JOURNAL OF MATERIALS SCIENCE 16 (1981) 1023–1028

# $Ba_2TiGe_2O_8$ and $Ba_2TiSi_2O_8$ pyroelectric glass-ceramics

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Pyroelectric glass-ceramics of composition $Ba_2TiGe_2O_8$ and $Ba_2TiSi_2O_8$ were prepred by crystallizing the glasses in a temperature gradient. High pyroelectric responses up to 50% of the single-crystal values were observed because of the high degree of orientation of the crystallites in the glass-ceramic samples. The piezoelectric and dielectric properties of the glasses and the glass-ceramics are also consistent with the properties of the single crystals.

## 1. Introduction

Pyroelectric lithium disilicate glass-ceramics have recently been prepared by growing highly orientated surface layers of lithium disilicate crystals by crystallizing the glasses of stoichiometric glass compositions $Li_2O \cdot 2SiO_2$ in a temperature gradient [1]. This technique provides a method of fabricating large and inexpensive pyroelectric devices. However, one difficulty encountered in working with the lithium disilicate pyroelectric glass-ceramic was that thin targets (of thickness, $d < 200\,\mu m$) cut perpendicular to the growth direction (the polar $c$-axis of $Li_2Si_2O_5$) were extremely fragile and could not be prepared routinely.

In this study pyroelectric glass-ceramics of barium titatnium silicate (BTS: $Ba_2TiSi_2O_8$ or fresnoite) and barium titanium germanate (BTG: $Ba_2TiGe_2O_8$) are described, the physical properties of which are superior to $Li_2Si_2O_5$. Thin sections of these glass-ceramics, less than $100\,\mu m$ in thickness, can easily be prepared since they are mechanically much stronger. Glass-ceramics of BTG and BTS were prepared by crystallizing glasses of stoichiometric compositions of BTG and a silica-rich composition ($64SiO_2$–$36BaTiO_3$) of BTS in a thermal gradient. The dielectric and pyroelectric properties were measured and compared with the properties of single crystals.

In the single-crystal form fresnoite belongs to the crystallographic point group 4mm and is pyroelectric [2]. $Ba_2TiGe_2O_8$ is reported to be a ferroelastic [3, 4] below 810° C and belongs to the orthorhombic polar point group mm2. In the paraelastic phase above the transition temperature, $T_c$, BTG also belongs to the tetragonal point group 4mm.

Glass-ceramics in the $BaTiO_3$–$SiO_2$ system have been previously investigated. Herczog [5] studied the crystallization of $BaTiO_3$ in a silicate glass matrix. Dielectric and electro-optic measurements on transparent glass-ceramics containing ferroelectric $BaTiO_3$ in a glass matrix have also been reported [6]. However, the primary interest in these materials has been concerned with the dielectric and electro-optic properties of the glass-ceramics, and in the ferroelectric nature of $BaTiO_3$ crystallites surrounded by a glass matrix. In these studies no efforts have been made to develop glass-ceramics containing orientated crystallites. The present study describes the preparation and characterization of glass-ceramics containing orientated crystallites of the pyroelectric (but non-ferroelectric) BTS and BTG phases.

## 2. Experimental details

Glasses of composition $64SiO_2 \cdot 36BaO \cdot 36TiO_2$ were prepared by mixing reagent-grade silicic acid*, barium carbonate† and titanic oxide‡,

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‡Eagle–Picher Industries, Inc., Quapaw, Oklahoma, USA.

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followed by melting in a globar furnace. Fresnoite has a high melting point (1400° C) and thus, it was difficult to obtain bubble-free glasses of the stoichiometric composition. To avoid this problem, a composition was selected which lies near the eutectic point on the silica-rich side of the $BaTiO_3$–$SiO_2$ binary phase diagram [7]. This composition lies well within the range of glass formation in the $BaTiO_3$–$SiO_2$ system.

In the case of BTG, reagent-grade barium carbonate, germanium oxide* and titanic oxide were mixed and melted in the furnace. In both cases, the melts were maintained at 1375° C for 24 hours for fining and homogenization. Transparent samples were obtained by pouring the melt into a graphite mould. The samples which crystallized during pouring of the melt were remelted and poured again into the graphite mould in order to ensure transparent glass samples. All the glass samples were annealed at 600° C for 12 hours and then cut and polished in the form of thick disks in preparation for the crystallization studies. To determine the crystallization temperatures of the glass compositions, differential thermal analysis (DTA) measurements were performed on the glass samples. Exothermic peaks were observed at 860° C in the case of BTS and at 800° C in the case of BTG, as shown in Fig. 1.

