Fig. 4. Scanning electron micrograph and nondispersive X-ray analysis of SiC specimen hot-pressed with 2 vol% Al_2O_3 and oxidized for 20 h at 1370°C in pure dry O_2 at 1 atm pressure.

covered with a glassy layer which was thicker over the streaks, but obscured their distinct boundaries. The specimen was therefore successively polished to remove the glassy layer from the surface, after which the exact streak geometry was revealed again. It is clear from these micrographs that a massive scale is formed over these streaks during oxidation.

A scanning electron micrograph of the oxidized surface of an Al_2O_3-streaked SiC specimen (Fig. 4) shows the gas pores through which CO gas escapes during oxidation.[8] These pores are concentrated in the oxide covering the streak. This observation, along with the glassy appearances of this scale, strongly suggests that, at the

*The presence of a liquid was inferred by the glassy appearance of the oxide scale, which also contained crystalline phases as reported above.

oxidation temperature, a liquid phase is formed over the streak. The results of a nondispersive X-ray analysis (Fig. 4) show that Si, Al, K, and Fe are present in the oxide formed over the streak, whereas only Si is detected in the oxide layer covering the rest of the SiC material. The presence of K and Fe (as oxides) can explain the formation of the liquid phase covering the streak, since a liquid phase should not be formed by the reaction between Al_2O_3 and SiO_2 until $\approx 1600°C$.[9]

This evidence suggests that the greater concentrations of impurities associated with either the Al_2O_3 residual phase or the Al_2O_3-SiC phase boundaries cause the formation of a liquid, Al-rich silicate at the oxidation temperature. It is likely that oxygen transport through an impure aluminosilicate liquid is faster than that through the pure SiO_2 scale, thus causing decreased oxidation resistance. Based on the hypothesis that a liquid forms over the Al_2O_3 streaks,* it can be inferred that increasing the amount of residual Al_2O_3 increases the area fraction of the liquid formed during oxidation at 1370°C, thus explaining the oxidation behavior of SiC hot-pressed with different amounts of Al_2O_3.

It should also be noted that the cracks radiating from the corners of the indentation (Fig. 3) are filled with the oxidation product. As suggested by crack-healing experiments,[10] any reduction in strength caused by the introduction of large cracks in hot-pressed SiC might be restored after prolonged oxidation.

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Pyroelectric Response in Transparent Ferroelectric Glass-Ceramics

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When the network system is limited, most ferroelectric glass-ceramics will produce a fully crystallized transparent body when cerammed at low temperatures. Higher-temperature heat treatment results in crystal growth and gradual loss of transparency. In the transparent state, the crystal size is limited to ≈ 2000 Å. Piezoelectric and hysteresis loop measurements have failed to detect evidence of ferroelectricity, but the present pyroelectric measurements show that fully transparent glass-ceramics can be ferroelectric.

I. Introduction

SINCE Herczog[1] investigated the devitrification of complex glasses to form a ferroelectric crystalline phase, studies have shown that a wide range of ferroelectrics can be crystallized from glass. By proper control of the glass composition and ceramming schedule, the ferroelectric phase can be completely crystallized while the crystallite size is maintained at ≤ 500 Å. Borrelli and

Layton,[2] who attempted to determine the ferroelectric nature of these crystallites, found that neither the electrooptic effect nor ferroelectric hysteresis could be detected in crystallites smaller than 500 Å. They proposed a stress-induced effect, analogous to that proposed by Buessem et al.[3] for $BaTiO_3$, which would result in the preservation of the high-temperature paraelectric state in the very small crystallites. The present pyroelectric measurements, however, show that even these minute crystals are ferroelectric.

II. Experimental Procedure

The glass from which the experimental samples were prepared contained the constituents of the ferroelectric phase, $0.9Na_2O\cdot$
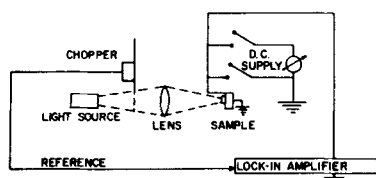
Fig. 1. Measuring apparatus.

Fig. 2. Pyroelectric response of glass-ceramics.

