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Study of the piezoelectric properties of $Ba_2Ge_2TiO_8$ glass-ceramic and single crystals

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Glass-ceramics of composition $Ba_2Ge_2TiO_8$ with oriented crystallites were prepared by crystallizing the glasses in a temperature gradient. The degree of preferred orientation of the crystallites as a function of depth was studied. Piezoelectric resonance properties of both the glass-ceramics and the single crystals were studied. The piezoelectric d_{33} coefficient, the frequency constants and the electromechanical coupling coefficients of the glass-ceramic were comparable to the single-crystal values.

1. Introduction

A technique for fabricating glass-ceramics of lithium disilicate ($Li_2O \cdot 2SiO_2$) and barium germanium titanate ($Ba_2Ge_2TiO_8$; BGT) has been reported in our earlier studies [1–3]. It was observed that the crystallization behaviour of glass-ceramics is influenced strongly by the heating cycle employed during the crystallization of the glasses. Two kinds of heat treatments were investigated: (a) heating under uniform isothermal environment and (b) heating with temperature gradients across the sample. Detailed studies of the microstructure and X-ray diffractometer patterns of the crystallized samples showed a considerable degree of crystallographoc orientation, in both cases. However, the piezoelectric d_{33} values and the pyroelectric responses of BGT glass-ceramics prepared under the temperature gradient were much higher than the respective properties of the samples prepared in isothermal conditions, indicating a strong polar orientation in the samples prepared by the former method. In addition, the d_{33} value of the BGT glass-ceramic was comparable to that of single crystals. These facts led us to investigate the piezoelectric properties of BGT glass-ceramic in greater detail.

Barium germanium titanate is a non-ferroelectric–ferroelastic [4] below 810° C, belonging to the orthorhombic polar points group mm2. In the paraelectric phase above 810° C it is in tetragonal point group 4 mm. Some of the elastic and piezoelectric properties of BGT single crystals have been reported [4–5], but detailed investigations of the piezoelectric properties have not been carried out. Single crystals of BGT have been grown by Czochralski and Bridgman techniques. However, the Bridgman technique yields a poor quality crystal, and Czochralski-grown crystals often contain a small cloudy core, perhaps associated with radial microcracks. Frequently the crystals contain microtwin domains. Hence, it was felt that it might be useful to investigate the piezoelectric properties of BGT glass-ceramics. In the case of several piezoelectric materials, which can be prepared easily in the form of glass, it is possible that simple glass-ceramic processing techniques could be useful in making large-area non-ferroelectric–piezoelectric resonant elements.

Since the thickness of the highly oriented region in the glass-ceramic depends on the heating cycle employed for crystallization, a systematic study to obtain well-oriented samples of desired thickness has been carried out. Also, in the present study, the piezoelectric resonance properties of BGT glass-ceramic and single crystal are compared. To our knowledge this is the first time that the resonance properties of non-ferroelectric–piezoelectric glass-ceramics have been reported.

2. Experimental details

The procedure for preparing BGT glass-ceramic with oriented crystallites is essentially the same

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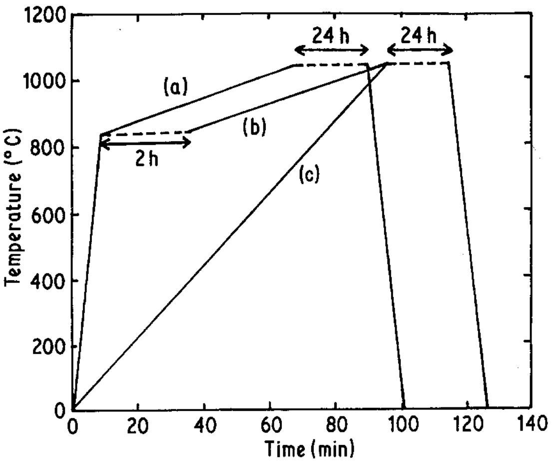

Figure 1 Heating cycles for crystallizing BGT glasses.