Crystalization was carried out in a temperature gradient by placing the polished glass samples, in the form of thick disks, on a microscope hot stage.† The temperature gradient near the hottest temperature zone was perpendicular to the surface of the sample and it was estimated to be about 100° C mm$^{-1}$. Typical heating cycles used for glass crystallization are shown in Fig. 2. The heating cycle consisted of an initial rapid rise in temperature to minimize volume nucleation, followed by a slow increase in temperature at a rate of about 3° C min$^{-1}$. After reaching the maximum crystallization temperature (1100° C for BTS and 1000° C for BTG), the samples were held at this temperature for 24 hours. The temperature was then decreased rapidly to room temperature. The thicknesses of the crystallized portions of the glasses ranged from 1 to 2 mm, depending on the heating cycle.

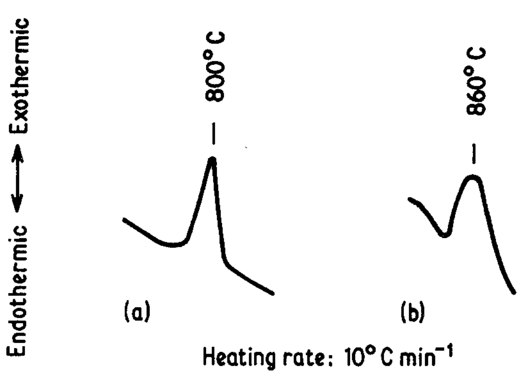

*Figure 1* DTA heating curves of (a) BTG and (b) BTS glasses.

The degree of preferred orientation of the glass-ceramic was evaluated from X-ray diffractometer patterns. X-ray diffraction (XRD) patterns were recorded on surfaces normal to the direction of the temperature gradient (Fig. 3). The XRD patterns were compared with the standard powder diffraction patterns to determine the relative degree of orientation. The dielectric constants of glass and glass-ceramic disks were measured with a capacitance bridge. The piezoelectric behaviour parallel to the crystallization direction was studied using a $d_{33}$-meter.‡ The samples were thinned down to about 200 $\mu$m in thickness and the pyroelectric response was measured by the dynamic Chynoweth technique [8] at a modulating frequency of 4 Hz. The pyroelectric signals on glass-ceramics were compared with the responses from single crystals of the BTG and BTS. The densities of BTG, BTS glasses and glass-ceramic samples were determined by a mercury porosimeter§ and compared with the densities of single crystals.

## 3. Results and discussion

Table I summarizes the data for the glass and glass-ceramic samples. Single-crystal values are also listed for comparison.

X-ray powder diffraction patterns of the crystallized samples showed that the principal crystallized phases were fresnoite in the BTS glass-ceramics and $Ba_2Ge_2TiO_8$ in the BTG glass-ceramic samples. A few low-intensity peaks of an unidentified phase were observed in the powder diffraction patterns of both compositions. The samples showed highly orientated crystal growth

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*Eagle–Picher Industries, Inc., Quapaw, Oklahoma, USA.

†Model No. 493, manufactured by E. Leitz, Inc., Rockleigh, NJ, USA.

‡Model CPDT 3300, manufactured by Channel Products, Chesterland, OH, USA.

§Model JS-7146, manufactured by American Instrument Co., Silver Spring, MD, USA.

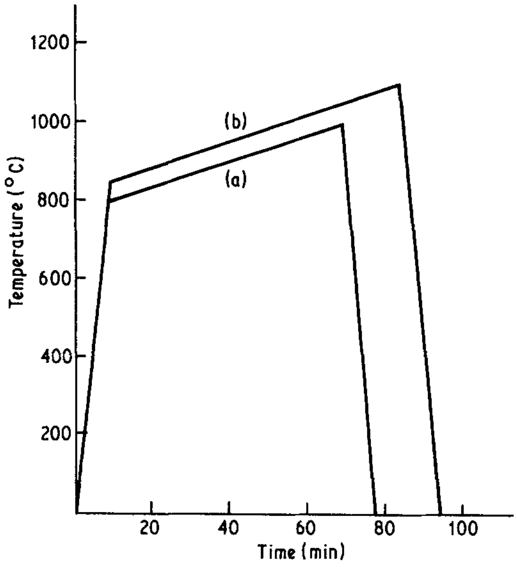

*Figure 2* Heating cycles used for crystallizing (a) BTG and (b) BTS glasses.

in a direction parallel to the temperature gradient, with the polar *c*-axis perpendicular to the hot surface of the sample. As shown in Fig. 4, the 0 0 2 reflection was the strongest in the X-ray patterns of the crystallized surfaces. The ratio of the intensity of the 0 0 2 peak to that of the 2 1 1 peak was taken as a measure of the relative degree of orientation. The intensity ratios are given in Table I. Comparison of the intensity ratios in the glass-ceramic samples with the intensity ratios of a standard powder pattern, showed a high degree of orientation of the crystallites in the glass-ceramics. An even higher degree of orientation was obtained in the samples with good surface finish.

