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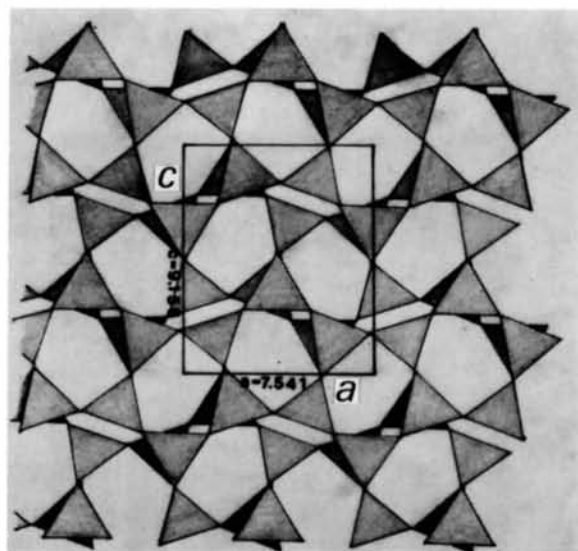
Electron microscopy of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass ceramics. By P. L. GAI and Q. Q. CHEN, *Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, England*

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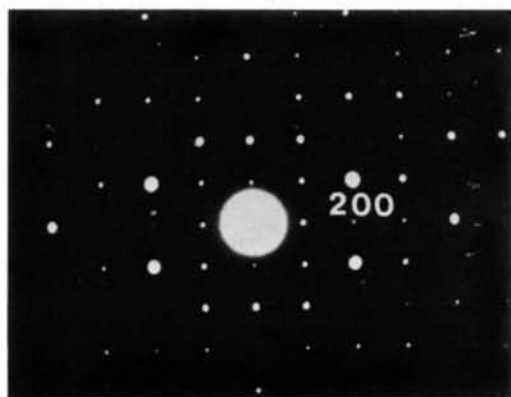
Abstract

A combination of high-resolution electron microscopy and electron diffraction methods is used to obtain microstructural information of lithium-bearing glass ceramics, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$ with TiO_2 as a nucleating agent (system *A*), and of the commercial system $0.68\text{Li}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 6.1\text{SiO}_2 \cdot 0.13\text{ZnO} \cdot 0.03\text{Na}_2\text{O} \cdot 0.01\text{K}_2\text{O} \cdot 0.11\text{TiO}_2 \cdot 0.077\text{ZrO}_2$ (system *D*). The experiments reveal the presence of small amounts of γ -spodumene in system *A*. In system *D*, the volume fraction of residual glass is estimated and the microstructure of various nucleating agents is elucidated.

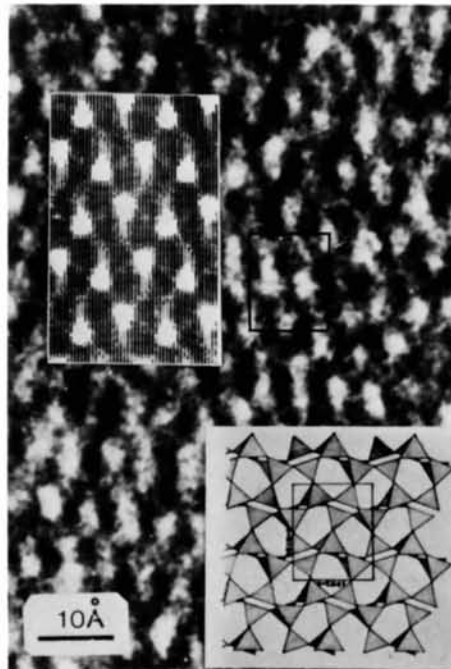
With the development of lithium-bearing glass ceramic materials for use in a diversity of commercial applications, the crystal structure and phase equilibrium studies in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass ceramics have become increasingly important. The superior properties of glass ceramics depend to a large extent on the crystal phases present, the microstructure, morphology and the residual glass (e.g. McMillan, 1975). Particular attention is paid to β - and γ -spodumene phases that can be formed in these low- or zero-expansion lithium-bearing glass ceramics. A combination of high-resolution electron microscopy of phase-contrast structure imaging and electron diffraction methods has been used here to examine crystallographic, microstructural and residual glass properties as well as the nature of nucleating agents of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$ glass ceramic with TiO_2 added as a nucleating agent (system *A*) and of the commercial glass ceramic system $0.68\text{Li}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 6.1\text{SiO}_2$ with nucleating agents $0.13\text{ZnO} \cdot 0.03\text{Na}_2\text{O} \cdot 0.01\text{K}_2\text{O} \cdot 0.11\text{TiO}_2 \cdot 0.077\text{ZrO}_2$ (system *D*) as such microstructural information is not revealed by conventional X-ray diffraction