as reported in the previous study [3]. The glass samples were prepared by mixing reagent grade chemicals in the required stoichiometric proportion and melting in a globar furnace. Differential thermal analysis (DTA) measurements indicated that the crystallization temperature of the glass was 800° C. The glass samples were crystallized in a temperature gradient by placing the polished glass samples in the form of thick discs on a microscopic hot stage.* An alumina substrate (0.5 mm thick) was placed below the glass samples to provide a uniform temperature gradient in the vertical direction. Heating cycles slightly different from the previous study [1] were used to compensate for the reduction in temperature near the hot face due to the alumina substrate. Three types of heating cycles were used, as shown in Fig. 1. The heating cycle (a) consisted of an initial rapid rise in temperature to minimize volume nucleation, followed by a slow increase in temperature at a rate of about $3^\circ \mathrm{C\,min^{-1}}$. After reaching the maximum temperature (1040° C), the samples were held at this temperature for 24 h. The temperature was then decreased rapidly to room temperature. Cycle (b) was the same as Cycle (a), except that it included a two-hour nucleation step at 840° C. Cycle (c) represents isothermal crystallization carried out in a furnace, with no temperature gradient. The thickness of the crystallized portions of the glasses ranged from 1 to 2 mm in the case of heating cycles (a) and (b).

The degree of preferred orientation of the glass-ceramic was evaluated from X-ray diffractometer patterns, recorded on surfaces normal to the direction of the temperature gradient [3]. The X-ray diffraction patterns of the glass-ceramics prepared by following the above three types of heating cycles were compared with the standard powder patterns to determine the relative degree of orientation.

The piezoelectric constant d_{33} parallel to the crystallization direction was determined using a d_{33}-meter.† For resonance studies, samples in the shape of circular discs of dimensions approximately 2.5 to 3 mm diameter and 0.5 to 0.75 mm in thickness were prepared. From single-crystal samples grown by Czochralski-pulling along the *c*-axis, circular discs were prepared in a similar way, with the *c*-axis perpendicular to the major faces. Gold electrodes were sputtered onto the polished surfaces. Resonance behaviour in the pure thickness mode and planar modes was studied by the resonance and anti-resonance method using a spectrum analyser.‡ The resonance frequency constants, the electromechanical coupling factors and the mechanical quality factor Q were determined both for the glass-ceramic and the single-crystal samples by measuring the resonance (f_r) and anti-resonance (f_a) frequencies. The temperature coefficient of the resonance frequency in a thickness mode was studied by measuring the resonance frequency at intervals of 5° C.

3. Results and discussion

3.1. Crystallization behaviour

The glass-ceramic samples showed highly oriented growth of crystallites in a direction parallel to the temperature gradient, with the polar *c*-axis perpendicular to the hot surface of the sample [3]. The 0 0 2 reflection was the strongest in the X-ray diffraction 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 were measured for glass-ceramic samples at various depths from the surface facing the hotter temperature zone by polishing-off successive layers. Fig. 2 shows the variation of I_{002}/I_{211} as a function of depth for the glass-ceramic samples prepared by following the three different heating cycles mentioned earlier. In general, a high degree of orien-

*E. Leitz, Inc., Rockleigh, New Jersey, USA; Model No. 493.

†Channel Products, Chesterland, Ohio, USA; Model CPDT 3300.

‡Hewlett-Packard, Loveland, Columbia, USA; Model 3585 A.

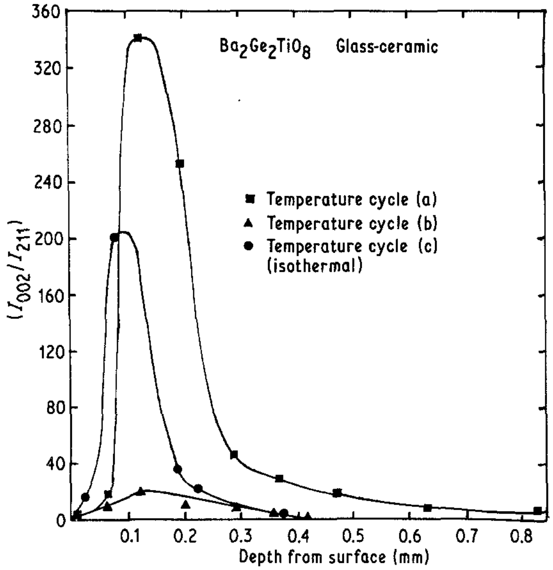

Figure 2 The degree of preferred orientation as a function of depth for different heating cycles.

tation is observed in all the cases, at a depth of about 100 μm from the high-temperature face. In all three cases it was observed that the flatness of the glass surface was lost after crystallization. Hence, it is possible that the apparent reduction in the degree of orientation observed near the high-temperature face is due to the unevenness of the glass-ceramic surface after crystallization rather than to the actual misorientation of the crystallites near the hot face. This was evident from the fact that the I_{002}/I_{211} ratio showed a maximum value at a depth where the surface of the glass-ceramic became completely flat after polishing. As is to be expected, the samples prepared by following the Cycle (b), which included a nucleation step also, showed a poor degree of orientation compared to the samples prepared by following the Cycles (a) or (c).