The degree of preferred orientation in crystallized samples of BTS and BTG was similar to that observed previously [1] in $Li_2Si_2O_5$. It was observed that the degree of orientation of the crystallites in the isothermally crystallized glass-ceramics was poor compared to the samples crystallized in a temperature gradient. In addition, detailed studies of the microstructure of the crystallized samples showed that the thickness of the well-orientated region was larger in the case of samples crystallized in a temperature gradient, indicating that thermal gradient crystallization is preferable for obtaining well orientated glass-ceramics.

The main reason for the orientation of the crystallites is surface-nucleated crystallization which takes place in both the isothermal and temperature-gradient crystallization. A higher degree of electrical and crystallographic orientation is obtained in the temperature-gradient crystallization method due to the absence of volume nucleation; however, in the case of isothermal crystallization, the orientation of the crystallites is limited to a layer only a few micrometers thick due to the simultaneous occurrence of volume nucleation. Atkinson and McMillan [9] attempted to produce a $Li_2Si_2O_5$ glass-ceramic with an aligned microstructure by a hot-extrusion method. They were partially successful in obtaining glass-ceramic samples with the disilicate crystal crystallographically-aligned parallel to the extrusion axis. However, the degree of orientation of the crystallites was less than that obtained in glass-ceramic samples prepared by crystallizing the glasses in a temperature gradient [1].

The density of BTG glass was about the same as

TABLE I Summary of data for glass and glass-ceramic samples

| Sample | X-ray intensities, $\frac{I(0\,0\,2)}{I(2\,1\,1)}$ | Dielectric constant, $\epsilon$* | Dissipation factor* | Density ($g\,cm^{-3}$) | $d_{33}$ ($\times 10^{12}\,C\,N^{-1}$) | Pyroelectric response |
|---|---|---|---|---|---|---|
| BTG glass | — | 17 | 0.003 | 4.74 | — | 50% to 60% of single-crystal value |
| BTG glass-ceramic | 85 | 15.0 | 0.002 | 4.56 | 5 to 7 | |
| $Ba_2Ge_2TiO_8$ single crystal | 0.2 (standard powder pattern) | $\epsilon_{11} = 20$<br>$\epsilon_{22} = 20$<br>$\epsilon_{33} = 13$ | 0.003 | 4.84 | 8 | |
| BTS glass | — | 15 | 0.002 | 4.01 | — | 50% to 60% of single-crystal value |
| BTS glass-ceramic | 15 | 12.5 | 0.002 | 3.90 | 2 to 3 | |
| $Ba_2Si_2TiO_8$ single crystal | 0.2 (standard powder pattern) | $\epsilon_{11} = \epsilon_{22} = 15$<br>$\epsilon_{33} = 11$ | 0.003 | 4.45 | 3.8 | |

*Measurements were made at 1 MHz for the glass and glass-ceramic and at 1 kHz for single crystals.

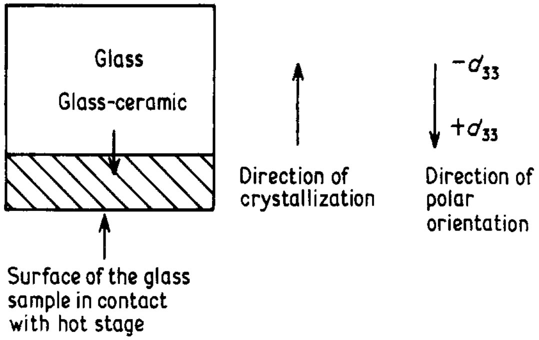

*Figure 3* The direction of polar orientation in glass-ceramic samples.

the single-crystal form (Table I), while that of BTS glass was slightly lower than the density of fresnoite single crystals because of the excess silica used in the BTS composition. Only a small decrease in density occurred on crystallization of the glass phases, indicating a low concentration of voids in the glass-ceramic samples. Samples as thin as 100 μm could be prepared without difficulty because of the absence of pores and cracks.

