

Development of textured antimony sulphoiodide

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Processing and characterization techniques which were used to obtain a dense well aligned antimony sulphoiodide ceramic body are described. A technique in which an a.c. field is used to electrically align SbSI crystals for subsequent orthogonal hot pressing is described. Characterization of the microstructure, the mechanical and the electrical properties disclosed that a reasonably strong (~ 20 MPa) piezoelectrically active ($d_{33} = \sim 500$ pC N⁻¹) body could be produced. These properties are then compared to those obtained on bodies prepared by other techniques and to those of single-crystal "boules" of SbSI.

1. Introduction

Conventional piezoelectric materials such as barium titanate (BaTiO₃) and lead zirconate-titanate (PbZrO₃-PbTiO₃) exhibit poor hydrostatic charge response, d_h , e.g. ~ 10 pC N⁻¹, unless used in a manner which negates the transverse responses (d_{31} and d_{32}). This poor response, which is related to their nearly isotropic crystal structure, considerably complicates their use in hydrophones and limits resultant output. In contrast to this Berlincourt *et al.* [1] found that the highly anisotropic (orthorhombic) crystal structure of SbSI produced a hydrostatic piezoelectric strain constant, d_h , of 1500 pC N⁻¹ (Table I). This value approaches the longitudinal piezoelectric strain constant d_{33} of 2000 pC N⁻¹ since the transverse piezoelectric strain constants, d_{31} and d_{32} , are nearly zero. The high d_{33} results [1, 2] were obtained when the electrodes of samples grown by a Bridgman technique were positioned normal to the "boule" c -axis. Such "boules" actually consisted of many fine long c -axis crystal rods aligned parallel to the boule-axis. This high response gives SbSI the potential for use in a simple design, high output hydrophone. However, while the use of such boules may not be altogether practical because of size, shape and/or cost, the over-riding constraint has been their very limited mechanical strength, especially perpendicular to the c -axis.

The primary purpose of this study was thus to investigate the feasibility of fabricating polycrystalline SbSI bodies with a significant c -axis texture in an attempt to optimize both the mechanical strengths and d_h values. The d_{33} value of Okazaki and Narushima [3] of 300 pC N⁻¹ at 30° C (Table I) suggested that reasonable texturing might be achieved. They cold-pressed fine, needle like SbSI grains in a rectangular cavity die, then the resulting green bodies were hot pressed in a direction orthogonal to the original. The combination of sequential pressing in orthogonal directions and the needle shape of the grains with the c -axis along their long direction, resulted in some mechanical alignment. Another purpose of this work was to observe effects of alloying on the Curie temperature and the depoling character of SbSI. This is important since the Curie temperature is typically low (19 to 24° C), but it has been shown (Table I) to vary with impurity or additive content (e.g. oxygen and sulphur [4-6] produce a higher Curie temperature).

The Naval Research Laboratory (NRL) studies were designed as a key step in evaluating whether SbSI could be a practical hydrophone material itself, and as a guide in determining whether other similar highly anisotropic materials might be suitable for such applications. That studies of SbSI could be a guide in evaluating the utility of

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TABLE I Previously reported data on SbSI and several alloys

Material ^a	Density (g cm ⁻³)	Dielectric constant ϵ_r ($\times 10^{-3}$)	Curie temperature T_c (°C)	Piezoelectric charge constants		Depoling temperature T (°C)	Source
				d_{33} (pC N ⁻¹)	d_h (pC N ⁻¹)		
C	5.23	20–40	19	2000	1500	15	[2]
C	—	—	—	2000	1500	—	[1]
C	5.27	25	20	—	—	—	[3]
P	5.10	3	30	300	—	20	[3]
P	—	10	19	—	—	—	[4]
pb	4.91	21	38	220	—	34	[5]
pc	4.79	16	43	180	—	36	[5]
pd	—	3	43	—	—	—	[4]

^aC = single crystal, P = polycrystalline.

^bComposition: SbS_{0.95}O_{0.05}I.

^cComposition: SbS_{0.8}O_{0.2}I.

^dComposition: SbSI + 12% Sb₂S₃.

other materials is based on the fact that orientation methods and the trade-off between strength and electrical properties should have direct relevance to other highly anisotropic materials with similarly high d_h responses but higher Curie temperatures.

2. Experimental procedure

Two types of material were available. The first type was chemically prepared SbSi fine grain powders available from two sources.* These powders consisted of fine needle grains 0.5 to 1.5 or 1.5 to 3 μ m in diameter with aspect ratios of 10 to 1 (e.g. Fig. 1a and b) in which the long grain direction was the c -axis. The second type of material was in the form of boules, grown by a modified Bridgman–Stockbarger technique.† These boules, like those of earlier workers, consisted of many fine rod crystals (~ 10 mm long and 2 to 10 μ m diameter) with their lengths and c -axis aligned along the boule axis (Fig. 1c and d).

Three processing approaches were investigated. The first was mechanical alignment and hot pressing of the powders in a manner similar to that of Okazaki and Narushima [3]. The second, and most extensively developed method, was electrical alignment and subsequent hot pressing of powders, which is somewhat analogous to the preparation of a ferrite by Stuits via magnetic alignment of the powders before hot pressing [7]. In this study fine powders, large grains (obtained from crushed

boules) or a combination of the two were hot pressed into a high-density body after electrical alignment. The hot-pressing system used is shown in Fig. 2. The third method of processing was press forging, i.e. slow compressive deformation of boule sections with the stress axis normal to the c -axis of the boule in the same stainless-steel die used for hot pressing.

Densities were measured on all as-received boules as well as on all processed polycrystalline bodies using Archimedes principal (ethanol was used as the fluid to avoid some attack and contamination from water). Furthermore, all bodies (as well as starting powders) were characterized for microstructure by optical and scanning electron microscopy. Fracture surfaces from modulus of rupture tests were generally used since these revealed the grain structures more clearly than polished samples because of the difficulties involved in polishing such soft materials.

Conventional diamond sawing was used along with hand finishing with dry 180 to 220 grit SiC metallurgical paper to prepare bars (3 mm \times 5 mm \times 15 mm) for the mechanical tests. It was found that mounting the SbSI samples in a room-temperature curing epoxy‡ before most machining operations minimized mechanical damage. The fracture strengths were then determined by three-point flexure on a span of 0.4 to 1 cm with a head travel rate of 1 mm min⁻¹ at 22° C and $\sim 50\%$ relative humidity in a mechanical test machine.§

*Commercially available from Gallard-Schlesinger or courtesy of P. E. Morgan, formerly at University of Pittsburgh, now at Rockwell Science Centre.