Fig. 3. Weak-field permittivity.

$0.1CdO \cdot Nb_2O_5$, plus a network-forming phase consisting of 14 wt% SiO_2 and 2 wt% TiO_2. The glass was melted at 1500°C in a Pt crucible and quenched. The transfer of the molten material into the quenching mold was mechanized to obtain a large number of disks 1 cm in diameter and 1 mm thick. The glass was heat-treated in a small tube furnace using a controlled rate of heating and cooling (100° C/h) at several ceramming temperatures.

After heat treatment, evaporated electrodes consisting of successive layers of Al-Ni-Au were applied, and dielectric measurements were made on a bridge.* These samples were then ground and polished to a thickness of 2 mils, and $^3/_{32}$-in.-diam. Au[†] electrodes were applied for pyroelectric measurements.

The circuit used to measure the pyroelectric response is shown in Fig. 1. The light from a Zr arc lamp[‡] was focused onto the electrode of the sample by a fused-silica lens 1.5 in. in diameter with a focal length of 5 cm. The lens was adjusted so the lamp light essentially covered the electrode of the sample. The sample was connected to the dc bias supply by fine Au leads cemented to the periphery of the electrodes by air-drying Ag paint. These leads were also used to connect the sample to the lock-in amplifier used to measure the pyroelectric response. The lock-in amplifier was phased with the rotating sector disk by a photocell.

The sample was initially biased to a predetermined level for 2 min. The bias supply was then removed, and the sample was short-circuited for 10 s to remove any surface charge. After 2 min, the pyroelectric response was read with the lock-in amplifier. The chopping speed was 27 Hz with an off-on ratio of 10:1.

No apparatus was available which could accurately measure the total energy incident on the electrodes; in fact, without knowledge of the absorbing characteristics of the electrodes used, such information would be of little value. To give some basis for comparison, however, a single crystal of $BaTiO_3$ was electroded and poled in a similar manner to 15 kV/cm. The pyroelectric response from this sample was 350 μV.

III. Results

The results obtained for samples heat-treated under various conditions are shown in Fig. 2. The sample treated at 800°C for 2 h was clear, that treated at 900°C for 24 h was hazy, and the others were white and opaque. After each sample had been poled and examined at the various field levels, the polarity of the bias field was reversed, and the sample was poled for 5 min at the same maximum field strength it had experienced previously. In all cases, the sign of the pyroelectric signal reversed, indicating the existence of a reversible spontaneous polarization, positive proof of ferroelectric behavior.

The data in Fig. 2 show that the magnitude of the pyroelectric output increases with poling field strength, as is to be expected, and, more significantly, that the output at the maximum bias field strength increases with heat treatment up to 960°C for 2 h and then decreases for the sample treated at 1075°C for 8 h. These results should be compared to the weak-field permittivity data shown in Fig. 3, which indicates that the magnitude of the weak-field permittivity increases with increasing severity of heat treatment, with the temperature of the peak moving continuously upward.

