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Dielectric, piezoelectric and pyroelectric properties of $Sr_2TiSi_2O_8$ polar glass–ceramic: a new polar material

A. HALLIYAL, A. S. BHALLA, L. E. CROSS, R. E. NEWNHAM
Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

Polar $Sr_2TiSi_2O_8$ glass–ceramics were prepared by recrystallizing glasses in a steep temperature gradient. The dielectric, piezoelectric and pyroelectric properties were studied as a function of temperature in the temperature range −150 to 200° C. The sign of the pyroelectric coefficient is positive at room temperature and is attributed to the dominance of the secondary pyroelectric effect over the primary effect. Anomalies were observed in the dielectric, pyroelectric and piezoelectric properties and a large hysteresis was observed in all these properties. Probable causes for the anomalies are discussed.

1. Introduction

Fresnoite ($Ba_2TiSi_2O_8$, hereafter designated BTS) is a polar but non-ferroelectric crystal with tetragonal space group P4bm. Single crystals of fresnoite have been grown successfully by the Czochralski technique by several workers [1–3]. Fresnoite has been shown to be a promising substrate material for surface acoustic wave (SAW) devices [1–5]. Its SAW properties are intermediate between those of $LiNbO_3$ and $LiTaO_3$. For fresnoite z-cuts with wave propagation along the [1 1 0] direction, the electromechanical coupling factor k_s^2 is 1.5% and the temperature coefficient of delay (TCD) is 50 ppm.

Recently, Ito and co-workers [6, 7] have shown that the TCD of fresnoite can be greatly lowered through the partial substitution of strontium for barium. Crystals of composition $(Ba_{2-x}Sr_x)TiSi_2O_8$ with uniform strontium concentration can be grown by edge-defined film-fed growth (EFG), for the compositions ranging from $x = 0$ to 0.8. It was found to be difficult to grow crystals of homogeneous composition by the Czochralski technique [7]. The strontium concentration in a Czochralski-grown crystal varies according to the normal freezing distribution. Z-cut crystals with strontium concentration of $x = 0.8$ give a TCD value of 20 ppm with practically no reduction in the value of k_s^2, and look to be very useful for SAW devices.

In compositions with $x \geqslant 1.0$, $SrTiO_3$ and $SrSiO_3$ also crystallize along with fresnoite, making it impossible to grow pure strontium titanium silicate ($Sr_2TiSi_2O_8$, hereafter designated STS) single crystals by the usual crystal growing techniques. However, X-ray diffraction studies on ceramic samples have shown that all compositions with $x = 0$ to 2.0 prepared by conventional ceramic processing techniques give single-phase fresnoite-type structure. The crystal symmetry of STS is the same as that of BTS. However, there are no measurements reported for the piezoelectric and pyroelectric properties of STS because of the difficulties in single-crystal growth. Moreover, since STS is a non-ferroelectric material, it is not possible to reorient the polar axes in individual crystallites and hence randomly axed ceramic samples will be of no use in studying the piezoelectric and pyroelectric properties.

In our earlier work it has been demonstrated that polar glass–ceramics with the fresnoite structure can be prepared by recrystallizing glasses of slightly modified fresnoite compositions [8–11]. In these glass–ceramics, the polar texture results from needle-like crystals growing from the glass surface during crystallization. These fresnoite polar glass–ceramics showed piezoelectric and pyroelectric properties comparable to the single-crystal properties.

In the present study, polar STS glass–ceramics were prepared from glasses of non-stoichiometric composition. The dielectric, piezoelectric and pyroelectric properties of STS glass–ceramics were studied as a function of temperature in the temperature range −150° C to 200° C. Since our previous studies have shown that the properties of BTS single crystals and polar glass–ceramics are very similar [11], we expect that the properties of STS glass–ceramics reported in the present paper might be very similar to the single-crystal properties.