†Courtesy of A. S. Bhalla and L. E. Cross, MRL Pa. State University, USA.

‡Epo-kwick fast cure epoxy, Buehler Corp.

§Model No. 1122, Instron Corp.

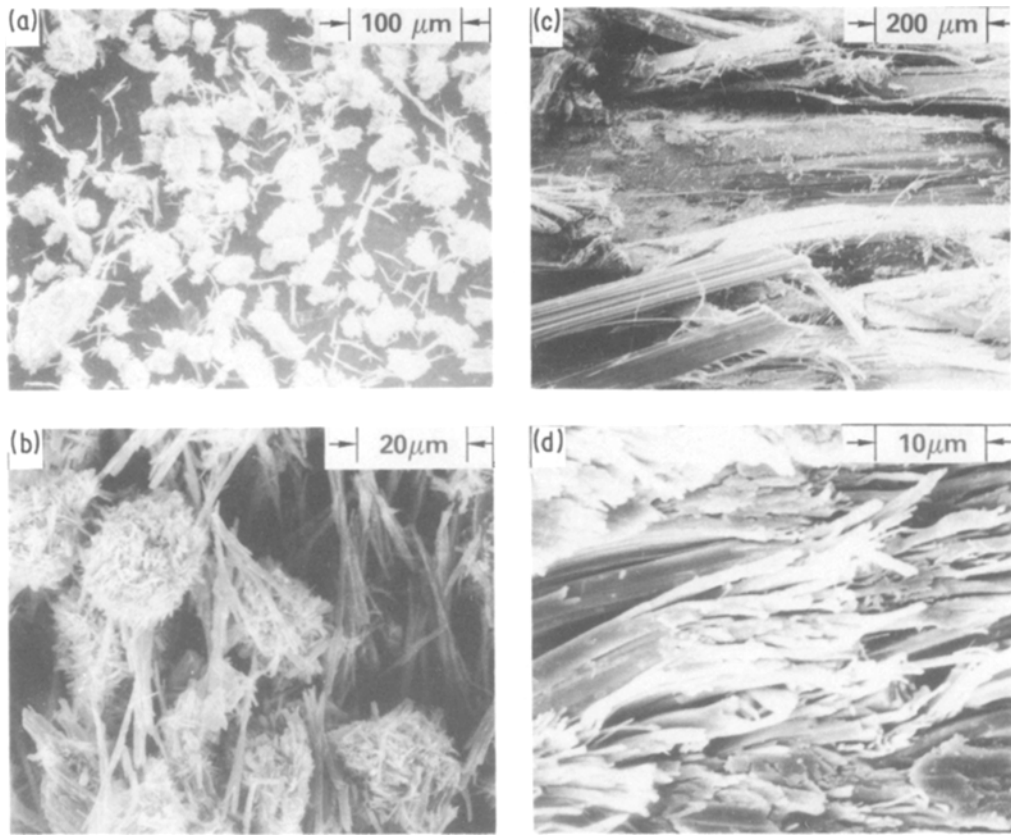


Figure 1 SbSI raw materials. (a) and (b) are respectively lower and higher magnifications of chemically prepared powders from Morgan. Note the approximately spherical agglomerates of fine needle grains with larger, especially longer needle grains between the agglomerates. (c) and (d) show respectively lower and higher magnifications of cross-sections of boules fractured approximately parallel with the boule *c*-axis. Note the highly aligned but quite fine needle grains and that some of their alignment has been distorted by the fracture process.

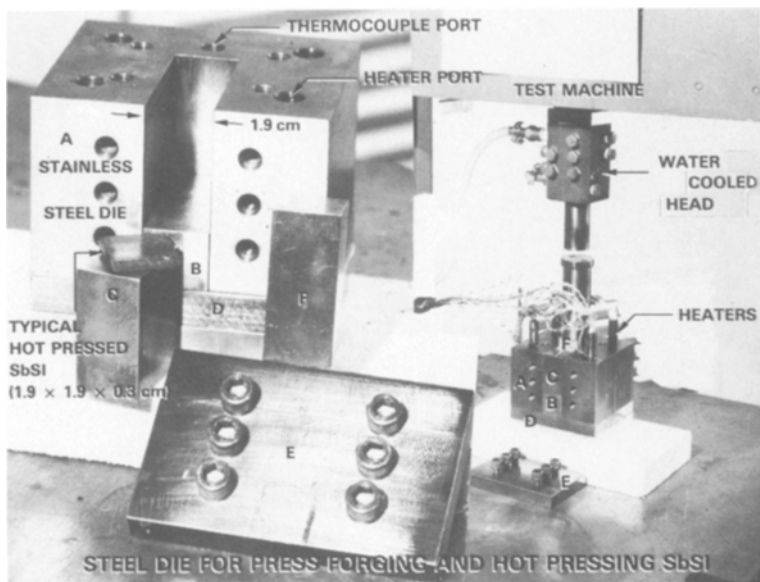


Figure 2 Steel die for hot pressing and press forging SbSI. A – die body; B – bottom spacer; C – front spacer; D – bottom plate; E – face plate; F – plunger. Note the ports for heaters and a thermocouple probe in the insert. In the main photograph, note the heaters, the test machine, the brick insulator below the die and the water cooled head. During hot pressing, a thermal blanket (not shown) was wrapped around the die to limit heat losses.

TABLE II Measured physical and electrical properties of processed SbSI materials

Sample ^a precursor processing	Average ^b density (g cm ⁻³)	Average ^c strength		Dielectric ^d constant ϵ_r ($\times 10^{-3}$)	Curie ^e temperature, T_c ($^{\circ}$ C)	Piezoelectric ^f charge constant, d_{33} (pC N ⁻¹)	Depoling temperature, T ($^{\circ}$ C)	Sensitivity ^h d_{33}^2/ϵ_r ($\mu\text{m}^2 \text{N}^{-1}$)
		σ_{\parallel} (MPa)	σ_{\perp} (MPa)					
B – L1	5.2	weak	weak	6–10	19–25	1000–1500	19–24	22
B – L2	4.8	20	weak	10–30	26–32	1500–2000	23–27	17
B – L1 – PF	5.0	6	4	3–4	35–40	350–450	19–24	5
B – L2 – PF	4.9	40	6	2–10	40–60	600–850	20–22	10
FG – ME	5.0		50	2–4	20–30	50–60	– ^g	0.1
FG – EL	5.2	60	50	2–5	25–35	30–60	– ^g	0.1
LG – EL	4.8	40	20	2–10	45–65	500–600	– ^g	6
FG + LG – MA	4.8	8	3	2–4	40–50	300–550	21–23	7
FG + LG – EL	4.8	30	–	2–10	50–70	350–390	19–23	3

^aB = boule, L = lot number, PF = press forged, FG = fine grain, LG = large grain, ME = mechanically aligned, EL = electrically aligned, MA = manually aligned.