(a)



(b)



(c)

Fig. 1. (a) Structure of β -spodumene with Si–Al tetrahedra in an aluminosilicate framework. The unit cell is outlined. (b) [010] electron diffraction pattern of β -spodumene. (c) Direct structure image of β -spodumene in (010) projection. Computer simulated image is inset for a defocus of -700 \AA (200 keV).

methods. Phase-contrast structure imaging is a powerful technique providing structural information at unit-cell level and is therefore very useful in the studies of mixed phases including minor phases and other inhomogeneities where microanalytical information may be obtained. The nucleating agents are added to the glass ceramics to modify their properties favourably.

The preparations of *A* and *D* using lithium carbonate, alumina and quartz with the nucleating agents have been described by Barry (1976) and Bold & Groves (1978). Powdered samples and thin foils were used for electron microscopy. The foils were prepared by ion thinning and were carbon coated to minimize charging of these very beam-sensitive materials. The thickness of the foils was estimated by stereo microscopy. High-resolution electron microscopy (HREM) was carried out using a JEOL JEM 200CX electron microscope at 200 keV with a point resolution of 1.7 Å and a CTF first zero of 2.4 Å at optimum defocus (Boyes *et al.*, 1980). The results are as follows.

$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2-\text{TiO}_2$: Three different polymorphs have been reported in the literature for the spodumene composition $\text{LiAlSi}_2\text{O}_6$, termed either (α, β, γ) spodumene or $\text{LiAlSi}_2\text{O}_6$ I, II, III. When a glass of the spodumene composition is heat treated the first crystallization product is hexagonal $\text{LiAlSi}_2\text{O}_6$ III (also known as β -quartz solid solution). As the temperature and time of the heat treatment is increased γ -spodumene transforms into tetragonal β -spodumene. The diffraction pattern and direct structure images of the heat-treated samples confirmed the main crystalline phase to be β -spodumene, with $a = 7.541$, $c = 9.156$ Å, space group $P4_32_12$ (or $P4_12_12$) and $Z = 4$. The structure of β -spodumene is described by Li & Peacor (1968). It consists of interlocking five-membered rings of Si-Al tetrahedra in an aluminosilicate framework with rings parallel to a and b axes, creating channels as in zeolites (Fig. 1a). Lithium is located between two tetrahedra and Si and Al

are distributed randomly. The occupancies are determined accordingly. Fig. 1(b) shows the electron diffraction pattern in (010) projection. The direct structure image in (010) is shown in Fig. 1(c) together with a computer-simulated image (inset) calculated using the crystal-structure data of Li & Peacor (1968). The image is at a defocus value (Δf) of -700 Å and for a foil of thickness (t) 75 Å. The Δf value

