

New Ferroelectrics of the Tetramethylammonium-Trihalo-Mercurate Family

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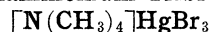
Three new ferroelectrics belonging to a family of the general formula $[X(\text{CH}_3)_4]\text{HgY}_3$ (where $X = \text{N}, \text{P}$; $Y = \text{Cl}, \text{Br}, \text{I}$) were discovered. They are: $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$, $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$, and $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$. The preparation of single crystals of these compounds (monoclinic, space group $P2_1$) is described. The dielectric constants are of the order of 10, the spontaneous polarizations between 1 and 3 $\mu\text{coul}/\text{cm}^2$. Curie points could not be observed because of thermal decomposition of the compounds around 170°C. The switching time varies with the seventh power of the applied field E .

I. INTRODUCTION

IN a recent publication¹ we reported on a new ferroelectric compound: tetramethylammonium-trichloro-mercurate (TTM), $[\text{N}(\text{CH}_3)_4]\text{HgCl}_3$. This paper is concerned with the preparation and some physical properties of ferroelectric isomorphs, obtained by substitution of the chlorine by bromine and iodine and of the nitrogen by phosphorus. These substitutions have led to the following new ferroelectrics: $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$, $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$, and $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$.

II. CRYSTAL PREPARATION

A. Tetramethylammonium-Tribromo-Mercurate

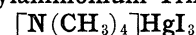


If a saturated aqueous solution of $[\text{N}(\text{CH}_3)_4]\text{Br}$ and HgBr_2 in the molar ratio 1:1 is prepared, the following equilibrium will be established: $2[\text{N}(\text{CH}_3)_4]\text{HgBr}_3 \rightleftharpoons [\text{N}(\text{CH}_3)_4]_2\text{HgBr}_4 + \text{HgBr}_2$. It determines whether the ferroelectric trisalt or the nonferroelectric tetrasalt will crystallize out. The equilibrium can be influenced by temperature and by the addition of HBr to the solution. The latter also greatly increases the solubility of the $[\text{N}(\text{CH}_3)_4]\text{Br}-\text{HgBr}_2$ mixture in a given volume. In Fig. 1 solubility curves are shown as a function of temperature and HBr concentration. They also indicate under which conditions the trisalt or tetrasalt is obtained. The points were obtained by slowly cooling down a stirred, saturated solution and microscopic

observation of the shape of the occurring crystals. The trisalt grows in elongated plates which show a typical extinction at 45° under crossed polarizers, whereas the tetrasalt shows extinction parallel to the crystal edges. It can be seen that from a neutral solution the ferroelectric salt can be grown only above 30°C. Since it is desirable for crystal growth to work at relatively high concentrations of the solute we chose to work in 1.3-normal HBr between 65 and 50°C. By slowly cooling down a saturated solution in this temperature range it is possible to obtain crystals of $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$ either by random nucleation on the bottom of the vessel or from seeds suspended from nylon threads. The cooling process has to be carried out in a closed system in order to avoid a change in acid concentration by evaporation of HBr. The crystals have the form of white needles (average size $10 \times 3 \times 3 \text{ mm}^3$), the ferroelectric axis being perpendicular to the needle axis. The growth of large crystals is difficult since twinning and dendritic growth occur easily.

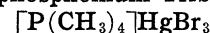
The structure of $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$ has been determined by White.² The compound is monoclinic, space group $P2_1$ with the following parameters: $a = 9.05 \text{ \AA}$; $b = 15.90 \text{ \AA}$; $c = 7.94 \text{ \AA}$; $\beta = 93.6^\circ$.

B. Tetramethylammonium-Triiodo-Mercurate



Since HgI_2 is only slightly water-soluble it was not possible to obtain measurable crystals of this compound from an aqueous solution, similar to the bromide. However, by stirring a finely powdered equimolar mixture of $[\text{N}(\text{CH}_3)_4]\text{I}$ and HgI_2 in cyclohexanone, a fairly concentrated solution of $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$ was obtained. By slowly evaporating the solvent, pale-yellow crystals of $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$ in the form of polyhedra up to $1 \times 1 \times 1 \text{ cm}^3$ could be grown.

C. Tetramethylphosphonium-Tribromo-Mercurate



Tetramethylphosphonium-bromide was not commercially available as a starting material. It was synthesized by Grignard reaction of PBr_5 with methylmagnesium-

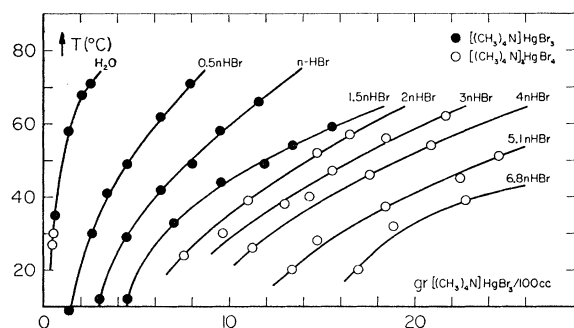


FIG. 1. Solubility of $[\text{N}(\text{CH}_3)_4]\text{Br}-\text{HgBr}_2$ mixtures versus temperature.