^bTheoretical density (X-ray) 5.275 [2].

^c σ_{\parallel} , σ_{\perp} – strengths for loads applied parallel or perpendicular to the aligned grain c -axis, respectively, weak means sample was too weak to measure.

^dMeasured at 1 kHz to 1 mHz with the force parallel to the c -axis.

^eRange is due to differences from sample to sample, occasional values obtained outside this range.

^fMeasured at the depoling temperature.

^gThe low flat shape of d_{33} response prevented identification of depoling temperature.

^hPZT typically has a sensitivity of 2 to 7 $\mu\text{m}^2 \text{N}^{-1}$.

For dielectric and piezoelectric measurements sections (5 mm \times 5 mm \times 15 mm) were cut with their plane perpendicular to the c -axis texture in a fashion similar to that used for mechanical test bars. These plates were then coated with a silver conducting paint after the surfaces were first roughened on 180 grit SiC paper and then cleaned with acetone. Subsequently, the silver coating was generally dried with a hot-air gun.

After coating, samples were poled in a carbon tetrachloride/dry ice mixture at $-5 \pm 5^{\circ}$ C. The best results were obtained by cycling the 0.6 cm thick samples to a colder temperature, then warming before poling at 1 to 1.5 (kV) d.c. for 2 to 5 min between two polished copper or aluminium plates. The samples were kept cold (either refrigerated or kept in a box with dry ice) while awaiting measurement. The piezoelectric charge constants, d_{33} , were measured on epoxy potted samples as a function of temperature by enclosing the head of the measuring device* in an atmospheric control chamber designed to control temperatures from 0 to 50 $^{\circ}$ C. The hydrostatic piezoelectric charge constants, d_h , are to be measured in the near future at the Naval Underwater Systems

Center.[†] The relative dielectric constants, ϵ_r , were derived from capacitances which were measured from 0 to 100 $^{\circ}$ C using another atmospheric control chamber in conjunction with an automatic capacitance bridge.[‡] Temperatures were monitored with chromel–alumel thermocouples mounted in intimate contact with the sample. The temperatures at which the maximum ϵ_r and d_{33} responses occurred were taken to be the Curie temperature, T_c , and the depoling temperature, T , respectively.

3. Results and discussion

3.1. Processing

3.1.1. Hot pressing and mechanical alignment

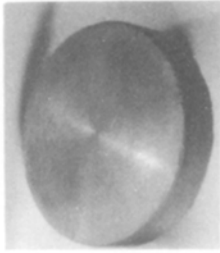
Early experiments showed that SbSI chemically attacked alumina dies and that graphite dies caused decomposition of the SbSI. However, stainless-steel dies (e.g. Fig. 2) were found to be relatively inert and were adopted for all the pressing and forging shown in this study (Fig. 3). Following a sequential pressing technique similar to that of Okazaki and Narushima [3], the fine powders (Fig. 1a and b) were cold pressed in one direction at 7 MPa (1 ksi) to roughly align the

*Berlincourt Model Number PDT3300 Piezo d_{33} Meter, Channel Products, Inc.

[†]Measurements courtesy of Mr C. LeBlanc.

[‡]Automatic Capacitance Bridge Model 4270A, Hewlett Packard Inc.

HOT PRESSED
FINE GRAIN SbSI POWDER

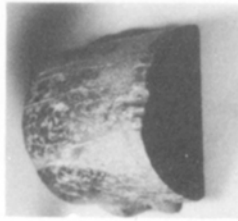


3 cm

SbSi "BOULE" SECTION

LARGE GRAIN POWDER
FROM SbSI "BOULE"

AS-RECEIVED



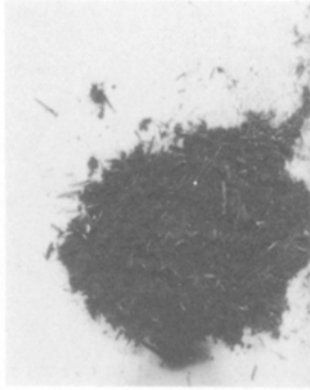
1.9 cm

PRESS FORGED



2.6 cm

RANDOM ORIENTATION
AS-PREPARED



2.5 cm

ELECTRICALLY ALIGNED
HOT PRESSED



1.3 cm

Figure 3 Examples of SbSI bodies. The top centre shows a body made by hot pressing fine grained powder; the lower left shows a boule section as-received and as-press forged; the lower right shows randomly oriented grains from an SbSI boule and a body prepared by electrically aligning and hot pressing these powders (note the horizontal alignment of large grains seen on the surface).