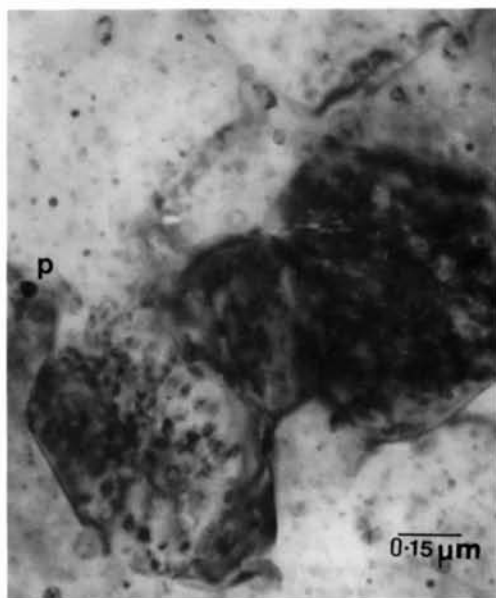
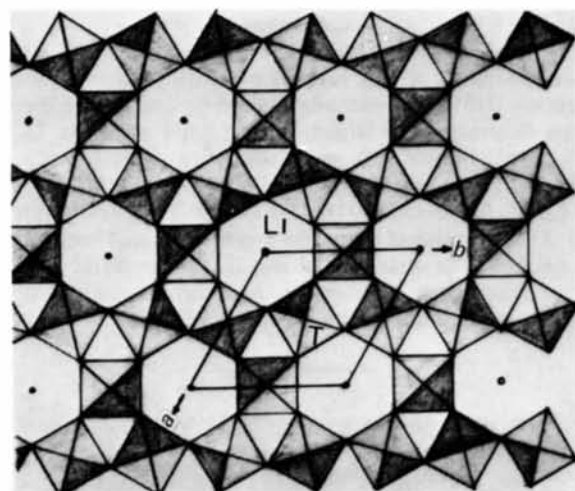
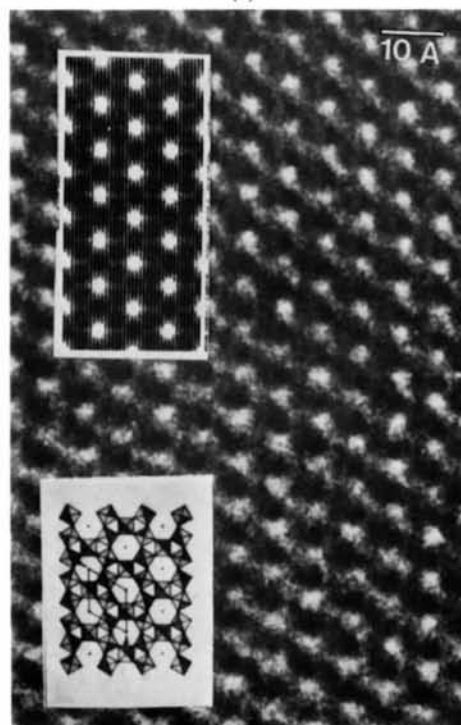


Fig. 2. Microstructure of β -spodumene showing TiO_2 particles, e.g. at *P*.



(a)



(b)

Fig. 3. (a) Structure of hexagonal γ -spodumene in (0001) projection. Li atoms are four-coordinated and each Li tetrahedron shares edges with Si-Al tetrahedra. Si-Al tetrahedra (e.g. *T*) form six- to eight-membered interconnecting rings creating channels. (b) Direct structure image on (0001) with simulated image inset, defocus = -800 Å (200 keV).