2. Experimental details

Glass samples were prepared by mixing reagent-grade chemicals followed by melting in a platinum crucible at 1400 to 1450° C. The melt was retained in the furnace for 4 to 6 h for fining and homogenization. The fined glass melt was air quenched by pouring it into graphite moulds to form cylinders of approximately 0.8 to 1 cm in diameter and 1 to 1.5 cm in length. Initially, an attempt was made to prepare glasses of stoichiometric STS composition. It was not possible to obtain clear glasses with uniform composition because of phase separation in the melt. Addition of excess silica to the composition helped to eliminate the phase separation problem. Glass samples containing one mole of excess silica (composition: $2SrO–3SiO_2–TiO_2$) were prepared for the present study. Glass–ceramic samples with polar texture were prepared by crystallizing the glasses in a temperature gradient as described elsewhere [8–11]. Microstructure studies indicated that needle-like crystals grow from the surface into the bulk along the direction of temperature gradient. X-ray powder diffraction patterns of glass–ceramic samples showed that the only crystalline phase in glass–ceramics was STS. Property measurements were carried out on sections (8 mm diameter and 0.5 mm thick) cut normal to the temperature gradient and with gold electrodes sputtered on the major surfaces.

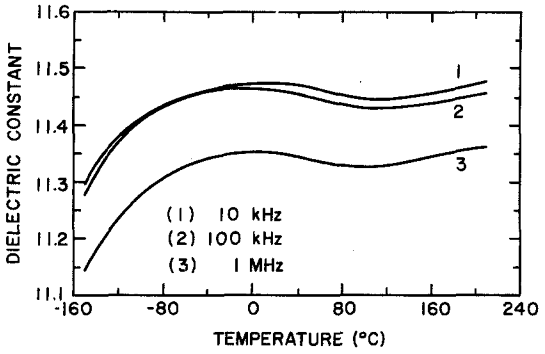

Figure 1 Dielectric constant of $2SrO–3SiO_2–TiO_2$ glass–ceramic as a function of temperature and frequency, over temperature range −150 to 200° C.

The dielectric constant and dissipation factors were measured at different frequencies using a capacitance bridge, and pyroelectric coefficients were measured by the Byer–Roundy [12] technique. The heating and cooling rates employed were 4° C min^{-1}. The electromechanical properties were determined by standard resonance techniques. All the above properties were measured as a function of temperature in both heating and cooling cycles. The hydrostatic voltage coefficient g_h was measured by a dynamic method described by Safari [13].

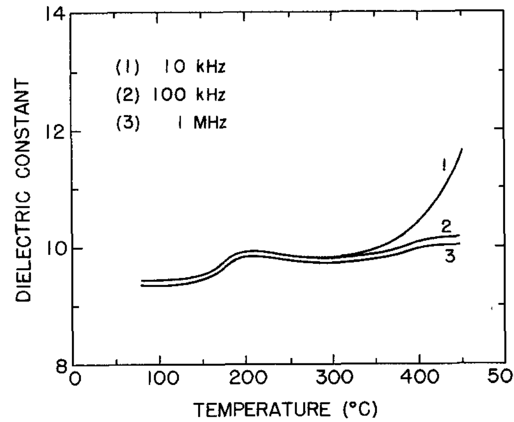

Figure 2 Dielectric constant of $2SrO–3SiO_2–TiO_2$ glass–ceramic as a function of temperature and frequency, over temperature range 80 to 450° C.

3. Results

The dielectric constant and dissipation factor of STS glass–ceramic are shown in Figs. 1 to 3. Broad peaks in dielectric constant were observed near 20 and 200° C. Below −20° C, the dielectric constant slowly decreased with decreasing temperature. There was an increase in dielectric

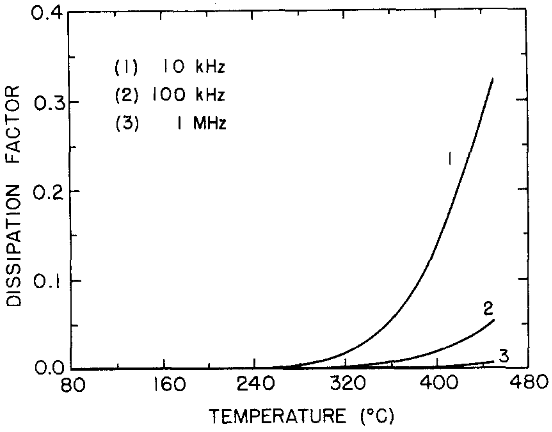

Figure 3 Dissipation factor of $2SrO\text{–}3SiO_2\text{–}TiO_2$ glass–ceramic as a function of temperature and frequency.

