treated at 750, 800, 850, 1050 and 1150°C for 0.5 h. The heating rate is ~10°C/min. After heating, the samples were cooled in the furnace. The heat treatment temperature ranges were chosen based on the results of the published literatures.7,11)
XRD and XANES were used to characterize the evolution of microstructure of the sample. Owing to the small amount of newly formed phase, an intense X-ray source at wiggler beamline, BL-17A, BL-17B12 and BL-01C2 at National Synchrotron Radiation Research Center (NSRRC), was employed for XRD measurement. An X-ray area detector, Mar 3450 image plate, was used to collect the patterns of diffraction rings. By examining the intensity uniformity of the diffraction ring, the non-uniform orientation distribution and large size of the microcrystallines can be identified. XANES was used here to show the structure changes around Fe ions during the crystallization process. For the data collection of XAS spectra, the Si (111) double-crystal monochromator and Lytle detector at BL-17C and BL-07A13 were employed. The Fourier-transformed EXAFS spectra with k^2-weighting were acquired by using the program Artemis14 for k range from 2.9 to 12 Å\(^{-1}\) with a hanning window function. The IR microscopy at BL-14A of NSRRC was used to understand the phase distribution of a glass-ceramic sample.

3. Results and discussion

3.1 Microstructural evolution by XRD

The XRD results show the microstructural development of LAS glass-ceramic samples, which include the possible phase separation phenomenon of a parent glass. The crystallization temperature of the main phase (\(\beta\)-quartz solid solution) and the transformation temperature of the main phase (\(\beta\)-quartz solid solution to \(\beta\)-spodumene solid solution), is significantly affected by the doping concentration of iron. For the as-quenched sample or the sample annealed at 650°C, the vitreous nature is confirmed with XRD patterns in which only one single amorphous halo appeared [see pattern (A) in Fig. 1 as an example]. As the annealing temperature increased to 750°C for 0.5 h, there exist two or even three broad peaks in the XRD patterns as shown in Fig. 1. This result might be due to the formation of crystallites with nanometer size (~4 nm, estimated by Scherrer formula). However, the possibility of glassy phase separation, which means two or three different kind of glassy phases coexist, cannot be excluded. Comparing with the position of amorphous halo in Fig. 1 and diffraction peaks shown in Fig. 2, it suggests that the composition of the first amorphous halo (h1) is a lithium aluminosilicate rich vitreous phase and the second broad peak (h2) is a Ti-rich one. When the concentration of dopants is increased, the peak position of h2 shifts to higher angles and the third broad peak (h3) becomes more pronounced. The shift of h2 peak implies that the higher ionic field strength of the doped transition element causes a shrink in averaged bond distance. The pronounced h3 peak indicates that the doped Fe ions might enhance the formation of nanocrystals or phase separation.

Furthermore, for samples heated at 750°C with Fe doping concentration higher than 0.6% (see Fig. 1 as an example), no diffraction peak belonging to hexagonal \(\beta\)-quartz solid solution, the XRD features of main crystalline phase of a LAS glass-ceramic at low temperatures, can be identified in these highly doping samples; while a sample contains < 0.6% dopants, two sharp diffraction peaks belong to \(\beta\)-quartz solid solution appear under the same thermal treatment condition. When the heat treatment temperature is further increased, sharp and distinct diffraction peaks belong to the two main crystalline phases (\(\beta\)-quartz solid solution and \(\beta\)-spodumene solid solution) of LAS glass-ceramics in the XRD patterns are observed. Figure 2 shows that the different Fe doping concentration results in a different main crystalline phase composition of the LAS glass-ceramic sample under the same heat treatment condition. When a sample heated at 850°C and doped with equal or less than 0.6% iron oxide, the main phase is tetragonal \(\beta\)-spodumene solid solution (marked as “s” in the bottom line of Fig. 2), which is a more stable main crystalline phase at high temperatures; while the main phase for a high-doping sample (e.g. 2% in Fig. 2, upper line) is still \(\beta\)-quartz solid solution, although accompanied with a trace amount of \(\beta\)-spodumene solid solution. From more detailed XRD data, it can be summarized that trace amounts of the Fe oxide (< 0.2 wt%) doped in a LAS glass-ceramic material decreased the crystallization temperature of \(\beta\)-quartz solid solution by about 50°C. Doping with ~0.6–3.0 wt% of Fe oxide results in a raised formation temperature of \(\beta\)-quartz solid solution and a retarded phase transformation of \(\beta\)-quartz solid solution to \(\beta\)-spodumene solid solution (i.e. this phase change temperature is increased).

![Fig. 1](image1.png)

Fig. 1. (Color online) XRD patterns of samples containing different amounts of FeO\(_3\) from 2.0% [pattern (B)] to 0.6% [pattern (D)] heated at 750°C for 0.5 h (Shifted for clarity). \(\lambda\) (wavelength) = 1.37756 Å. The peaks of \(\beta\)-quartz solid solution are labeled with “q”. Pattern (A) with only one amorphous halo shows the XRD data of the sample with 1.2% FeO\(_3\) annealed at 650°C for 1 h. The as-quenched samples exhibit the same XRD features as pattern (A).