¹ E. Fatuzzo and R. Nitsche, Phys. Rev. 117, 936 (1960).

² J. C. White, RCA Laboratories, Princeton, New Jersey (private communication).

bromide in anhydrous ether and hydrolysis of the reaction product with HBr. The resulting solution was passed through a cationic ion exchange column (Dowex 50 W) which adsorbed the tetramethylphosphonium ions. Elution with HBr gave a pure tetramethylphosphonium-bromide solution to which an equivalent amount of HgBr_2 was added. Vacuum evaporation of the resulting solution gave the crude $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$ salt. Crystals were grown by dissolving the salt in dimethylformamide and slowly evaporating the solution. Flat white plates of $5 \times 5 \times 2 \text{ mm}^3$ were obtained, the ferroelectric axis being perpendicular to the plane of the plates. Crystallization from aqueous solution yielded only tiny, poor crystallites.

D. Other Substitutions

A number of other substitutions were tried; the salts obtained, however, had different structures as shown by x-ray analysis and thus were not ferroelectric.

Tetramethylphosphonium-triiodo-mercurate was prepared similar to the bromide by eluting the ion exchange column with KI and addition of HgI_2 . Its structure is different from TTM. The corresponding chloride was not obtained so far since the solution decomposed on concentrating. Substitution of Hg in TTM by Cd, Zn, and Cu and of the tetramethylammonium ion by tetraethylammonium-, trimethyl-, and dimethylammonium ion gave structures unidentical with TTM in all cases.

III. PHYSICAL MEASUREMENTS

The component ϵ of the dielectric constant tensor along the monoclinic axis, the spontaneous polarization P_s and the coercive field E_c of the above substances were measured. We found ϵ at room temperature to be of the same order of magnitude (about 10) in all three compounds. It is independent of temperature in the range -40 to $+100^\circ\text{C}$. Hysteresis loops were measured with the loop tracer described by Diamant *et al.*³ Remarkably square loops were observed and no compensation for losses was necessary. Due to the high coercive force in $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$ and $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$ loops could be observed only above 50°C , whereas in $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$ the loop can be observed already at -40°C . The coercive field E_c has a different temperature dependence in the three compounds. It can be seen from Fig. 2 that E_c decreases normally with temperature in $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$. In the other two compounds E_c shows a remarkable behavior. The sudden drop of E_c in $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$ is not accompanied by a transition (no peak in dielectric constant, no essential change in polarization) and can be compared with a similar drop observed in the temperature dependence of E_c of triglycine sulfate by Triebwasser.⁴ Thermal decomposition sets in around 170°C in all compounds.

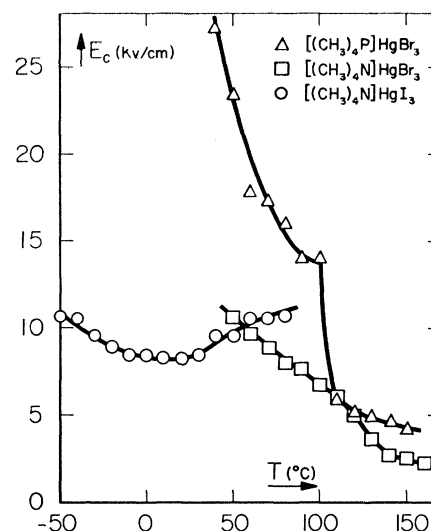


Fig. 2. Coercive field E_c versus temperature for $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$; $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$, and $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$.

The spontaneous polarization P_s of $[\text{N}(\text{CH}_3)_4]\text{HgBr}_3$ is $1 \text{ microcoulomb/cm}^2$, that of $[\text{P}(\text{CH}_3)_4]\text{HgBr}_3$ is $3 \text{ microcoulomb/cm}^2$. In both cases P_s is independent of temperature between -40 and $+160^\circ\text{C}$. The room temperature value of P_s for $[\text{N}(\text{CH}_3)_4]\text{HgI}_3$ is $1.7 \text{ microcoulomb/cm}^2$; however, in this material P_s increases slightly with temperature (similarly to TTM) and goes from $1.2 \text{ microcoulomb/cm}^2$ at -40°C to $2.3 \text{ microcoulomb/cm}^2$ at $+80^\circ\text{C}$.

From these results it follows that P_s increases by about a factor of 3 on substitution of nitrogen by phosphorus, whereas substitution of the halide ion in TTM does not alter P_s appreciably. In no case could a Curie point be observed because of thermal decomposition of the compounds.

The switching of the new members of the TTM family is even slower than in TTM because of their higher coercive fields. The dependence of switching time t_s on the applied field E in TTM has been studied in detail by one of us.⁵ Contrary to the exponential dependence of t_s on E observed in many ferroelectrics,^{6,7} in TTM t_s varies with the 7th power of E .