IV. Discussion

In such compositions, where the content of the network-forming phase is limited, crystallization is very rapid and results in the
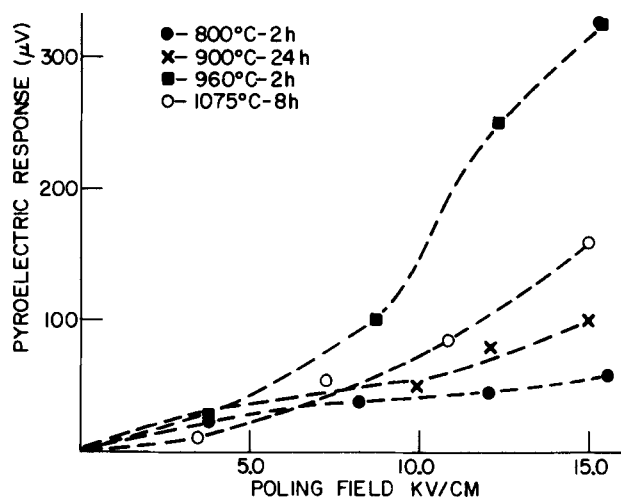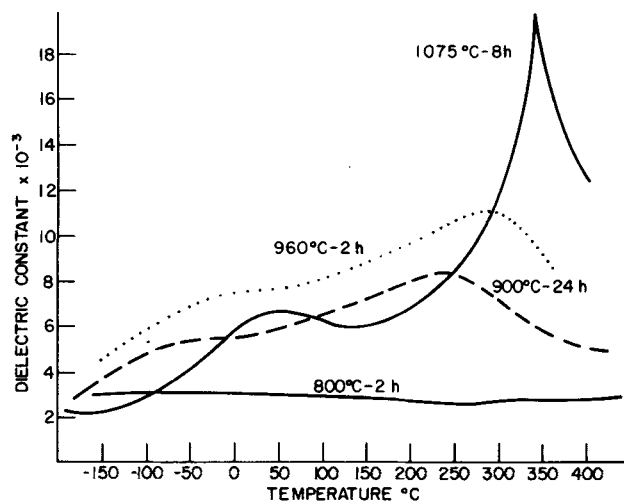
formation of a very large number of small crystallites. Electron micrographs show that, in the early stages of crystallization (Fig. 4), a dendritic type of growth occurs which is visible only in transmission. Further heat treatment results in consolidation of the spherulite and exsolution of the silicate phase (Fig. 5). This behavior frequently results in apparent shrinkage of the crystallite when it is viewed by standard replication techniques (compare the samples cerammed at 800° and 900°C). After the crystallite has consolidated, further heat treatment results in grain growth, and, in many glass-ceramics, crystallization of a second phase. In the case of the present Na_2O-CdO-Nb_2O_5 system, this second phase is cristobalite.

The experimental data obtained establish the existence of ferroelectric phenomena in heat-treated glass-ceramic specimens. Moreover, this phenomenon is shown to be manifest in transparent materials with very small localized crystalline regions of the order of ≤ 1000 Å. It is quite remarkable that these very small crystalline species can support a field-reversible spontaneous polarization. More importantly, the electron micrographs indicate that, whereas the aggregate diameter of the crystalline regions is of the order of 1000 Å, the actual contiguous crystalline areas (i.e. the individual spires of the dendritic crystallites) are much smaller, perhaps of the order of 50 to 60 Å in diameter and several hundred angstroms long. In such a crystalline species, it is difficult to imagine the occurrence of less than 180° polarization reversal, i.e. it is postulated that the axis of the polar vector lies parallel to the individual spire and that polarization reversal lies along this axis. The depolarization field
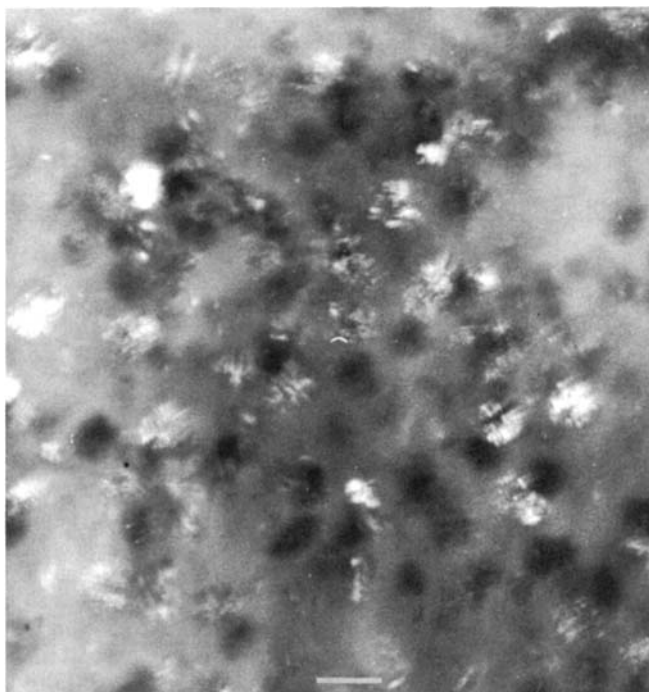
Fig. 4. Transmission electron micrograph of glass-ceramic cerammed at 800°C. Marker = 1000 Å.

