

Ferroelectricity in SbSI

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The photoconducting compound SbSI was found to be ferroelectric with a Curie point at 22°C. It has a high spontaneous polarization of $P_s = 25 \mu\text{C}/\text{cm}^2$ and a small coercive field strength of $E_c = 100 \text{ V}/\text{cm}$ at 0°C. The dielectric constant at the Curie point reaches values as high as 50 000. The switching is relatively fast and depends on the applied field according to a power law. It appears that the unusually large field-induced shift in absorption edge in SbSI and its electromechanical behavior can be explained by the fact that the material becomes ferroelectric below room temperature.

I. INTRODUCTION

TWO years ago, the photoelectric properties of several V-VI-VII compounds (where V=Sb, Bi; VI=S, Se, Te; VII=Cl, Br, I) were investigated by Nitsche and Merz.¹ Single crystals of 11 compounds of this family were prepared by cooling from the melt or by sublimation. They have the form of thin needles which cleave easily parallel to their axis. According to Dönges² the structure is orthorhombic, space group D_{2h}^{16} . The wavelength of maximum photoconduction lies between 5400 and 7840 Å depending on the compound. With increasing atomic weight the maximum in photocurrent and the optical absorption edge are shifted to longer wavelengths.

SbSI is a photoconductor with a maximum sensitivity at 6300–6400 Å.¹ It has the remarkable feature that the temperature coefficient β of the energy gap with $\beta = 15 \times 10^{-4} \text{ eV}/\text{deg}$ is unusually large.¹

Kern³ has investigated the optical properties of SbSI and found that the absorption edge is shifted towards shorter wavelengths upon application of an electric field along the needle axis (c axis of the orthorhombic crystal).² The shift per unit field strength is more than an order of magnitude larger and opposite in sign than that expected from the Franz effect.⁴ Furthermore, the crystal expands noticeably along the c axis upon application of an electric field along it.

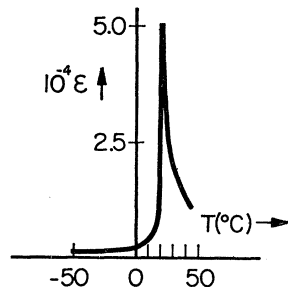


FIG. 1. Temperature dependence of the dielectric constant of SbSI parallel the c axis.

II. EXPERIMENTAL RESULTS

On account of the electromechanical effect at room temperature and of the coupling between optical, electrical, and mechanical properties we suspected that this material must have a high dielectric constant or might even be ferroelectric.

Measurements of the dielectric constant and of the hysteresis loop showed that SbSI is a ferroelectric with a Curie point at room temperature (22°C). The ferroelectric axis is the needle axis (c axis).

The dielectric constant ϵ perpendicular to the needle axis, at room temperature, shows a value of about 25 independent of frequency in the range 1 kc/sec to 100 kc/sec. Parallel to the needle axis the dielectric con-

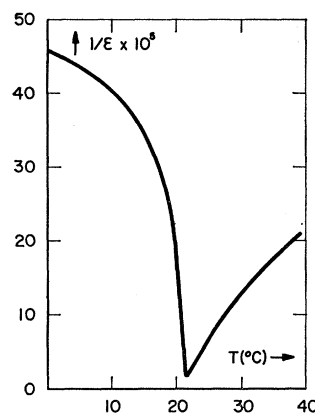


FIG. 2. Temperature dependence of $1/\epsilon$ below and above the Curie point.

stant is extremely high, reaching values up to 50 000 at the Curie point. Figure 1 shows that in SbSI the temperature dependence of the dielectric constant is typical for a ferroelectric material. As it appears from Fig. 2 the ratio of the slopes of the $1/\epsilon$ vs T plots, above and below the Curie point, is much larger than 2, thus indicating a first-order transition.