In most other ferroelectrics a minor loop is observable already at small fields; it then gradually grows and finally saturates with increasing E . In TTM-type ferroelectrics, on the other hand, upon application of an ac field, one first observes a straight line up to fields in the vicinity of E_c ; then suddenly a minor loop shows up which very rapidly reaches saturation. This behavior, however, is not caused by a true coercive field—as suggested by Pulvari⁸ for the case of sodium vanadate niobate—but by the very rapid decrease of t_s with E in the TTM ferroelectrics.

Summarizing, it can be said that the TTM family

³ H. Diamant, K. Drenck, and R. Pepinsky, *Rev. Sci. Instr.* **28**, 30 (1957).

⁴ S. Triebwasser, *IBM J. Research Develop.* **2**, 212 (1958).

⁵ E. Fatuzzo, *Proc. Phys. Soc.* **76**, 797 (1960).

⁶ W. J. Merz, *Phys. Rev.* **95**, 690 (1954).

⁷ C. F. Pulvari and W. Kuebler, *J. Appl. Phys.* **29**, 1742 (1958).

⁸ C. F. Pulvari, *Phys. Rev.* **120**, 1670 (1960).

represents an interesting class of ferroelectrics because of the following features:

(a) Chemical composition: they are the first ferroelectrics containing mercury and halogens.

(b) Temperature independence of the dielectric constant.

(c) The polarization does not decrease with temperature.

(d) Unusual switching behavior.

The difficulties in growing large, perfect crystals and the slow switching time, however, are serious limitations for technical applications.

Edge Emission in CdS Crystals that Show Mechanically Excited Emission

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The characteristic green fluorescence of CdS single crystals that exhibit mechanically excited emission has been examined spectroscopically at 4.2° and 77°K. The fluorescence of the crystals was stimulated by either ultraviolet irradiation, or the application of an electric field. The uv-stimulated and field-induced emission spectra are compared and discussed. The low-temperature behavior of the conductivity (storage properties) in these crystals is also discussed. The uv-stimulated edge emission peaks in these crystals differ from those in normal CdS; these differences are discussed and quantitative comparisons are made. A simple trapping model is applied to the uv-stimulated emission data at 77°K. On the basis of this model, the mean number of optical phonons cooperating in the optical transitions is shown to be higher than in normal CdS. The field emission, believed to be due to carrier injection, is explained on the basis of a previously proposed energy model of Warschauer and Reynolds for mechanically excited emission.

I. INTRODUCTION

THE phenomenon of mechanically excited emission is one in which radiative emission is obtained by mechanical excitation of optically or thermally stimulated CdS crystals. It has been previously shown by Warschauer and Reynolds¹ that selected cadmium sulfide crystals, cooled to 77°K and then stimulated with light, will respond to mechanical excitation; moreover, it has been determined that the threshold

for the stimulating radiation is 6900 Å. After stimulation, the crystal is completely shielded from light. If the crystal is now tapped in the dark in the direction of the *c* axis, one finds that a green flash of light is emitted from the body of the crystal. From a reasonably well stimulated crystal, several hundred flashes at the rate of one flash per tap can be obtained. It has also been determined that ultraviolet or visible light is not necessary for stimulation of the crystal. In fact, thermal background radiation is of sufficient intensity in the proper wavelength range to stimulate the crystal. It has further been shown that a crystal of this type, cooled to 77°K, then warmed in total darkness to approximately 200°K, with subsequent immersion in liquid nitrogen, will show flashes of the green edge emission when mechanically tapped. However, the emission is completely exhausted after only a few taps.

These CdS crystals, hereafter referred to as "tap-effect" crystals, as distinguished from "normal" or "ordinary" CdS crystals, also show storage properties. A given crystal at 77°K may increase in conductivity by as much as eleven orders of magnitude when exposed to the stimulating radiation. If the stimulating radiation is removed, the conductivity remains high and will remain so indefinitely. During stimulation, the conductivity increases slowly to a relatively high level after which it is observed to hold constant (in the dark at 77°K) for periods as long as 66 hr. Figure 1 shows how the storage varies as a function of temperature. Here current through the crystal is plotted as a func-

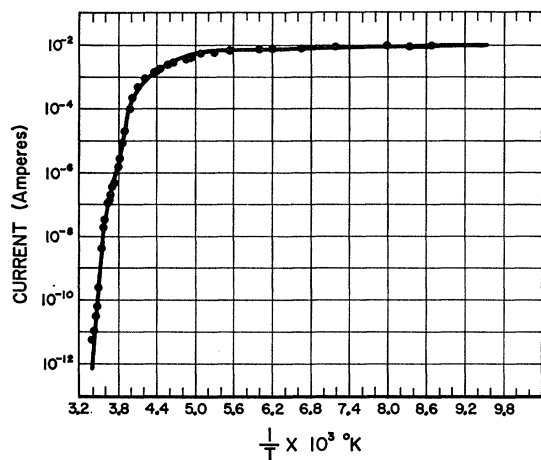


FIG. 1. Current through a "tap-effect" CdS crystal vs $10^3/T$. The temperature ranged from 115°K to 300°K.

¹ D. M. Warschauer and D. C. Reynolds, J. Phys. Chem. Solids 13, 251 (1960).