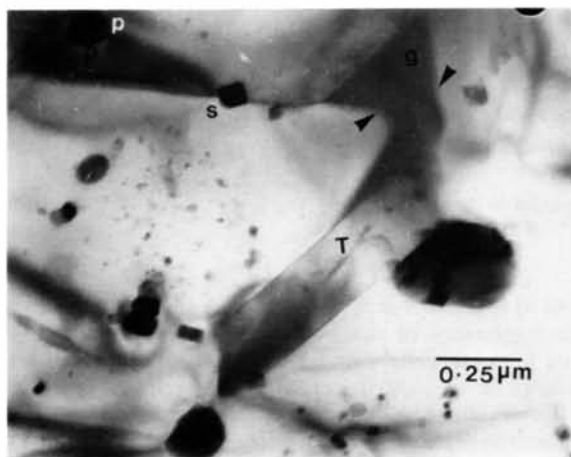


Fig. 4. Microstructure of system *D* ($0.68\text{Li}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 6.1\text{SiO}_2$ with nucleating agents) showing TiO_2 in the form of anatase/rutile particles (at *P*), $\text{TiO}_2\text{-ZrO}_2$ solid solutions as needles (*T*), gahnite crystals (at *S*) and a glass pocket (at *g*).

was determined experimentally using the minimum contrast at zero focus as a reference. The agreement between computed and observed image is satisfactory given the uncertainties in determining Δf and t . The rows of bright white spots correspond to rows of five-membered rings. The rings parallel to the a and b axes have a free diameter of $\sim 3 \text{ \AA}$ and are responsible for ion-exchange properties of β -spodumene. The presence of β -spodumene as the main phase was also confirmed by X-ray diffraction.

The typical microstructure of the ceramic is shown in Fig. 2. The TiO_2 added as a nucleating agent remains in the form of anatase particles inside the grains, e.g. at *P*, confirmed by analytical electron microscopy (AEM) and HREM. Some particles at grain boundaries grow into larger particles. Direct structure imaging of the intergranular regions showed that system *A* contained very little residual glass, extending in some cases to only about 10 \AA or less (Chen & Gai, 1982). High-resolution electron microscopy of the system also revealed some crystallites with hexagonal $\text{LiAlSi}_2\text{O}_6$ III structure (γ -spodumene), which were not revealed by X-ray diffraction methods. The unit-cell parameters of the structure are $a = 5.217$, $c = 5.464 \text{ \AA}$ and its space group is $P6_222$. The structure consists of Si-Al tetrahedra (with randomly distributed Si and Al) which form interconnecting six- or eight-membered rings creating channels (Li, 1968). Lithium is four-coordinated and occupies interstitial positions. The projection of the structure on (0001) and the direct structure image are shown in Figs. 3(a) and (b), respectively. The computed image (inset) is based on the X-ray structure data of Li (1968) and corresponds to $\Delta f = -800 \text{ \AA}$, $t = 100 \text{ \AA}$, estimated as before. The agreement between the two images is again satisfactory. The amount of

γ -spodumene was estimated to be roughly of the order of 1–2%.

In system *D*, however, the main crystallographic phase was found to be β -spodumene solid solution and residual glass existed in larger amounts occurring as pockets or intergranular films. The volume fraction of glass in *D*, measured by point counting, was 14–16%. The microstructure of *D* is shown in Fig. 4 with TiO_2 occurring as anatase/rutile particles (e.g. at *P*) or $\text{TiO}_2\text{-ZrO}_2$ solid solutions as needles at *T*, and gahnite (ZnAl_2O_4) crystals at *S*, all confirmed by AEM and HREM. The presence of a residual glass pocket is shown at *g*. In *D*, in the heat treatment studies, the particles, needles, etc. arising from the nucleating agents were observed to grow in size at higher temperatures but they retained their chemical composition. The amounts of the particles were consistent with the glass composition described earlier.

In summary, examination of crystal-structure properties of glass ceramics by electron microscopy methods has revealed that in system *A*, apart from β -spodumene as the main phase, a small amount of hexagonal γ -spodumene is present in the ternary system, not detected by conventional X-ray diffraction methods. In system *D*, the main crystal phase is β -spodumene solid solution. The nature, microstructure and locality of the various phases due to nucleating agents (which are vital components in glass ceramics) have also been described. Detailed work describing the composition of the grain boundaries and characteristics of grain growth is to be published (Chen, Gai & Groves, 1982).

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