![Fig. 2](image2.png)

Fig. 2. (Color online) XRD patterns of samples containing 0.6% (bottom) and 2.0% (top) FeO\(_3\) (Shifted for clarity). All the samples are heat-treated under 850°C for 0.5 h. \(\lambda\) = 1.37756 Å. The peaks are labeled with “q” for \(\beta\)-quartz solid solution, “s” for \(\beta\)-spodumene solid solution, and “t” for ZrTiO\(_4\).
Two possible mechanisms, stoichiometry change and viscosity drop, are proposed to explain the changes in the crystallization and phase transformation temperatures mentioned above. Due to the stoichiometry change from the composition of the main crystalline phase, the higher doping concentration results in a smaller driving force of crystallization of the main crystalline phase. The crystallization and phase transformation temperatures are thus increased. On the contrary, a small amount of transition elements in the parent glass usually decreases the viscosity of the matrix drastically and results in a decrease of the energy barrier of crystallization or phase transformation. The mechanism of decrease in glass viscosity via doping is dominated when the doping content is very low. Therefore, the crystallization and phase transformation temperatures are decreased. It is usually acceptable for a glass network to tolerate the formation of very few broken bonds (non-bridging oxygen) due to the presence of small amount of transition element ions. These broken bonds usually cause a sharp drop in viscosity and reduce the barrier of ion diffusion. However, when the doping concentration is high, the structural role of transition elements would not be acted as a network modifier anymore; weak-bonded network former seems a better choice to prevent the collapse of the glass network (less broken bonds). The decrease in viscosity, in general, is thus not always so effective for the further addition of transition elements. As a result, not only the stoichiometry change factor, the structural role of transition element ions might also be responsible for retarding the main crystalline phase change under a high doping level.

Moreover, it is unlikely that the structural role of Fe ions behaves as nucleating agents. Although the color of samples bearing more than 1% Fe₂O₃ is usually black (similar to the color of magnetite), there is also a thin red brown layer (similar to the color of hematite) at the surface of samples (with >1% doping) heating at higher than 1050°C. However, no clear XRD peak belonging to Fe-rich secondary phases, such as magnetite (Fe₃O₄) or hematite (Fe₂O₃), can be identified inside the samples at each heating stage. It seems that no Fe-rich precursor nanocrystalline phase exists to help the succeeding crystallization. The thin red brown layer at the sample surface implies that excess Fe ions prefer to stay away from the main crystalline phase or residual glassy phase under high temperature heat treatment and avoid a distortion of lattice structure or glass network.

### 3.2 Microstructural uniformity

Not only the crystalline phase composition but also the microstructural uniformity of grains is affected by the doping level of transition elements. The crystal size distribution and grain distribution position in a glass matrix result in a great influence on the mechanical and other properties of a glass-ceramic. When the doping concentration is high, these distributions become irregular. For example, XRD image plate pattern shown in Fig. 3(a) demonstrates that the diffraction rings of the reference sample (without doping) are continuous; while for highly doping concentration samples (~3% in Fig. 3(b) as an example), the rings consist of discontinuous array of spots. It indicates that the uniformity of crystalline phase assembly (crystal size distribution and grain distribution in a glass matrix) in high-doping samples is poorer than that of the reference sample. This result might be due to the enhanced phase separation phenomenon or the formation of larger amount of precursor phases. Precursor phases (usually Ti-rich crystalline phases) are usually easier to precipitate at the glassy phase boundaries in a phase-separated sample and these precursor particles can be acted as nucleation sites of the succeeding main phase, which may result in a high grain growth rate at specific sample positions. To further understand the distribution of the two main phases in μm length scale, IR microscopy was performed in this work. The IR microscopy image in Fig. 4(a) reveals the difference of IR spectra at different sample positions, which shows different phase compositions at each position. More detailed difference in IR absorption spectra is plotted in Fig. 4(b). In Fig. 4(b), the blue dash line shows IR data at site A (concave position) and the black solid line (normal position) shows the data at site B. Spectra features of site A are similar to that of amorphous samples or samples heated at lower temperatures (<750°C). The sharp, split and shifted IR bands at site B indicates that these regions are highly crystallized. The phase change seems not completed in this sample due to the lack of heat treatment time. This result is consistent with the XRD data which shows a mixing phase in the sample of Fig. 4.