Even though the samples crystallized isothermally (Cycle c) exhibited crystallographic orientation to a certain extent, these samples had a lower d_{33} (3 to 4×10^{-12} C N^{-1}) compared to the samples crystallized in a temperature gradient (5 to 7×10^{-12} C N^{-1}) (Cycle a), indicating that crystallization in a temperature gradient leads to a better polar orientation also. However, the highest degree of orientation was observed in the case of samples prepared by following Cycle (a), which did not include the intermediate nucleation step. Also, the depth of oriented region was much greater in this case.

Hence, for studying the piezoelectric properties of the glass-ceramics, the samples were prepared by crystallizing the glasses according to the Cycle (a). All the piezoelectric properties of the glass-ceramic samples mentioned in this paper refer to the glass-ceramic samples prepared by following Cycle (a).

3.2. Piezoelectric properties

Resonance spectra for the thickness mode are shown in Fig. 3 for both the glass-ceramic and single-crystal samples. Resonance in the planar mode was weak compared to the resonance signal in the thickness mode. Resonance spectra in the radial mode are shown in Fig. 4. The radial mode of vibration was very weak for the glass-ceramic samples. This is not surprising, since the crystallites in the glass-ceramics are oriented only along the c-direction, there being no preferred orientation along the a- or b-axes. In addition, there is a glassy phase surrounding the crystallites. Both these factors might be responsible for the weakening of the radial mode vibration in the glass-ceramic samples. In Table I, the measured resonance properties of the glass-ceramic and the single crystal are summarized. The reported values for

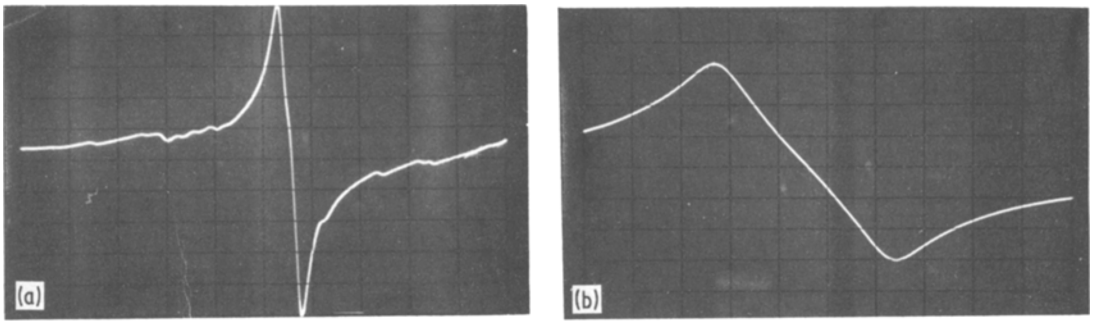

Figure 3 Resonance spectra in the thickness mode. (a) BGT glass-ceramic, horizontal scale = 31 kHz; (b) BGT single crystal, horizontal scale = 3.06 kHz.

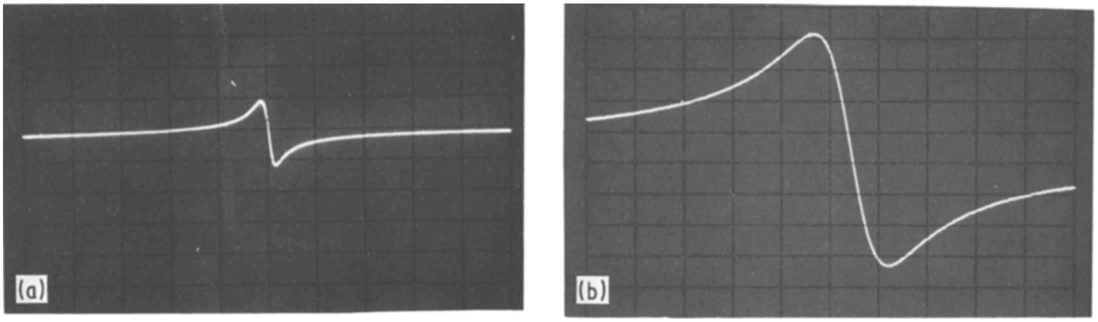

Figure 4 Resonance spectra in the radial mode. (a) BGT glass-ceramic, horizontal scale = 3 kHz; (b) BGT single crystal, horizontal scale = 1.1 kHz.

the 3–3 coupling are also given for comparison. The measured values of N_t and k_t in our single-crystal samples were higher than the reported value. This is perhaps because the Czochralski-grown crystals used in our experiments were of better quality than the crystals used in previous studies [4], which were grown by the Bridgman technique.