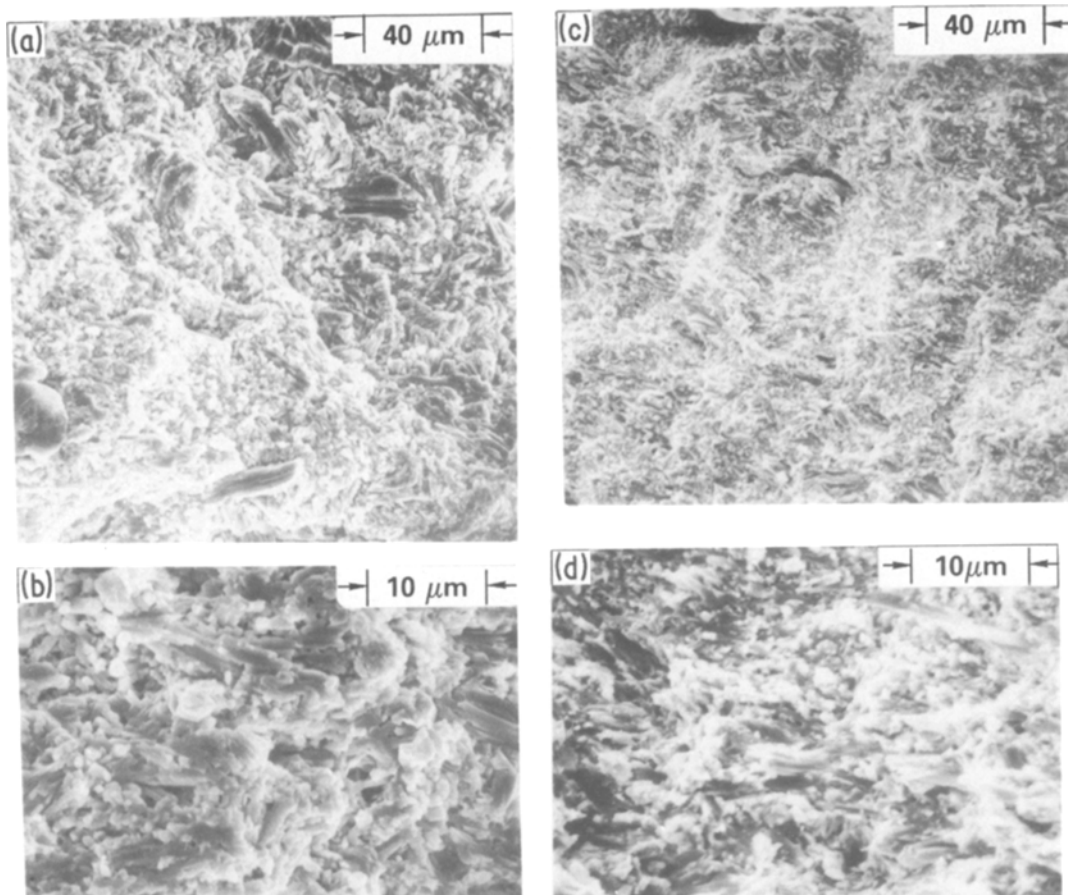


Figure 4 Microstructures of SbSI bodies hot pressed from fine grain powders. (a) and (b) are respectively lower and higher magnification photographs of fracture surfaces of material processed by hot pressing orthogonal to the original cold-pressing direction to achieve some mechanical alignment. (c) and (d) are respectively lower and higher magnifications of a fracture of a body hot pressed from electrically-aligned fine grain powders. In both cases, the hot-pressing direction was in the vertical direction. Note that there is very little resultant orientation (horizontal alignment) of the elongated grains in (a) and (b) but there is a fair amount in (c) and (d).

c-axis crystals in one plane and then hot pressed along an orthogonal axis at 70 MPa (10 ksi) at 340°C for 3 to 4 h to approach a rod or uniaxial texture. This procedure produced good densification (Table II, Fig. 4a and b) but limited alignment. A later experiment utilizing large grains obtained by crushing part of a boule resulted in better alignment and reasonable densities (Table II). However, this latter approach was unsatisfactory since the large grains from the boule had to be physically aligned and interspersed with fine grain powders, a time-consuming procedure which produces an irregular grain distribution and density.

3.1.2. Electrical alignment

Since mechanical alignment was not satisfactory and manual alignment was neither optimum nor

practical, an electrical alignment procedure was developed. Electrical alignment of fine grains between two d.c. electrodes was attempted first as suggested by Morgan [8]. After limited success, this process was altered to one using a 60 Hz a.c. field in the apparatus shown in Fig. 5 which produced excellent alignment. As expected, carbon tetrachloride, a non-polar liquid, was found to be sufficiently resistant to dielectric breakdown and to leave almost no residue on the SbSI crystals upon drying. Therefore, it was employed to carry the crystals in the electrical alignment device as they were dropped through the liquid between the electrodes for alignment at 2 to 4 kV. As can be seen in the insert of Fig. 5, the *c*-axes of the powder particles align parallel to the electric field during this process. After the grains settled in a

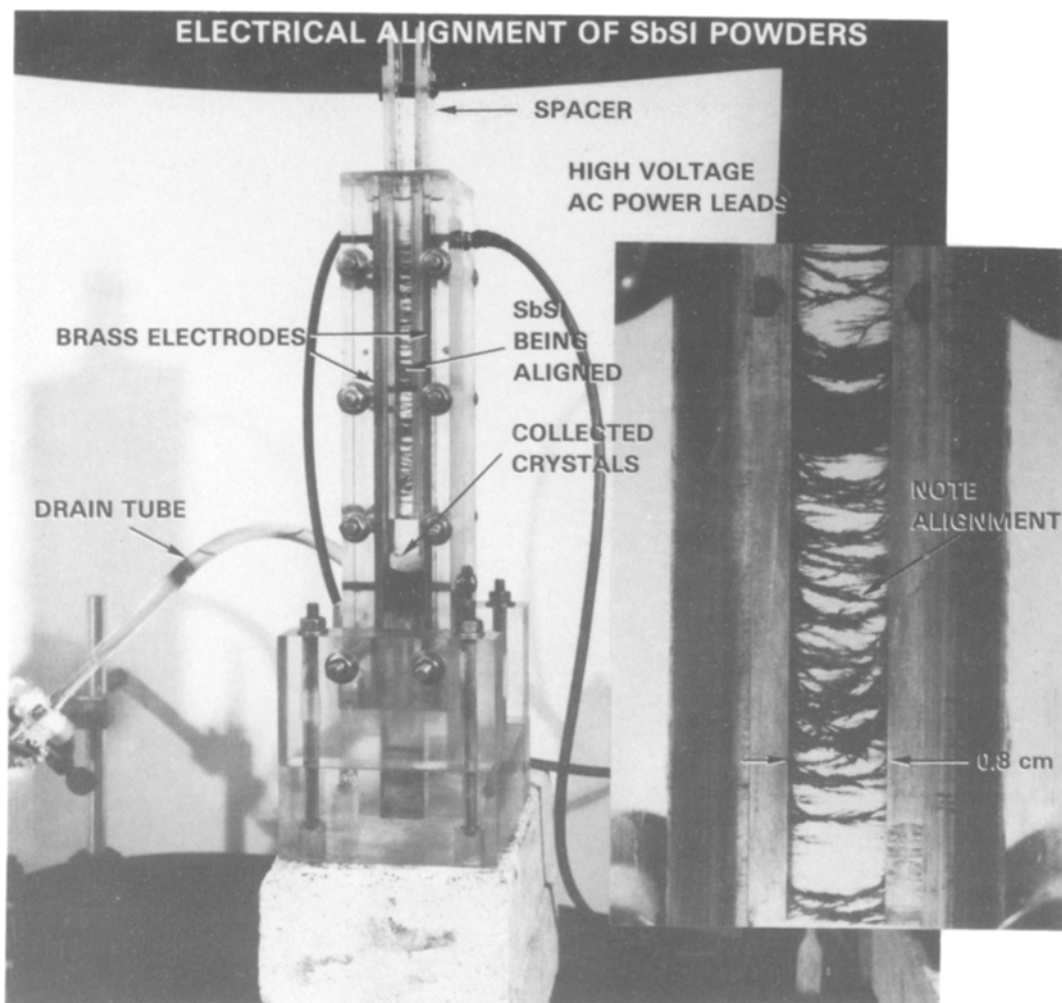


Figure 5 Electrical alignment apparatus and actual degree of alignment of SbSI powders (shown at higher magnification in the insert to the right).