TABLE I Room-temperature properties of $2SrO\text{–}3SiO_2\text{–}TiO_2$ glass–ceramics

Density (g cm^{-3})	3.55
Dielectric constant K_{33}, at 1 kHz	11.5
Dissipation factor	< 0.001
Pyroelectric coefficient p_3 (μC m^{-2} K^{-1})	+ 7.5
d_{33}(pC N^{-1})	14
d_{31}(pC N^{-1})	1.6
d_h(pC N^{-1})	8.7
g_{33}(10^{-3} V m N^{-1})	138
g_h(10^{-3} V m N^{-1})	85
$d_h g_h$(10^{-15} m^2 N^{-1})	740
Frequency constant N_t (m Hz)	2550
Frequency constant N_p (m Hz)	3300
k_t	0.08
k_p	0.10
Mechanical quality factor Q	700
Temperature coefficient of resonance (ppm °C^{-1})	50

constant and dissipation factor at higher temperatures, probably because of conduction. The dissipation factor curve was featureless up to 250° C and the losses were very low (<0.001).

The variation of pyroelectric coefficient p_3 as a function of temperature is shown in Fig. 4. The pyroelectric coefficient p_3 is positive at room temperature and shows a very broad peak at about -20° C. An anomaly is observed in p_3 at about 120° C. A large hysteresis was observed between heating and cooling cycles above -10° C and this was particularly absent below -10° C. This behaviour in $p_3(T)$ was confirmed by repeating the heating and cooling measurement twice. Plots of $p_3(T)$ recorded during the two heating cycles were exactly the same, as were the plots for the two cooling cycles.

The variation of frequency constant N_p and electromechanical coupling factor k_p are shown in Figs. 5 and 6. Frequency constant N_p showed a minimum at about 150° C in the cooling cycles and at about 200° C in the heating cycles. A large hysteresis similar to the one in pyroelectric coefficient measurement was observed between heating and cooling cycles in N_p and k_p. At the inflection point the value of temperature coefficient of resonance (TCR), defined as

$$\mathrm{TCR} = \frac{1}{f_r}\frac{\partial f_r}{\partial T} \qquad (1)$$

is zero. Here, f_r is the resonance frequency at temperature T. The minimum in N_p during the heating cycle and the small anomaly in the dielectric constant occur at the same temperature (~200° C). The room-temperature properties of STS glass–ceramics are listed in Table I.

4. Discussion

In our previous study on BTS single crystals and

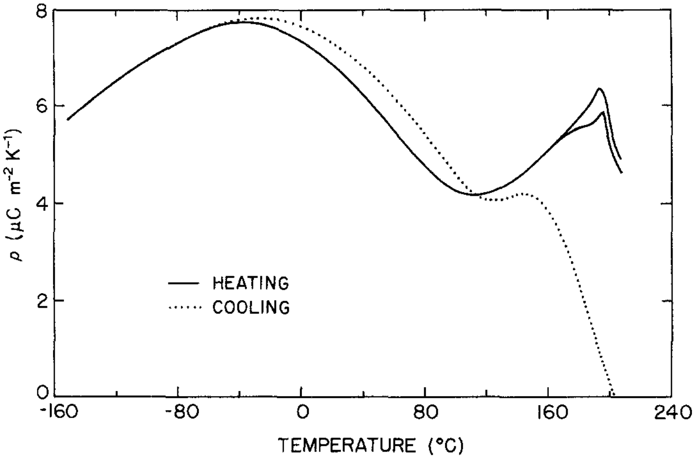

Figure 4 Variation of pyroelectric coefficient with temperature for $2SrO\text{–}3SiO_2\text{–}TiO_2$ glass–ceramic.

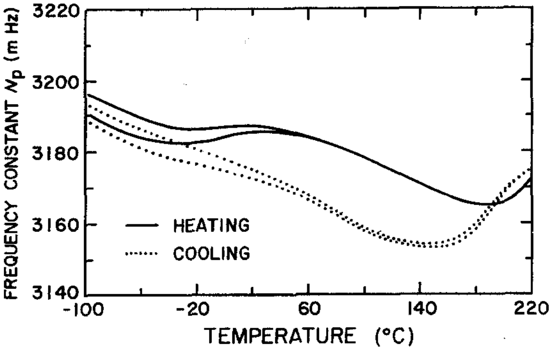

Figure 5 Temperature dependence of frequency constant N_p of $2SrO-3SiO_2-TiO_2$ glass–ceramic.

glass–ceramics [11], it was clear that all the properties of glass–ceramics containing one mole of excess silica (composition: $2BaO-3SiO_2-TiO_2$) were very similar to those of BTS single crystals. In the case of STS glass–ceramics (composition: $2SrO-3SiO_2-TiO_2$) we can also expect the properties of glass–ceramics to be similar to the properties of STS single crystals. In addition, we can expect the same anomalies in the dielectric, piezoelectric and pyroelectric properties of single crystals also.