The variation in resonance frequency constant, N_t, with temperature was studied in the temperature range − 10 to 150° C. The relative resonance frequency Δf_R as a function of temperature for both the glass-ceramic and single crystal is plotted in Fig. 5, where

$$\Delta f_R = \frac{f_T - f_{RT}}{f_{RT}}.$$

Here f_T is the resonance frequency at temperature T and f_{RT} is the resonance frequency at room temperature. The temperature coefficients of resonance (TCR), calculated from the slopes of Δf_R against T plots are given in Table I.

The electromechanical coupling factor k_t was calculated by using the equation

$$k_t^2 = [(\pi/2)f_r/f_a] \tan [(\pi/2)\Delta f/f_a].$$

The room-temperature values of k_t are given in Table I. The temperature dependence of k_t is shown in Fig. 6. For single crystal, k_t is practically constant in the temperature range − 10 to 150° C, increasing slightly with temperature. For the glass-ceramic, k_t increases slowly with temperature.

Values of the mechanical quality factor Q are given in Table I. Difficulties were encountered in the measurement of Q, due to the small values of capacitances of the sample. Spurious resonance signals were observed with large-area glass-ceramic samples. Measurements indicated that $Ba_2Ge_2TiO_8$ has a high Q of about 700.

The temperature coefficients of resonance of some of the commonly used piezoelectric materials [7] are given in Table II for comparison. The TCR of $Ba_2Ge_2TiO_8$ single crystals is comparable to that of $Ba_2Si_2TiO_8$. It has been reported [8, 9] that $Ba_2Si_2TiO_8$ (fresnoite) is a good candidate material for surface acoustic wave (SAW) devices. The shear-mode piezoelectric surface wave of $Ba_2Si_2TiO_8$ has a coupling coefficient $k^2 = 0.0053$,

TABLE I Piezoelectric properties of $Ba_2Ge_2TiO_8$ determined by the resonance method

Property	Glass-ceramic	Single crystal	Reported values in the 3–3 mode
ϵ_{33}/ϵ_0	15	13	–
d_{33} ($\times 10^{-12}$ C N^{-1})	5–7	10	–
Frequency constant N_t (Hz m)	2500	2150	$N_{33} = 1900$
Thickness coupling coefficient k_t	0.075	0.10	$k_{33} = 0.07$ $k_{15} = 0.27$ $k_{24} = 0.31$
Mechanical quality factor Q	700	650	–
Temperature coefficient of resonance, $T_{fr} = \frac{1}{f_r}\frac{\partial f_r}{\partial T}$ (ppm/° C)	95	48	–
Frequency constant N_p (Hz m)	3100	2900	
Planar coupling coefficient k_p	0.044	0.062	

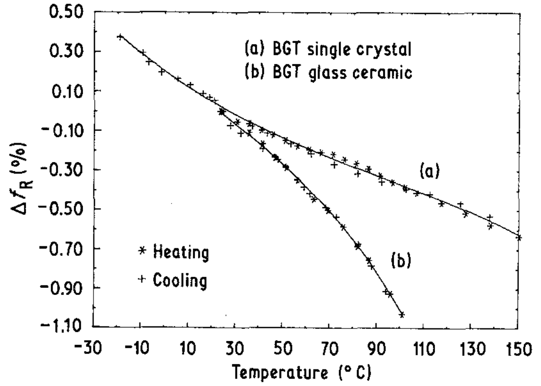

Figure 5 Relative resonance frequency as a function of temperature.

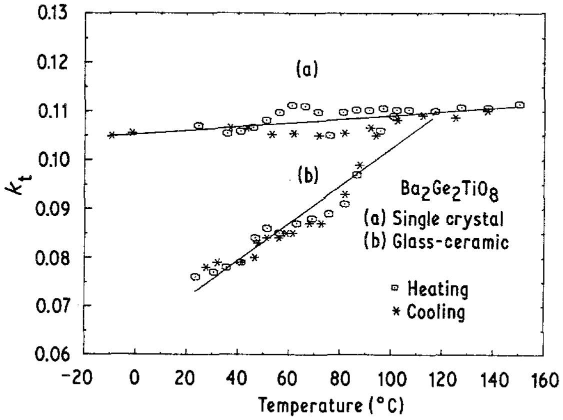

Figure 6 Variation of k_t with temperature.