layer at the bottom, the CCl_4 was filtered off while retaining the electric field to minimize loss of alignment from fluid motion. The residue was then cold pressed in the alignment device at 7 MPa into a green body nominally 1.5 cm square and about 0.3 cm thick. Such bodies were then hot pressed in the square stainless-steel die at pressures of 60 to 70 MPa and temperatures of 330 to 340°C for 5 h. This produced high-density ($>90\%$ of theoretical) electrically-aligned bodies (Fig. 4c and d).

As discussed later, the piezoelectric properties of the mechanically-aligned hot-pressed fine-grained ceramics were inadequate even though good grain alignment was obtained (Table II). This was not too surprising since Mansingh *et al.* [9] have shown that the piezoelectric properties of

the needle-like SbSI crystals decreased with decreasing diameter below $\sim 150\ \mu\text{m}$. Therefore, larger grains (Fig. 3) were obtained by crushing boules (since large grain powders were not available) and these were successfully aligned electrically (Fig. 6a and b). Hot pressing these aligned large grains under the same conditions used for fine grains produced an aligned body (Fig. 3) with a slightly lower density ($\sim 4.8\ \text{g cm}^{-3}$) and with slightly less strength ($\sim 20\ \text{MPa}$) than those obtained using the fine grains ($\sim 5.2\ \text{g cm}^{-3}$ and 50 MPa).

3.1.3. Press forging

Although the as-received boules already had a near-maximum degree of alignment, sections of several boules were press forged in a radial direction (i.e.

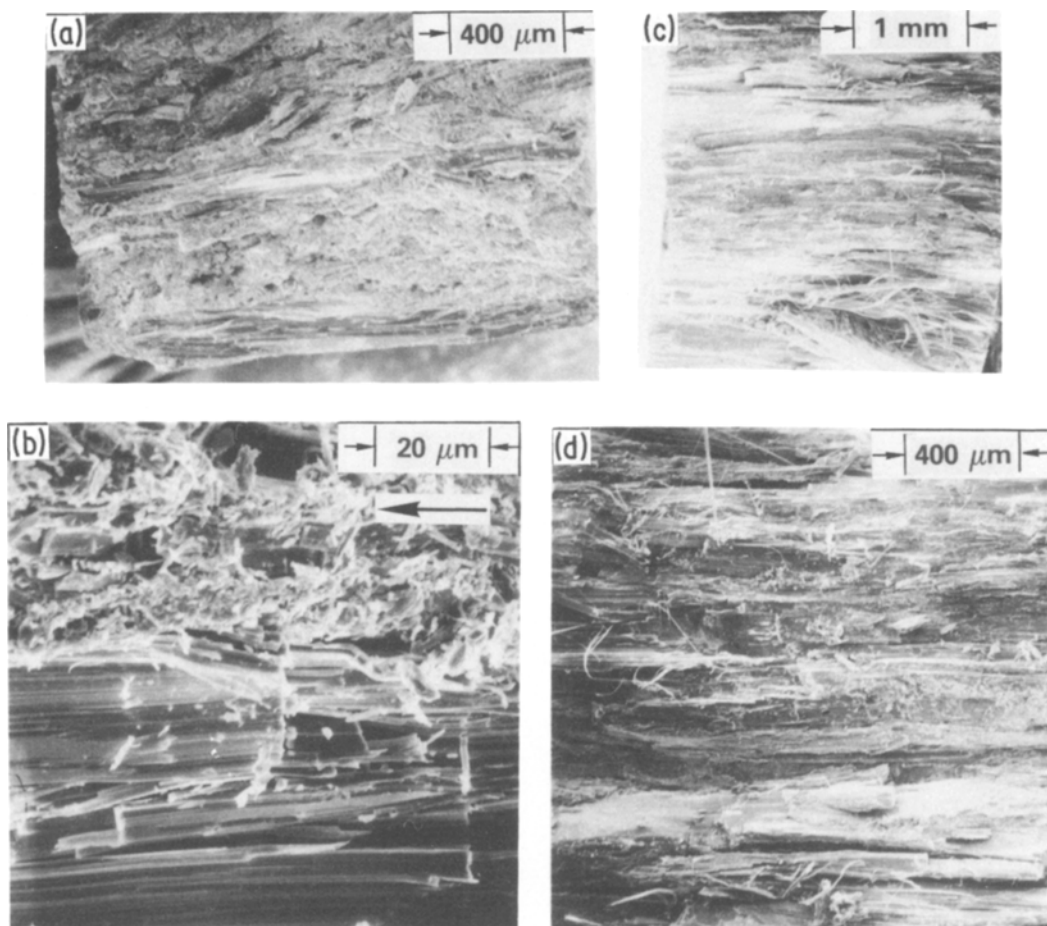


Figure 6 SbSI bodies processed from boule materials. (a) and (b) are respectively lower and higher magnifications of the fracture of a body made by hot pressing electrically-aligned large grains obtained by crushing a boule. (c) and (d) are fracture cross-sections of a press forged boule. In both cases, the pressing and forging directions are vertical. Note in (a) and (b) there is substantial alignment of large clusters of grains. Also note in (b) that even within regions not first appearing to have a high degree of alignment that there is some alignment, e.g. note larger grain segments in line with the arrow. (c) and (d) show near perfect alignment from the original boule retained in the press-forging process from the original boule. Note in both cases that the fracture may have distorted the alignment of some of the surface grains.

perpendicular to the boule *c*-axis, Fig. 3) to determine if grain sizes could be reduced and/or bonding between grains improved. A medium strength (~ 5 MPa) reasonably dense (5.0 g cm^{-3}) well-aligned press-forged body (Fig. 6c and d), $1.5 \text{ cm} \times 1.5 \text{ cm} \times 0.6 \text{ cm}$, was formed from a 1.5 cm long and 1.1 cm diameter section of an SbSI boule by using the same conditions as those used for hot pressing of powders (60 to 70 MPa and 330 to 340° C for 5 h).