### 3.3 Local environment change around Fe ions

To further understand the structural role of Fe ions during devitrification, XANES study of Fe K-edge of LAS samples under different heat treatment conditions was carried out. The result shows that Fe ions exhibit different structural states under different doping levels. From XANES spectra shown in Fig. 5(a), it can be found that when more than ~0.6 wt% of Fe₂O₃ was doped, a multiple scattering peak (denoted as “s”) in XANES spectra can be observed for the sample heated at higher than 850°C, which implies these elements located at more ordered local environments. According to XRD data, samples heated at higher than 850°C are highly crystalline solid. In Fig. 5(b), no...
significant change of XANES features can be observed when the doping concentration is low (<0.2%). This result implies that most Fe ions in the low doping samples remained in a vitreous state because all the XANES features of high temperature samples are the same as that of amorphous samples. In an amorphous system, the main feature mainly comes from the first shell and the contribution from outer shells submerges due to the lack of long range order and thus no multiple scattering peak will appear. The statistical variation in the edge positions among various absorption sites from the aperiodicity results in a broadened XANES and EXAFS features.16) The XANES features of as-quenched and as-annealed (650°C) samples with different doping concentrations are also nearly identical and are consistent with our XRD data. This result indicates that the Fe ions, independent on the doping level, all present in an amorphous state in the matrix. For samples with high-doping level, when the heat treatment temperatures increased (>750°C), the main absorption peaks usually become sharper than that of as-quenched ones.

In addition, the normalized intensities of pre-edge peaks (p) of high doping-level samples are decreased (~30% in Fig. 5). Combined with the phenomena of sharper main edge peak (white line), lowered pre-edge peak intensities and the presence of multiple scattering peaks, it can be inferred that some Fe ions present in a more ordered environment in a high-doping level sample. The lowered pre-edge peak intensity is due to that Fe ions located at ordered centro-symmetry sites (e.g. octahedral site of Li⁺ at the main phase) will result in a reduced possibility of 1s to 3d core orbital transition.17) The high intensity of main absorption peak indicates that some Fe ions are octahedral (six-) coordinated, and the low intensity of main absorption peak indicates a reduction of coordination number (e.g. four-coordinated at tetrahedral site).18) As a result, it suggests that the doped Fe ions might substitute into Li ion site of the main crystalline phase due to the similar ionic radii (Li⁺ = 0.074 nm, Fe²⁺ = 0.078 nm, both six-coordinated)19) when the concentration of these ions exceeds the solubility of residual glass phase. No diffraction peak belongs to Fe oxide can be clearly identified by synchrotron XRD which also favors the model of substitution.

The phenomenon of Fe ions substituted into Li sites of the main crystalline phase or precipitated in a Fe rich secondary crystalline phase in a LAS sample could also be understood by comparing the difference of their EXAFS spectra. Figure 6(a) shows the Fourier-transformed experimental EXAFS data of Fe ions in a LAS sample with the calculated and Fourier-transformed EXAFS data of possible Fe compounds (secondary crystalline phases) and EXAFS data of Fe-substituted Li site in α-quartz solid solution or β-spodumene solid solution, the difference of Fe EXAFS features in different crystalline phases could be observed. For example, the relative amplitude of the second peak “b” in Fig. 6(a) is stronger in highly doping samples. The amplitude decreases as a linear function of doping concentration under the
same heating condition. The lowered intensity of the second peaks indicates that the scattering contribution from second shell is lowered. This result implies that Fe ions in a low-doping sample exist in a more disordered environment; while in a high-doping and highly crystalline sample, some ions exist in an ordered environment. Additionally, from the relative intensity of the first and second shell of calculated and Fourier-transformed Fe EXAFS data in β-quartz solid solution [Fig. 6(b)], we can see this ratio is much weaker than that of bulk magnetite and hematite, which can exclude the existence of Fe ions to form these two most probable precipitates such as large magnetite and hematite particles. The result is also in agreement with XRD data. The Fourier-transformed experimental EXAFS peak position and relative intensity were more or less consistent with the calculated and Fourier-transformed EXAFS spectra of Fe-substituted β-quartz solid solution [see Fig. 6(b)]. Consequently, it can be suggested that those Fe ions in an ordered environment of high-doping samples tend to substitute into the main crystalline phase rather than precipitate into a Fe-rich compound as proposed from our XANES results. If the model is correct, peak “a” can be attributed to the distance to the first coordination oxygen approximately; peak “b2” could be assigned to the distance to alumina ions; peak “b” might be due to the combination of silicon and oxygen ions of the second shell; while peak “c” seems corresponding to the next shell of iron ions.

4. Conclusion

LAS glass-ceramic samples with commercial-like compositions doped with Fe ions have been prepared by the monolith glass-forming method and characterized by XRD and XAS. A few conclusions can be reached as follows:

1. The temperatures of crystallization and phase transformation of main crystalline phase are lowered for samples with very low doping concentration but are raised for samples with high doping concentration.

2. The microstructural uniformity becomes irregular as the doping level increased.

3. At low doping level (~<0.2%), most of Fe ions remain in disorder states during devitrification process; at high doping level (~>0.6%), some of these ions migrate into ordered environments. The doped Fe ions might substitute into the Li site of the main crystalline phase.

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