Fig. 5. Surface replicas of samples heat-treated at (A) 800°C for 2 h, (B) 900°C for 24 h, (C) 960°C for 2 h, and (D) 1075°C for 8 h. Marker = 1 μm.

would also be minimized in such a configuration. Displacements of ions as a result of thermal agitation would be minimal because of the internal stress inherent in such a configuration, thus accounting for the low value of the pyroelectric effect. Also, in such a crystalline array, the development of the crystalline phase must of necessity be very imperfect, so that probably only a small fraction of the crystalline phase would be sufficiently well developed to support a field-reversible spontaneous polarization.

At higher heat-treatment temperatures, as the crystalline regions consolidate and exsolution of the network-forming species occurs, the crystalline regions take on more of a 3-dimensional character. Less than 180° switching now becomes possible, clamping is reduced, and the full dielectric character of the crystalline species begins to manifest itself to external measurements. This behavior is shown by an increase in the weak-field permittivity, by better definition of the peak in the dielectric constant, and by an increase in the pyroelectric response. At still higher ceramming temperatures, i.e. ≈ 1000°C, a second phase (cristobalite) appears. In this temperature region, the weak-field dielectric properties become more pronounced, but in this system the pyroelectric response decreases. Studies in other systems show that this decrease in pyroelectric response is atypical of the behavior of ferroelectric glass-ceramics.

The reason for this decrease in pyroelectric response in $Na_{1-x}Cd_{x/2}NbO_3$ is not clear, although it may be associated with the proximity of a tetragonal-orthorhombic phase transition near room temperature. The transition causes a peak in the dielectric constant near room temperature. The measured height and actual temperature of the peak depend markedly on the previous history of the sample, i.e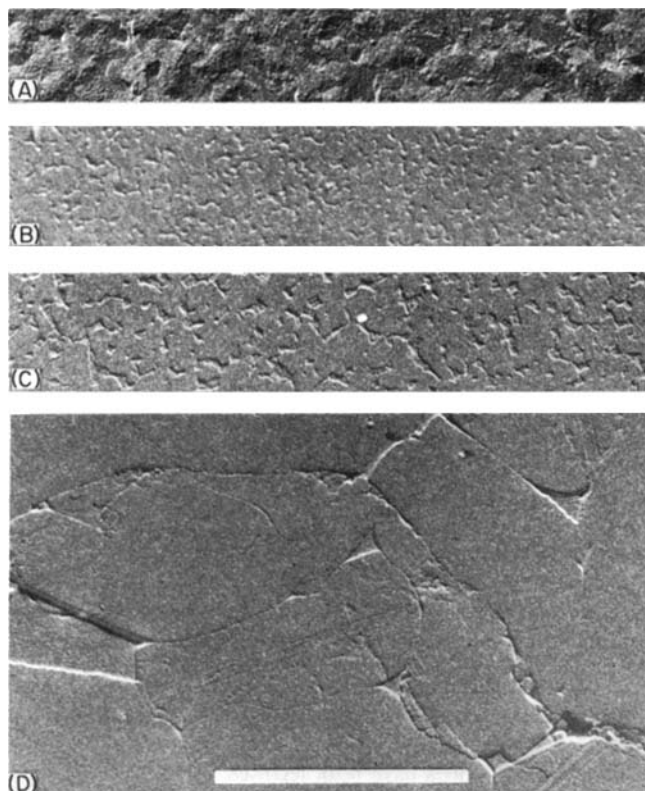. whether the dielectric constant was previously measured at high or low temperature. The thermal instability of this transition suggests that the individual crystallites may be highly subject to influences from external stimuli such as clamping.

V. Conclusions

At very early stages of heat treatment, glass-ceramics in the $Na_2O-CdO-Nb_2O_5$ system crystallize with a dendritic structure. These materials are transparent and show a field-reversible spontaneous polarization indicative of ferroelectricity.

Moreover, the pyroelectric effect increases with increasing heat treatment to a point where a decrease is noted. The temperature region in which this decrease occurs is characterized by the formation of cristobalite in the glass-forming network. The dendritic structures found in the early stages of heat treatment, while the materials are still transparent, may be the most minute ionic species ever shown to exhibit ferroelectric behavior.

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