X-ray Diffraction and Absorption Studies of the Crystalline and Vitreous Phases of a Low Thermal Expansion Lithium Aluminosilicate Glass-Ceramics Doped with Transition Oxides

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This main goal of study is to demonstrate the correlations among phase development, microstructure, and thermal expansion coefficient associated with the content of transition elements, especially Ti, Fe, Co and Zr, added in the raw bath of a lithium aluminosilicate (LAS) glass-ceramic with commercial-like recipes. Samples were prepared by the standard bulk, glass-forming method and heat-treated by two-step thermal programs to achieve a transformation of vitreous to crystalline state. X-ray powder diffraction (XRD), XANES, SEM and IR absorption spectroscopy were used in this study.

According to the preliminary results of XRD, XANES and IR, the microstructure development of LAS glass-ceramic largely depends on the doping of the transition elements studied (Ti, Fe, Co and Zr), including the change of the main-phase formation temperature, phase transformation temperature of hexagonal β-quartz solid solution (s.s.) to tetragonal β-spodumene s.s., crystalline phase assembly and the existence of secondary phases. The phase separation phenomenon in glass is often more pronounced with the addition of transition elements (Fe, Zr) and this result can be easily observed by XRD. This phenomenon indicates that the structure of these glasses have converted into several glassy phases because these glasses exhibit higher tendency of phase separation or ion aggregation behavior caused by the existence of higher concentration of Fe ions with higher cation field strength. The difference in cation field strength of different transition ions might be one important reason of the retarded phase transition and phase separation result that samples containing ~0.6-3 wt% Fe or Co oxide show a raised formation temperature of β-quartz s.s. and a retarded phase transformation behavior of β-quartz s.s. to tetragonal β-spodumene s.s. at lower temperatures. However, the substitute effect of theses ions into main crystalline solid solution phases can not be ignored. When two Li^+ ions are replaced by one Fe^{2+} or one Co^{2+} ion, the crystal lattices of the main phase experience large distortion. According to the IR experimental data, IR beams undergo anomalous dispersion in LAS glass-ceramic samples of this study. It can be observed that after Kramers-Kronig correction, the positions of absorption bands shifted several tens of cm^{-1} while the relative intensities of absorption bands changed more than 100%.

In some details of XANES, the spectra change of titanium K-edges for LAS glasses and glass-ceramics is interesting. Typical XANES spectra of Ti K-edge of a sample containing 2.2 wt% TiO_2 under different thermal schemes are shown in Fig. 1. The pre-edge peaks p1 corresponds to partially allowed *1s* to *3d* core level electron transitions with *p-d* mixing. The p1 intensity usually drops more than ~50% and approaches a constant gradually during devirtrification. The pre-edge peak intensity is proportional to the percentage of the unoccupied *p* states in the *p-d* hybridization. The bond angle variance and site distortion from disorder will give rise to an increased *3d-4p* orbital hybridization. As a result, the higher intensity of pre-edge peaks of vitreous samples indicates that most of the Ti atoms are in non-centrosymmetric environment of the glassy samples. In near edge structures, the peak of the first main feature denoted as m1 might be due to the multiple scattering contribution from the presence of next nearest neighbors around Ti or 1s to 4p transition which is associated with the shake down effect by creating a hole in the highest occupied ligand orbital. Another peaks, m2 and m3 attribute to the electron transitions from *1s* to *4p* and higher-lying *p*-states. In the present work, the main absorption features can be well resolved in a highly crystalline sample while only smooth and broadened shoulders of m1 and m3 can be observed in a vitreous sample. In an amorphous system, the main feature mainly come from the first shell and the contribution from outer shells submerges due to the lack of long range order. The statistical variation in the edge position among various absorption sites from aperiodicity results in a broadened XANES and EXAFS features. Moreover, the degree of Debye-Waller-like damping due to random phase decoherence among each set of closely similar multiple scattering paths is also another important factor for amorphous materials. In addition to the disorder stated above, another reason of the low main-edge peak intensity of a vitreous sample is the well-known f-sum rule.

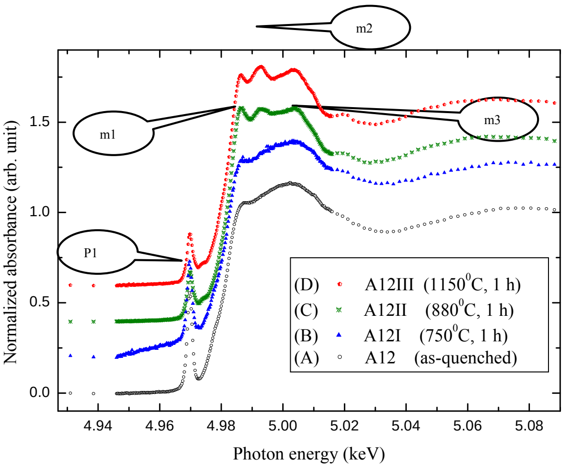

Figure 1. XANES spectra of Ti K-edge of a sample containing 2.2%TiO_2 under different heat treatment conditions (Shifted for clarity).