3.2. Characterization and properties

3.2.1. Density, microstructure and strength

Densities of the bodies were typically 90 to 95% of theoretical regardless of whether they were

electrically aligned and hot pressed or press forged and whether or not large or small grain powders were used (Table II). Mechanical alignment of fine grain chemically-prepared powders resulted in only limited *c*-axis alignment in the dense material (Fig. 4a and b). However, electrical alignment of these same powders resulted in an appreciable increase in *c*-axis alignment and a dense product (Fig. 4c and d). As with the mechanical alignment, no significant grain growth occurred. Similarly, electrical alignment of the large grains resulted in hot-pressed bodies with substantial grain (*c*-axis) alignment and little grain growth (Figs 3, 6a and b). Press forging of boule sections also resulted in well-aligned bodies with little or no loss of the

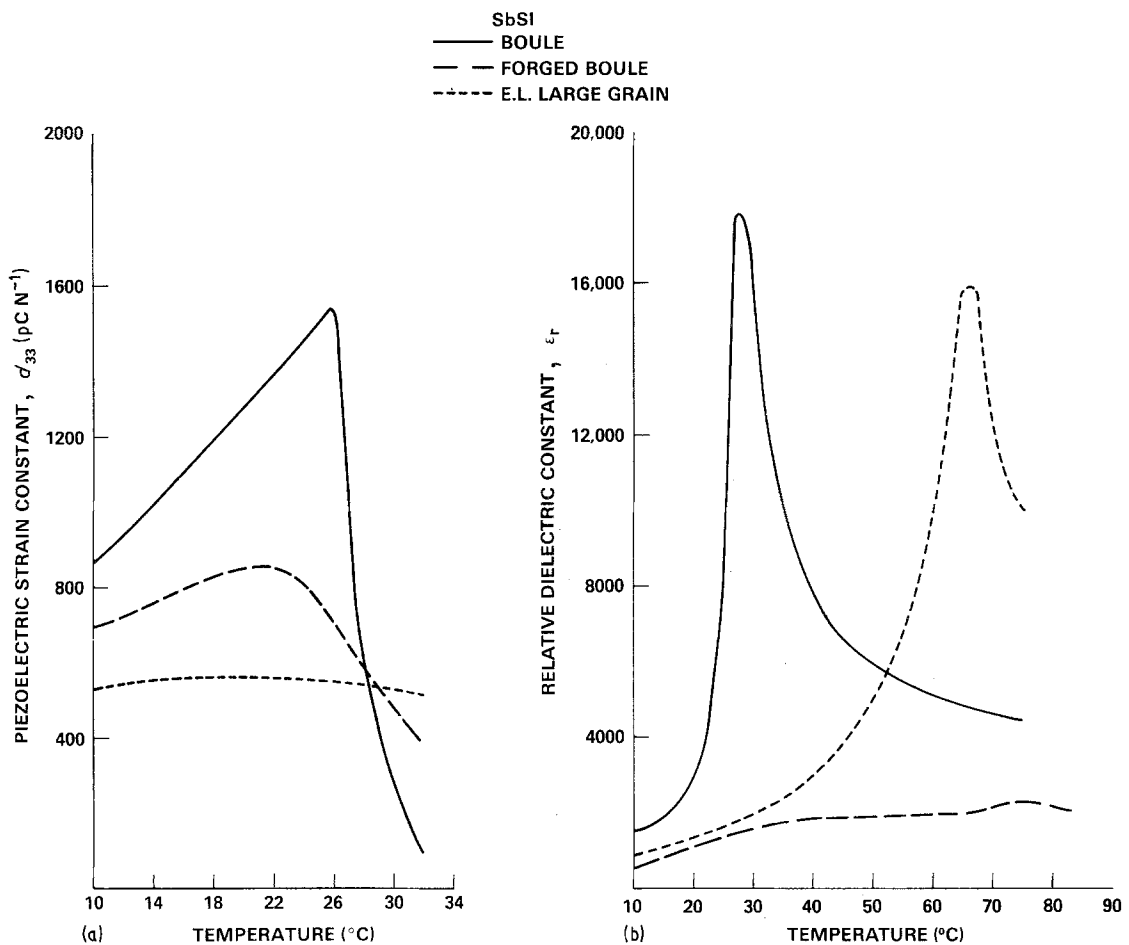


Figure 7 (a) Piezoelectric strain constant, d_{33} , and (b) relative dielectric constant, ϵ_r , as a function of measurement temperature for boule-derived materials. d_{33} values at 100 Hz and ϵ_r values at 10 kHz are shown for an as-received Lot 2 boule – (solid line), a press-forged section of that boule (long dashes) and a body (short dashes) hot-pressed from large grains extracted from the boule and electrically aligned prior to hot pressing. Note the flat shape of the d_{33} curve of the electrically-aligned hot-pressed sample. This behaviour combined with the high Curie temperature ($\sim 70^{\circ}\text{C}$) indicated by the ϵ_r , suggest that this material could be very useful.

near-perfect orientation of crystals from the starting boule (Fig. 6c and d). The final grain diameters were not significantly different from those in the starting boules which again indicates a stable grain structure.

Bend strength results are also summarized in Table II. The highest strengths were achieved in the finest grain bodies, as expected [10] but, as discussed later, such bodies had poor electrical properties. Also, as expected, there was a significant anisotropy of strength with substantial alignment, the highest strengths occurring for stresses parallel to the c -axis (Table II).

