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TEM Study of Nano Crystals in Li_2O-Al_2O_3-SiO_2 Glass-Ceramics

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Glass-ceramics have an amorphous glassy matrix and one or more crystalline phases that produced by controlled crystallization process (of base glass). These unique properties of glass-ceramics depend on their chemical composition and microstructure, including the shape, size and volume fraction of the crystalline phases in glassy matrix [1]. The Li_xO-Al_xO_x-SiO_2 (LAS) system is an important commercial glass-ceramic due to its extremely low thermal expansion coefficient [1, 2]. The main crystalline phases in LAS system are metastable solid solution of high-quartz or keatite depending on the crystallization temperature [2]. Crystal structures of high-quartz and keatites phases have non-cubic symmetry, thus, anisotropic thermal expansion induces thermal residual stresses due to the thermal and elastic mismatch between the crystalline phase and amorphous glassy matrix [2-3]. Characterization of the structure, shape and volume fraction of crystalline phases in LAS is important to understanding the glass-ceramics system. This paper presents a TEM study of the microstructure (size, shape, distribution and volume fraction) of crystalline phase in LAS glass-ceramic.

To prevent potential amorphization, the TEM sample was prepared by crushing a small piece of laboratory fabricated LAS glass-ceramic sample with ethanol using a pestle and mortar. A small drop of the fine suspension (after a brief ultrasonication) was pipetted onto a holey carbon coated Cu grid. TEM study was carried out using JEOL 2100FEG S/TEM equipped with Gatan Tridiem 863 EELS/GIF system. Electron tomography was performed using JEOL 2100 LaB6 TEM with a high tilt sample holder. Images for 3D reconstruction were obtained from 134 images (±67°) with one image per degree. Tomographic reconstruction and visualization were performed using TEMography software (System in Frontier, Inc.).

TEM/STEM micrographs, BF/DF/HAADF as shown in Fig. 1, of the LAS glass-ceramic reveal nano-size crystals in glassy matrix. Nano-crystals of various morphologies were observed: rod-like (6~9 nm L x 2~3 nm W) (arrows in Figs. 1a and 2a); round/spherical (~6 nm in diameter, open arrows in Figs. 1a and 2b) and irregular shapes. The SAD pattern (Fig. 2c) with sharp and clear diffraction rings overlapping on a broad diffused band indicated poly-nanocrystallites "submerged" in amorphous matrix. The crystalline phase, verified by SAD and EELS (Fig. 2d), is β-quartz $LiAlSi_2O_6$ ($P6_222$). A threshold energy of ~8.5 eV with sharply increasing intensity to the maximum of ~24 eV was observed in the low-loss region (Fig. 2d). These correspond to the energy band gap and volume plasmon (collective excitation of valence electrons) of LAS glass-ceramics, respectively. The energy band gap of 8.5 eV indicates not only an electrical insulator, but also optical transparency similar to other SiO_2-base glasses. HRTEM clearly revealed the lattice image of β-quartz $LiAlSi_2O_6$ nano-crystals in a glassy matrix (Figs. 2a and b). The β-quartz $LiAlSi_2O_6$ phase, however, was destroyed quickly under electron beam irradiation, and further study of atomic arrangement became impossible. Estimated volume fraction of nano-size β-quartz crystals in LAS was ~ 10% using TEM micrographs (total area of nano-size β-quartz crystals/total observation area). TEM images are 2-D images projection from 3-D objects (Figs. 3 a and b). Thus, the volume fraction of objects in the image will be underestimated using TEM images. Using reconstructed 3D images via TEMography software, homogeneous distribution of nano β-quartz crystals in LAS glass-ceramics was observed (Figs. 3 c and d). The rod-like, spherical and irregular morphologies were clearly shown in the 3D display. Assuming the morphology of nano β-quartz crystals are spherical with ~10 nm average diameter, and the calculated total number of nano β-quartz crystals is ~1500, a ~30% volume fraction of β-quartz crystals in glassy matrix can be estimated (the total volume of nano β-quartz crystals $1500 \times \sim 500\ nm^3$/the total reconstruction volume of $140nm \times 175\ nm \times 115\ nm$ is ~ 30%). Comparison of volume fraction of nano β-quartz crystals in LAS using different approaches is in progress.