The dielectric constants of BTS and BTG glasses measured at 1 MHz are very close to the mean dielectric constant, $(\epsilon_{11} + \epsilon_{22} + \epsilon_{33})/3$, of the corresponding crystalline phases. On crystal-

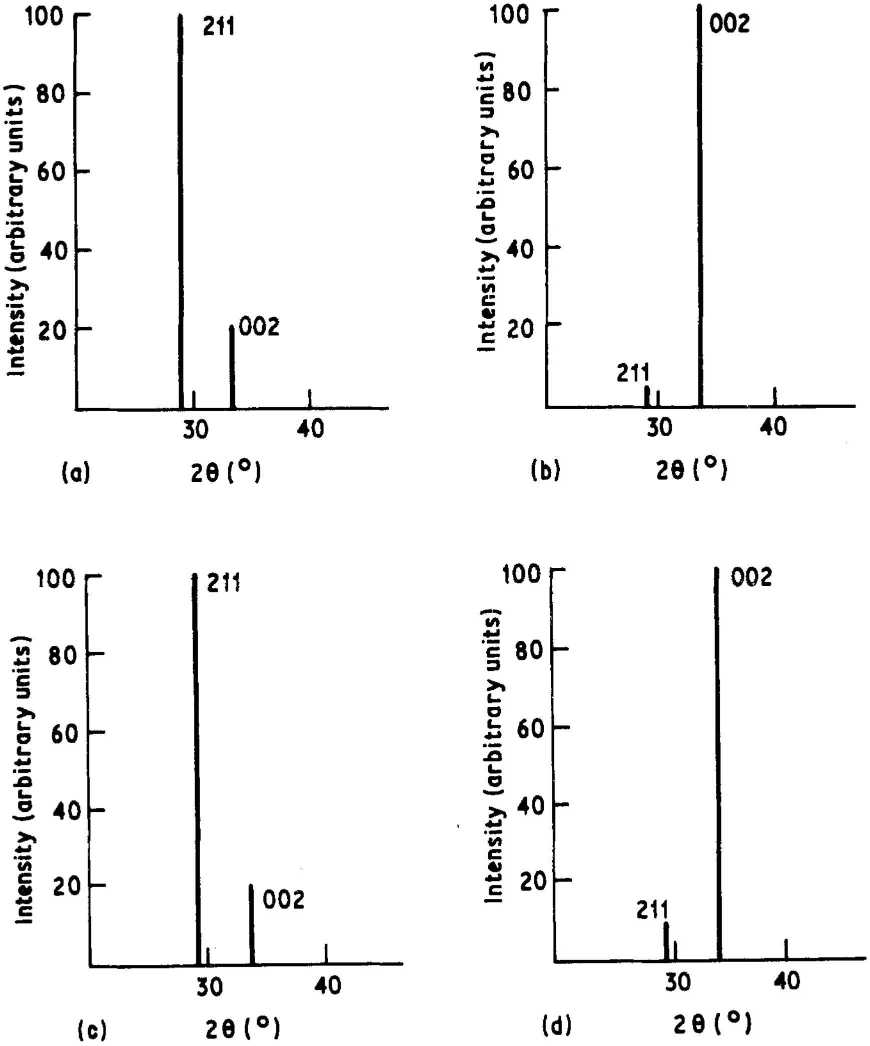

*Figure 4* X-ray diffraction patterns of (a) $Ba_2Ge_2TiO_8$ standard powder diffraction pattern, (b) BTG glass-ceramic, (c) $Ba_2TiSi_2O_8$ standard powder diffraction pattern, and (d) BTS glass-ceramic.

lization, the dielectric constants of the glass-ceramic samples show a slight decrease; the dielectric constant measured in the crystallization direction is closer to the $\epsilon_3$-values of the single crystals. This is consistent with the fact that the $c$-axis is the preferred orientation direction in the glass-ceramic, as indicated by X-ray diffraction analysis.

The loss tangent factors of the glass-ceramics were similar to those measured on single crystals.

Piezoelectric coefficients, $d_{33}$, measured in the crystallization direction in glass-ceramics were comparable to the single-crystal $d_{33}$ coefficient values reported [2–4] for BTS and BTG. Opposite faces of the sample gave opposite signs for the piezoelectric constant. The large magnitude of $d_{33}$-values and its sign reversal suggest that the crystallites in the glass-ceramics are not only orientated along the $c$-axis in the crystallization direction, but that most of the crystallites have the same polarity as well. The fact that the $d_{33}$-values remained constant over the entire surface of the glass-ceramic testifies to the uniformity and the homogeneity of the samples.