Of particular importance is the fact that rather

reasonable bending strengths (6 to 20 MPa) were achieved, even in the weakest direction (stressing perpendicular to the c -axis texture) in bodies either made with electrically-aligned grains from crushed boules or by press forging of a boule. Such boule-derived bodies also retained reasonable electrical responses, as discussed below. It should also be noted that, while the strengths of the starting boules, which were too low to measure initially (Table II), improved slightly (bend bars could not be prepared from early boules since they separated into individual fibre grains during machining attempts), press forging still significantly increased their strengths to ~ 5 MPa. This would

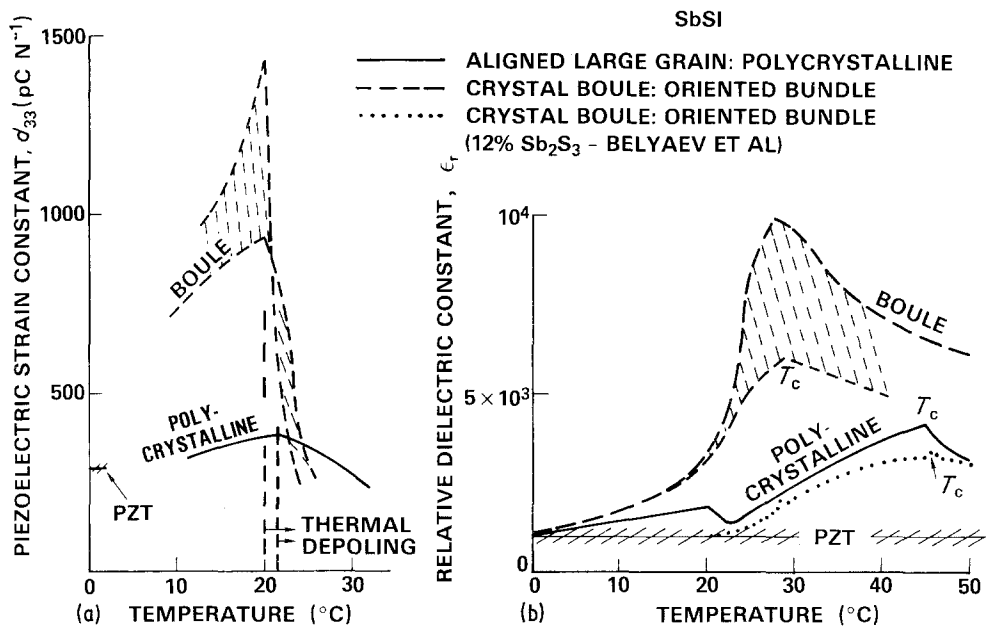


Figure 8 (a) Piezoelectric strain constant, d_{33} , and (b) relative dielectric constant, ϵ_r , against temperature. In both curves, the cross-hatched regions represent differences due to different frequencies. The upper limits were measured at 20 Hz and 1 kHz, respectively, while the lower limits were measured at 300 Hz and 100 kHz.

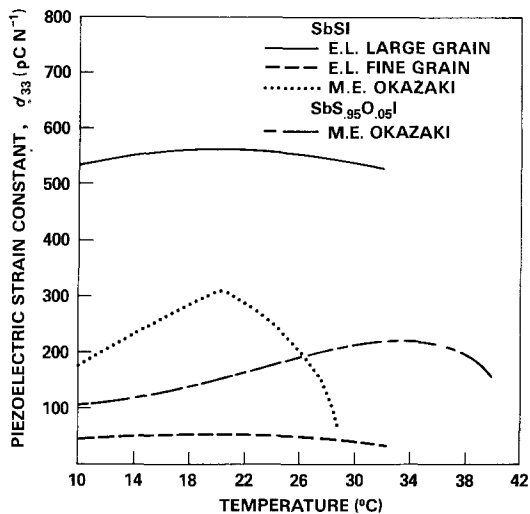


Figure 9 Piezoelectric strain constant, d_{33} , as a function of measurement temperature for fine grain SbSI material. The upper curves for large grain materials is a repeat from Fig. 7 for comparison. The lowest curve is from electrically-aligned fine grained material of this study. The intermediate curves are from Okazaki's previous work.

*In early NRL studies [11], it was noted that the available SbSI boules consisted of bundles of long thin orthorhombic crystals (SbSI) separated by large numbers of smaller rhombic or monoclinic crystals (probably unreacted SbI_3 and Sb_2S_3). Boules, especially the earlier ones, were found to have a yellow grain boundary phase (distinct from the reddish SbSI) under the optical microscope. Therefore, a semiquantitative method of analysis based on solubilities in CS_2 and ethanol was used to determine the amount of impurities. The SbSI was first treated with CS_2 in which SbI_3 is soluble, but in which neither Sb_2S_3 or SbSI are. Then the undissolved SbSI was put in ethanol in which Sb_2S_3 has high solubility, but SbSI is only slightly soluble. Approximately 5% of each of the above impurities were found which suggests an incomplete reaction of the SbI_3 and Sb_2S_3 during growth of the boules. Later boules contained much less impurity and appeared to have better electrical properties. Even so, EDAX measurements indicated a slight excess of sulphur was still present, as expected.

appear to be due to improved bonding between grains.*

3.2.2. Piezoelectric properties

Piezoelectric properties are also summarized in Table II where it can be seen that all fine grain materials had low d_{33} and ϵ_r values regardless of the degree of alignment. The results of Mansingh *et al.* [9] suggest that the diameter of these fine grains is too small for effective domain formation which leads to the poor piezoelectrical response. As seen in Fig. 7, bodies with higher d_{33} (400 to 800 pC N^{-1}), moderate ϵ_r (~ 2000) values, and reasonable bending strengths (Table II) were obtained by press forging bodies from recently acquired boules [12]. However, the level of the d_{33} (500 to 600 pC N^{-1}) and ϵ_r (5000 to 16000) values which can be obtained in bodies of hot pressed electrically-aligned large particulates obtained from these same boules, indicate that the development of chemical methods by producing

