Silicate melts with indications of ino structures.

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Summary. Evidence is presented for the existence of silicon-oxygen chains up to 1 000 Å. in length in melts of $CaMgSi_2O_6$ and of $LiAlSi_2O_6$ at temperatures a little above the melting point.

THE structure of silicate melts has pressing importance to geochemists, mineralogists, ceramicists, and slag metallurgists. Since ino-silicate compounds such as $CaMgSi_2O_6$ (diopside) and $LiAlSi_2O_6$ (spodumene) have petrological as well as industrial significance the synthetic melts of these compounds were chosen for this study.

Goldstein and Davies[1] in their work on phosphate linear polymers pointed out that the conflict between views concerning the presence and orientation of chain like structures in supercooled melts suggests the value of additional evidence for or against the existence of chain 'molecules' in glasses.

Preparation of the bulk samples. Pure $CaCO_3$, MgO, Al_2O_3, SiO_2, and Li_2CO_3 were used to prepare a homogeneous glass for each composition corresponding to either $CaMgSi_2O_6$ or $LiAlSi_2O_6$. Each mixture was thoroughly fused in platinum containers until free of gas bubbles, after which the glass was analysed for correct chemical composition. Each glass was then thoroughly devitrified. The polycrystalline aggregates were then examined by optical microscopy, and X-ray and electron diffraction in order to ascertain whether indeed the particular compound with its particular ino structure had been formed.

The polycrystalline material was then remelted and cooled into a glass. This bulk glass was then carefully examined for absence of crystalline matter by means of a polarizing microscope (using objectives with NA up to 1·4), electron transmission with a resolution between 10 and 15 Å., and X-ray and electron diffraction. All these techniques indicated absence of crystalline material.

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[1] M. Goldstein and T. H. Davies, Journ. Amer. Ceram. Soc., 1955, vol. 38, p. 223.

Experimental methods and results. The experimental glasses were examined in the bulk and fibre forms by means of high resolution petrographic microscopy, X-ray diffraction (von Laue type flat-back camera), and electron transmission (RCA EMU-2D electron microscope with double objective pole piece). The electron micrographs were selected on the basis of being in good focus and free of any astigmatism or image motion.

Diopside, an ino-silicate, was rapidly melted up to a temperature of 1 510° C. The supercooled bulk melt was examined for absence of crystalline material as described above. Numerous electron transmission photographs of this substance showed poorly oriented chain-like structures. The chains appeared to have lengths from 500 Å. down. An attempt was then made to ascertain whether longer linear elements could be formed in the diopside melt. Since the chains are preformed in the crystalline state where their maximum length theoretically would be the length of the crystal in the direction of its *c*-axis (to which they are parallel) and in general their minimum length the length of the *c*-axis for the unit cell, it was felt that pyrolytically grown crystals held just below the liquidus for 96 hours might furnish longer chains.

Since it appears that the devitrification rate of a one-component melt would be related among other factors to the size of the nuclei present, it was interesting to note that any attempt to pull glass fibres from the diopside melt prepared from larger crystals failed even at 1 510° C. owing to very rapid crystallization. A similar melt prepared from smaller crystalline material allowed glass fibres to be pulled at 1 393° C., or only about 2° C. above the liquidus.

Spodumene, also an ino-silicate, was examined in the bulk glass form by means of high resolution electron transmission. Linear elements were clearly visible in the photographs. The chain length ranged again from 500 Å. down. Attempts, similar to those employed on the diopside melt, to enlarge the Si–O chains resulted in chains approximately 1 000 Å. long (fig. 1).

It seemed reasonable to assume that if indeed Si–O types of chains are present in the melt it should be possible to orientate such units by mechanically pulling glass fibres at high speeds from such fluids. From an electrically heated platinum container with a small funnel in the bottom glass fibres with diameter ranging from 16×10^{-5} to 21×10^{-5} in. were pulled by means of a high-speed electrically driven spindle. These fibres were then examined by powder electron diffraction techniques and were found to be free of crystallites.