As in the previous study of lithium disilicate [1], it was observed that the temperature gradient dictated both the electrical and crystallographic alignment. In all samples the polar orientation was antiparallel to the direction in which crystallization proceeds into the glass, with the positive end of the dipole pointing toward the high-temperature end of the sample, as depicted in Fig. 3. There may be several causes for the polar alignment of the crystallites. One possible cause is the existence of high local electric fields resulting from surface pyroelectric charges [10]. These local electric fields might dictate the orientation of the dipoles as crystallization proceeds into the glass. A second possible cause is the nature of the surface chemistry. It is known that low charge cations such as $Li^+$ or $Ba^{2+}$ migrate to the surface upon heating [11]. This higher surface concentration of cations could influence the nature of both the crystallization and polar orientation. It is possible that as the crystallization proceeds into the bulk of the glass, starting from a cation-rich surface, the positive end of the dipole moments in the crystallites will be directed toward the hot surface.

The pyroelectric response on the glass ceramics was studied by the dynamic Chynoweth method. Pyroelectric voltage responses of between 50 and 60% of the single-crystal values were obtained reproducibly with the glass-ceramic samples. The sign of the pyroelectric coefficient is negative for BTG single crystals and positive for BTS. A similar difference in sign was observed with glass-ceramics. For a simple pyroelectric detector, the figure of merit is given by $p/\epsilon$, where $p$ is the pyroelectric coefficient and $\epsilon$ is the dielectric permittivity. The pyroelectric coefficients of single crystals of $Ba_2TiGe_2O_8$ and $Ba_2TiSi_2O_8$ are 3 and $10\,\mu C\,m^{-2}\,{}^\circ C^{-1}$, respectively [12]. Since the dielectric constants of the glass-ceramics are comparable with those of single crystals, it can be concluded that the pyroelectric coefficients of the glass-ceramics are of the same order of magnitude as those of the single crystals. Specimens of 100 to $500\,\mu m$ in thickness were studied during pyroelectric tests. Samples of large surface area and less than $100\,\mu m$ in thickness were mechanically strong and gave reproducible results, suggesting their use as pyroelectric detectors.

## 4. Conclusions

Glass-ceramics of composition $Ba_2TiGe_2O_8$ and $Ba_2TiSi_2O_8$ were prepared by crystallizing the glasses in a temperature gradient. The glass-ceramics show preferred orientation, with the polar $c$-axis parallel to the temperature gradient. Pyroelectric responses up to 50% of the single-crystal values were observed on these glass-ceramic samples. Measurement of the density, dielectric constant, and piezoelectric constant gave results comparable to the reported single-crystal properties.

## Acknowledgement

We wish to thank our colleagues at the Materials Research Laboratory for their advice and assistance. This work was sponsored by the U.S. Army Office of Research and Development (Contract Grant No. DAAG29-78-0033) and by Defense Advanced Research Projects Agency (Contract DARPA Project No. P-15124-MS).

## References

1. G. J. GARDOPEE, R. E. NEWNHAM, A. G. HALLIYAL and A. S. BHALLA, *Appl. Phys. Lett.* **36** (1980) 817.
2. M. KIMURA, Y. FUGINO and T. KAWAMURA, *ibid.* **29** (1976) 227.
3. M. KIMURA, K. DOI, S. NANAMATSU and T. KAWAMURA, *ibid.* **23** (1973) 531.
4. M. KIMURA, K. UTSUMI and S. NANAMATSU, *ibid.* **47** (1976) 2249.

5. A. HERCZOG, *J. Amer. Ceram. Soc.* 47 (1964) 107.
6. N. F. BORRELLI and M. M. LAYTON, *J. Non-Cryst. Sol.* 6 (1971) 197.
7. D. E. RASE and R. ROY, *J. Amer. Ceram. Soc.* 38 (1955) 393.
8. A. G. CHYNOWETH, *J. Appl. Phys.* 27 (1956) 78.
9. D. I. H. ATKINSON and P. W. McMILLAN, *J. Mater. Sci.* 12 (1977) 443.
10. P. E. BLOOMFIELD, I. LEFKOWITZ and A. D. ARONOFF, *Phys. Rev. B* 4 (1971) 974.
11. G. E. RINDONE, in Proceedings of the Symposium on Nucleation and Crystallization in Glasses and Melts, edited by M. K. Roser, G. Smith and H. Insley (American Ceramic Society, Columbus, Ohio, 1962) pp. 63–69.
12. A. S. BHALLA, unpublished work.

Received 4 July and accepted 22 September 1980.