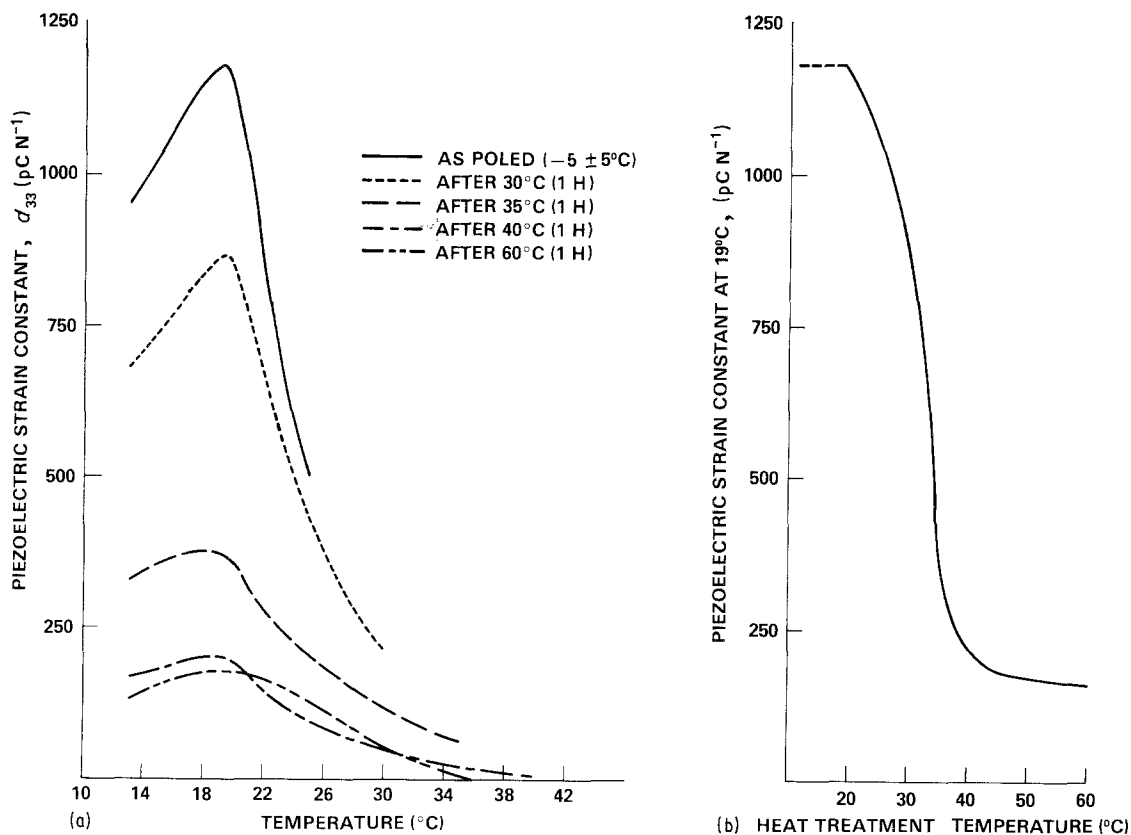


Figure 10 Piezoelectric strain constant, d_{33} , as a function of measurement temperature, and previous thermal history at 100 Hz. (a) shows the d_{33} values as a function of temperature for a boule specimen that was measured as-poled, without any heat treatment or after a 1 h heat treatment at each of the temperatures indicated. Note that so long as the measurement or heat treatment temperature did not exceed the preceding heat-treatment temperature, the response was reproducible. Curves for heat treated samples are the average of 2 to 3 heat treatment measurement cycles. (b) is simply a plot of the maxima from the other curves as a function of the heat-treatment temperature. All data shown are for an earlier (Lot 1) boule.

coarser powders could result in a practical product. By comparison, the d_{33} (1500 to 2000 pC N^{-1}) and ϵ_r (10 000 to 20 000) of the boules are larger but as shown before the strengths are probably too low to be practical.

Early SbSI boules, which contained an excess of iodide, were found to have lower Curie temperatures (e.g. 19 to 25 $^{\circ}\text{C}$) and low piezoelectric depoling temperatures (19 to 24 $^{\circ}\text{C}$) as expected [4]. However, Belyaev *et al.* [4] also indicated that substantial additions of Sb_2S_3 [12] (Fig. 8) can raise the Curie point substantially. In our work, it was found that boules (lot 2) grown with a slight excess of Sb_2S_3 [12] had slightly higher Curie temperatures and depoling temperatures (Table II). Fig. 7 shows that when these boules were either hot forged or broken up, electrically aligned, and then hot pressed, the resultant body had a higher Curie temperature of 45 to 65 $^{\circ}\text{C}$.

However, it appears that, within the limited operating temperature range of the piezo d_{33} meter, the depoling temperature has not been raised in a similar manner. This suggests that an alloy or addition (e.g. O^- or S^-) to the pure material might raise the Curie temperature more than it raises the depoling temperature which could limit its use. However, the flat shape of the d_{33} response in the electrically-aligned large grain bodies which may extend to the Curie temperature is an especially desirable characteristic. This latter effect would allow one to use alloying such as in the $\text{Sb}_{0.95}\text{O}_{0.05}\text{I}$ of Okazaki and Narushima [3] to further improve the usefulness of SbSI (Fig. 9).

The effect of frequency on the dielectric constant can be seen in Fig. 8 where the upper curve for the boule was measured at a frequency of 1 kHz and the lower curve at 100 kHz. The sensitivities shown in Table II indicate that a press-

forged boules may be equally as useful as the electrically-aligned large grain body provided its strength can be improved.

In addition to the studies already discussed, other experiments were carried out to determine the effect of temperature cycling on the magnitude of the d_{33} . The effect of the maximum cycling temperature on the degree of reduction of the piezoelectric constant of a boules section is shown in Fig. 10. Note that, unless the Curie temperature is exceeded, some degree of poling remains. In the NRL electrically-aligned hot-pressed material this behaviour should allow one to use the material up to 70° C (the Curie temperature shown by the dashed line in Fig. 7b).

4. Conclusions

Several processing techniques were developed for anisotropic piezoelectric materials, in particular, electrical alignment of crystalline grains followed by hot pressing, which was found to yield materials with exceptional potential. This electrical alignment process appears to offer advantages over either the press forging of boules sections or the orthogonal axis mechanical hot-pressing from a standpoint of practical application and from the potential ease and adaptability for tailoring material properties. Extensive microstructural, mechanical and electrical characterization illustrates that the polycrystalline SbSI bodies produced by the electrical alignment followed by hot pressing have very reasonable bend strengths, e.g. ~20 MPa, perpendicular to the c -axis (the weakest direction) and good hydrostatic piezoelectric charge responses, 500 to 600 pC N⁻¹. Similar characterization shows that bodies with similar electrical characteristics (d_{33} , 350 to 850 pC N⁻¹), but lower strengths (~6 MPa), can be obtained by press forging. However, the lower depoling

temperature 20 to 30° C might limit usage of this latter material. However materials from either of these processes could be incorporated into a device which uses electrical biasing to extend the zero-field depoling temperature. Finally, in the case of similar potential anisotropic materials which exhibit higher depoling and Curie temperatures, both the alignment technique and the interrelations between electrical and mechanical properties presented in this study should provide a basis for further development.

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