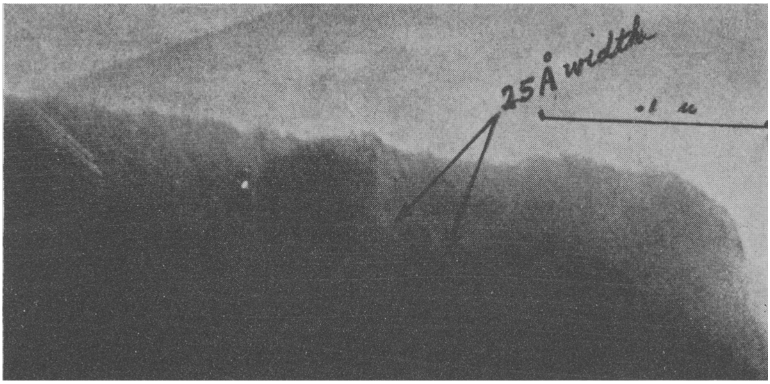

FIG. 1. Electron transmission picture of an $LiAlSi_2O_6$ glass fibre.

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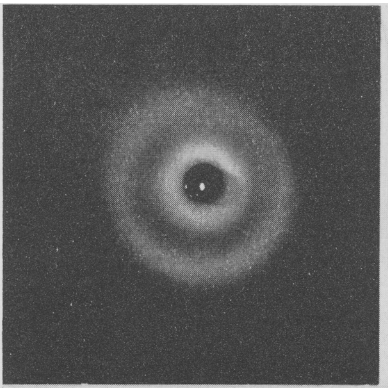

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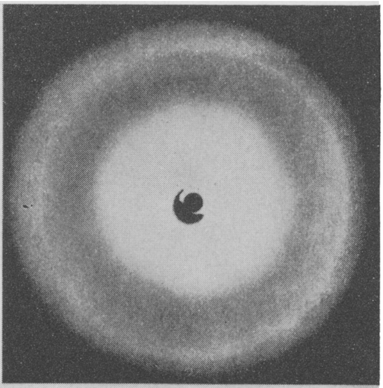

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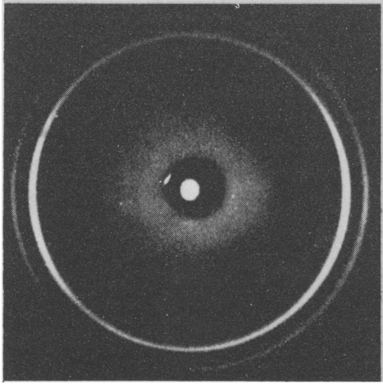

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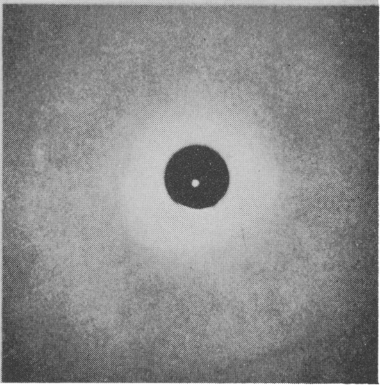

FIGS. 2–4. X-ray diffraction patterns of $LiAlSi_2O_6$ glass fibres.
FIG. 5. X-ray diffraction pattern of a commercial high-silica glass fibre.

The classical method of determining preferred orientation of polymers in fibres is by the use of von Laue type flat-back cameras. Such a unit employing copper radiation was employed. Figs. 2 to 4 show some of the typical results obtained. It appears that pulling rates and temperature strongly affect the results obtained. We are in the process of determining the effect of some of these variables on the degree of orientation. Examination of the patterns obtained indicated that diffraction is occurring from (*hk*0) planes at right angles to the long axis of the chains. Apparently groups of chains have locally aligned themselves so well as to form regions of order resulting in a few very mosaic *hk*0 reflecting units. For comparison purposes an X-ray pattern of normal commercial (high silica) glass is included, fig. 5. Optical examination of the fibres revealed a slight anisotropism resulting from different optical densities parallel and at right angles to the long axis of the fibres.

Conclusions. The author has attempted using some of the modern tools and techniques available to discover whether indications concerning the structure of some specific one-component silicate melt could be obtained. The experimental data so far assembled and the theoretical discussions brought forth in a previous paper appear to indicate to us that some hesitancy in the acceptance of the general network theory of silicate glasses might well be defensible. The author is well aware that considerable work remains to be done and in a later paper will publish some additional data on other specific one- and two-component silicate melts.