At 50 cps square hysteresis loops can be obtained. This is remarkable if one takes the unfavorable shape of the crystals into account (length 1 cm, cross section $1/10 \text{ mm}^2$). The measurements were made either along a few mm long needles or across tiny thin platelets cut out perpendicularly to the needle axis. The temperature dependence of the spontaneous polarization P_s is shown

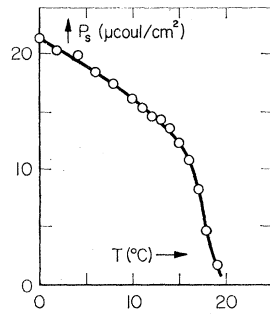
¹ R. Nitsche and W. J. Merz, *J. Phys. Chem. Solids* **13**, 154 (1960).

² E. Dönges, *Z. anorg. u. allgem. Chem.* **263**, 112, 280 (1950); **265**, 56 (1951).

³ R. Kern, *J. Phys. Chem. Solids*, **23**, 249 (1962).

⁴ W. Franz: *Z. Naturforsch.* **13a**, 484 (1958).

FIG. 3. Temperature dependence of the spontaneous polarization P_s of SbSI.



in Fig. 3 and the temperature dependence of P_s^2 is shown in Fig. 4. At 0°C a value of $P_s = 25 \mu\text{C}/\text{cm}^2$ is obtained, which is comparable to the spontaneous polarization of BaTiO_3 at room temperature. As it appears from Fig. 5, the polarization decreases with increasing temperature according to the law: $P_s^2 \propto (T - T_0)$, with T_0 about 5° higher than the Curie point. At the Curie point P_s^2 drops rather suddenly to zero as one would expect for a first order transition.

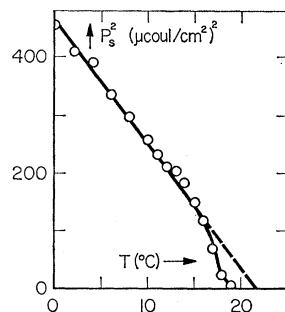
The coercive-field strength at 50 cps was found to be small, about 100 V/cm at 0°C. It decreases with increasing temperatures and drops suddenly at the Curie point. Although all these facts indicate a first-order transition, no double hysteresis loops above the Curie point could be observed.

Although the specimens were small, it was possible to investigate the switching properties of SbSI. In the range of 70–1400 V/cm the switching time t_s shows the following field dependence:

$$t_s = kE^{-n},$$

where the exponent n is about 3 (see Fig. 5). Two things are of interest. First, the switching is quite fast; a field of only 1400 V/cm gives a switching time of 3 μsec . Second, the usual exponential field dependence of the

FIG. 4. Temperature dependence of P_s^2 .

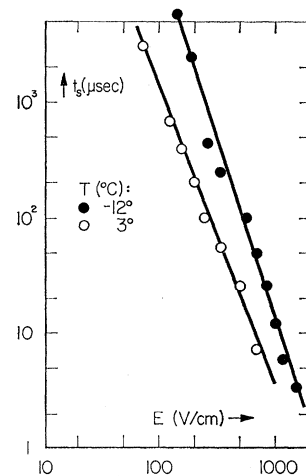


switching time cannot be observed. A similar law has up to now only been found for thiourea⁵ (exponent $n = 1.5$) and tetramethyl-ammonium-trichloro-mercurate⁶ (exponent between 3 and 7 depending on temperature).

III. DISCUSSION

SbSI is the first ferroelectric material which is also photoconductive. It can, therefore, conveniently be investigated for its photoconducting, semiconducting, and optical properties on the one hand and for its ferroelectric, dielectric, and electromechanical properties on the other hand. Strong interactions between these properties do exist as shown by the field-induced shift in absorption edge.

FIG. 5. Field dependence of the switching time of SbSI.



Dönges² found that the main feature in the crystal structure of SbSI is the existence of long chains parallel to the c axis. It should be noted that probably Dönges' measurements were performed above the Curie point, since he found a structure with a center of symmetry.

It is a natural step to check all the other compounds of the V–VI–VII family for ferroelectricity. Preliminary experiments have shown that some of the compounds do show transitions which may or may not be from the ferroelectric to the paraelectric phase. Measurements on better crystals will clarify this question. An investigation of the structure below the Curie point will also be necessary.

⁵ G. J. Goldsmith and J. G. White, *J. Chem. Phys.* **31**, 1175 (1959).

⁶ E. Fatuzzo, *Proc. Phys. Soc. (London)* **76**, 797 (1960).