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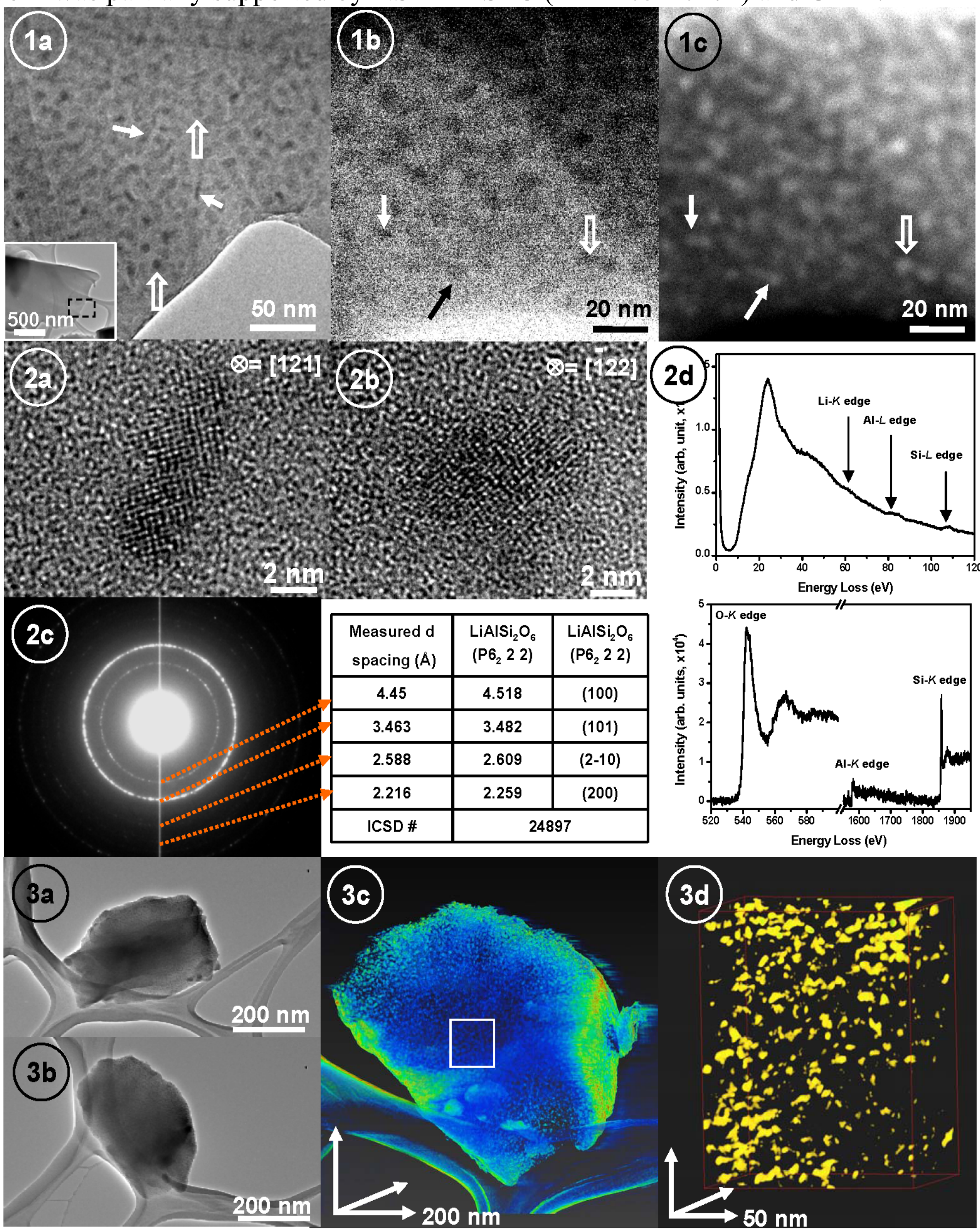

Measured d spacing (Å)	$LiAlSi_2O_6$ ($P6_2$ 2 2)	$LiAlSi_2O_6$ ($P6_2$ 2 2)
4.45	4.518	(100)
3.463	3.482	(101)
2.588	2.609	(2-10)
2.216	2.259	(200)
ICSD #	24897	

Fig. 1. TEM image (a), STEM BF (b) image and HAADF image (c) of LAS glass-ceramic shows rod-like (arrows) and round/spherical nanocrystals (open arrows).

Fig. 2. HRTEM images depict rod-like (a) and round/spherical (b) nano β-quartz crystals in glassy matrix. (c) SAD pattern obtained from area in Fig. 1(a). (d) EELS spectrum of LAS glass-ceramics.

Fig. 3. A series of TEM images of a LAS glass-ceramic particle obtained by tilting around the long axis of the particle, e.g., image at -50° (a) and +50° (b). (c) 3D reconstruction image of nano β-quartz crystals in LAS glass-ceramic. (d) Enlarged volume from the boxed area in (c).

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