which is three times larger than that of quartz ($k^2 = 0.0014$). It has a small TCR (38 ppm/° C for X-cut and Y-propagation) and a small surface velocity. The SAW characteristics of fresnoite can be further improved by partial substitution of Sr for Ba (i.e., $Ba_{2-x}Sr_xTiSi_2O_8$), with almost no change in the electromechanical coupling factor [10]. For Z-cuts with ⟨1 1 0⟩ propagating waves, the TCR drops from 51 to 21 ppm/° C at a Sr concentration of $x = 0.8$, which is comparable to the TCR of $LiTaO_3$. BGT also exhibits large electromechanical coupling in a pure thickness shear mode with values of $k_{15} = 0.27$ and $k_{24} = 0.31$. The SAW characteristics of $Ba_2Ge_2TiO_8$ single crystal are to be explored and this aspect needs further study.

The TCR of BGT glass-ceramics is about 95 ppm/° C, which is higher than the single-crystal value. However, further studies are necessary to explore the possibilities of fabricating BGT glass-ceramics with improved temperature compensation, by controlled crystallization of the BGT glasses, and by modifying the composition of the glasses. The present studies demonstrate the possibility of preparing glass-ceramic piezoelectric resonant elements with reasonably good piezoelectric properties from a non-ferroelectric–peizoelectric material. Piezoelectric glass-ceramics in which the crystalline component has tetragonal or higher symmetry should have a high degree of homogeneity in properties for the surface perpendicular to the polar crystallite axis and in consequence should show strong radial coupling. Such systems may have application in SAW devices.

Under controlled crystallization a desired thickness of the thin glass plate can be crystallized into a glass-ceramic layer and such composite elements may be useful for device applications based on flexural resonance modes.

4. Conclusion

Glass-ceramics of composition $Ba_2Ge_2TiO_8$ 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. The depth of the oriented region depends on the heating cycle employed. The piezoelectric resonance properties of the glass-ceramics are in agreement with the single-crystal properties. Measurement of piezoelectric d_{33} and electromechanical coupling coefficients

TABLE II TCR of some piezoelectric materials

Material	Orientation	TCR (ppm/° C)	Reference
$LiNbO_3$	Y-cut, Z-propagation	94	[7]
Quartz	ST-cut, X-propagation	0	[7]
$LiTaO_3$	Y-cut, Z-propagation	35	[7]
$Ba_2Si_2TiO_8$ (+ 10 to + 60° C)	X-cut, Y-propagation	38	[7]
	Z-cut, ⟨1 1 0⟩	51	[9]
$Ba_2Ge_2TiO_8$ (+ 10 to + 60° C)	Z-cut	48	Present data
$Ba_2Ge_2TiO_8$ (glass-ceramic, 0–60° C)	Z-surfaces	95	Present data
$(Ba_{1.2}Sr_{0.8})Si_2TiO_8$ (+ 10 to + 60° C)	Z-cut, ⟨1 1 0⟩	21	[9]

on both the glass-ceramic and single crystals gave comparable results. We suggest that in the case of piezoelectric materials which can be prepared in the form of glass, it is possible to employ simple glass-ceramic processing techniques to produce glass-ceramics with useful piezoelectric properties.

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References

1. G. GARDOPEE, R. E. NEWNHAM, A. HALLIYAL and A. S. BHALLA, *Appl. Phys. Lett.* **36** (1980) 817.
2. A. S. BHALLA, G. GARDOPEE and R. E. NEWNHAM, *Ferroelectrics* **27** (1980) 123.
3. A. HALLIYAL, A. S. BHALLA, R. E. NEWHAM and L. E. CROSS, *J. Mater. Sci.* **16** (1981) 1023.
4. M. KIMURA, K. DOI, S. NANAMATSU and T. KAWAMURA, *Appl. Phys. Lett.* **23** (1973) 531.
5. M. KIMURA, K. UTSUMI and S. NANAMATSU, *ibid.* **47** (1976) 2249.
6. L. DRAFALL and K. E. SPEAR, *J. Cryst. Growth* **33** (1976) 180.
7. A. J. SLOBODNIK, Jr, *Proc. IEEE* **64** (1976) 581.
8. M. KIMURA, *J. Appl. Phys.* **48** (1977) 2850.
9. H. YAMAUCHI, *ibid.* **49** (1978) 6162.
10. Y. ITO, K. NAGATSUMA and S. ASHIDA, *Appl. Phys. Lett.* **36** (1980) 894.

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