The unusual features in all the properties of STS glass–ceramics suggest the possibility of a structural phase transition, since in most of the ferroelectric crystals structural changes are accompanied by anomalies in dielectric and related properties. In the absence of data about the properties of STS single crytals, it may be fruitful to compare the properties of STS glass–ceramics with those of BTS single crystals which show similar anomalies in properties [11]. In BTS single crystals, the sign of the pyroelectric coefficient is positive at room temperature and becomes negative at about 190° C. Sharp peaks in K_{33}, p_3 and k_p are observed at 160° C and a minimum is observed in resonance frequency at the same temperature. A single-crystal X-ray study [14] did not indicate any phase transition in BTS. The origin of the anomaly in the dielectric and related properties of BTS is thought to be related to anomalous behaviour of some of the elastic constants near 160° C [11], and, because of the coupling between elastic and other properties, this could also lead to anomalies in the piezoelectric and pyroelectric properties.

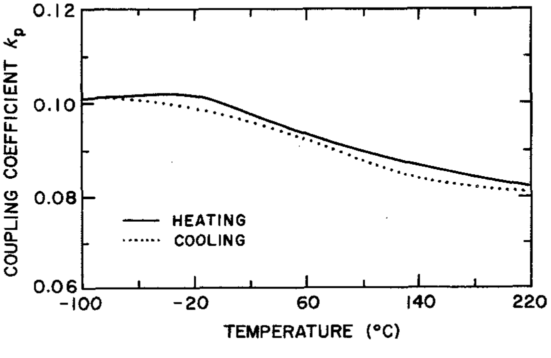

Figure 6 Variation of planar coupling coefficient k_p with temperature for $2SrO-3SiO_2-TiO_2$ glass–ceramic.

A comparison of the properties of BTS single crystals and STS glass–ceramics indicates that it is highly unlikely that there is a phase transition in STS in the temperature range $-150°$ C to 200° C. In STS also the reason for the anomaly in all the properties might be anomalous behaviour of some of the elastic constants. However, a detailed measurement of the temperature dependence of all the elastic constants and thermal expansion coefficients is necessary to support the above assumption.

The pyroelectric coefficient p_3 of STS is positive in the temperature range $-150°$ C to 200° C and shows a peak value of about 8 $\mu C\ m^{-2}\ K^{-1}$ at about $-20°$ C. In BTS also, p_3 is positive at room temperature and the reason for this is that the secondary component of p_3 (p_{sec}) is larger than the primary component of p_3 (p_{prim}) at room temperature [15]. The calculated value of p_{sec} in BTS is about 16.5 $\mu C\ m^{-2}\ K^{-1}$. Unfortunately it is not possible to separate the primary and secondary effects in STS as the full family of elastic, piezoelectric and thermal expansion constants required to assess the secondary effect have not yet been measured.

In the case of both BTS single crystals and glass–ceramics, all the properties were exactly the same in both heating and cooling cycles and the anomalies occurred at the same temperature without any hysteresis [11]. In STS glass–ceramic, there is a large hysteresis in piezoelectric and pyroelectric properties and the anomalies occur at slightly different temperatures in heating and cooling cycles. The reason for this hysteresis in STS is not clear at present. Measurement of dielectric constant and pyroelectric coefficient with an applied bias electric field might help in understanding the origin of this unusually large hysteresis.

5. Summary

The present study demonstrates the usefulness of preparing polar materials by the glass–ceramic route. For several non-ferroelectric materials, which are difficult to prepare in single-crystal form and can be prepared easily as glasses, the polar glass–ceramic technique described in the present work can be used to assess the piezoelectric and pyroelectric effects in the crystalline phase. Ceramic samples of such materials will not be useful for studying the above properties since they cannot be poled by an external electric field. If it is possible to prepare glasses of the required material with minor modification in the composition, the technique of preparing glass–ceramics with oriented polar texture provides an alternative method to study the properties of such materials. In the case of $Sr_2TiSi_2O_8$ it was possible for the first time to obtain reliable data on both pyroelectric and piezoelectric properties, by the glass–ceramic technique.

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