PHYSICAL REVIEW VOLUME 110, NUMBER 6 JUNE 15, 1958

New Room-Temperature Ferroelectric*

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(Received February 18, 1958)

The neutral-salt complex with glycine, di-glycine manganous chloride dihydrate, $(NH_2CH_2COOH)_2 \cdot MnCl_2 \cdot 2H_2O$, is found to be ferroelectric from low temperatures to +55°C. Above the latter temperature the conductivity suddenly becomes excessive. At room temperature the spontaneous polarization is 1.3×10^{-6} coulomb/cm^2 and the coercive field is 5.6 kv/cm. A nonreversible surface change is observable optically above 72°C, probably due to loss of H_2O. Thermal measurements indicate onset of water loss above 35°C; electrical conductivity increases sharply and irreversibly above 55°C, and care must be taken to prevent dehydration even at room temperature. No Curie temperature can be observed. X-ray measurements of this hitherto unreported salt show space group $P2_1$, $a=9.96$ A, $b=8.53$ A, $c=6.86$ A, $\beta=107\pm0.5°$, density $=1.875_0$ g/cc, and two formula units per cell. The ferroelectric axis is along b. The dielectric constants at room temperature are $\epsilon_a=6.6$, $\epsilon_b=8.1$, $\epsilon_c=7.4$; and these decrease linearly and only very slightly as the temperature is lowered to 77°K. The corresponding neutral-salt complex of two glycines with $MnBr_2$ is not isomorphous, occurring as a tri-hydrate, and is not ferroelectric. It has not been possible to find any metal which will replace manganese and form an isomorphous crystal.

I. INTRODUCTION

THE discovery of ferroelectric behavior in guanidinium aluminum sulfate hexahydrate (GASH) and isomorphs, by Holden, Matthias, and co-workers,[1] has eventually led to recognition of the importance both of substituted ammonium ions, and of the sulfate and closely related ions, in this very interesting type of dielectric anomaly. Following the GASH discovery, Pepinsky and associates[2] found similar anomalies in the ammonium and methylammonium alums. The phenomena in GASH and the alums led investigators to discovery of ferroelectricity in thiourea,[3] ammonium sulfate[4] and ammonium fluoberyllate[5] (the ferroelectric phases of which are quite dissimilar[6]), and di-ammonium di-cadmium tri-sulfate,[7] and eventually to the very important (room-temperature) ferroelectric tri-glycine sulfate $[(NH_2CH_2COOH)_3 \cdot H_2SO_4, =G_3S]$,[8] and its close relative tri-glycine fluoberyllate $[(NH_2CH_2COOH)_3 \cdot H_2BeF_4, =G_3F]$.[9]

As new classes of ferroelectrics are discovered, knowledge of the criteria for examination of still other materials grows. The importance of substituted acetates has been suggested, after the discovery of G_3S (glycine = aminoacetic acid), by ferroelectric behavior in ammonium chloroacetate,[10] glycine silver nitrate,[11] and di-calcium strontium hexapropionate[12] (propiononic acid = methylacetic acid). The essential features of the mechanism of ferroelectricity in G_3S has been indicated by a structural study,[13] which suggests involvement of a proton in a bifurcated bond, and also the strong tendency of one of the three glycine groups toward coplanarity (nonhydrogen atoms of this one glycine lie in a mirror plane, and one proton is shared by that glycine's amino nitrogen and two oxygens from a contiguous sulfate group, above the Curie point).

As a consequence of recognition of the importance for ferroelectricity of substituted acetates, a program of investigation of derivatives of alkyl and related carboxylic acids has been in progress in our Penn State Laboratory.

The first practical result of this new program has appeared in the discovery of a new room-temperature ferroelectric, $(\text{glycine})_2 \cdot MnCl_2 \cdot 2H_2O$ $(=G_2MCD)$, which shows useful behavior up to 55°C if care is taken to prevent dehydration below this temperature.

II. PREPARATION AND PROPERTIES OF DI-GLYCINE MANGANOUS CHLORIDE DIHYDRATE

Although the compound $(\text{glycine})_2 \cdot MnCl_2 \cdot 2H_2O$ (G_2MCD) has not been reported heretofore, complexes of glycine or other amino acids with neutral salts are well known. Glycine silver nitrate, $NH_2CH_2COOH \cdot AgNO_3$ (=GSN), and partially-substituted mixed crystals of that class $[\text{glycine} \cdot (Ag, Tl)NO_3$ and $\text{glycine} \cdot (Ag, Li)NO_3]$, the ferroelectric behavior of which was recently reported from this laboratory,[11] is one such salt. GSN becomes ferroelectric below −55°C; and substitution of Tl or Li for Ag, up to about 15%, raises the Curie temperature by as much as 10°C. Many other neutral-salt complexes of glycine have been prepared. One of the very first of these to be measured by us was

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* This investigation is supported by contracts with the Air Force Office of Scientific Research and the Army Signal Corps Engineering Laboratories.

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[12] B. T. Matthias and J. P. Remeika, Phys. Rev. **107**, 1727 (1957).

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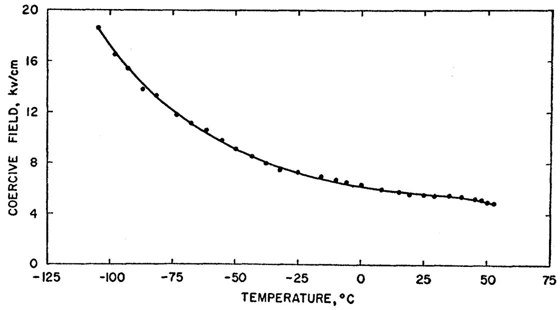

FIG. 1. $(CH_2NH_2COOH)_2 \cdot MnCl_2 \cdot 2H_2O$: coercive field *vs* temperature.

G_2MCD. It proved to be ferroelectric at room temperature.

G_2MCD grows readily from stoichiometric quantities of its constituents in aqueous solution: two moles of glycine to one of manganous chloride. Excellent crystals are easily obtained. The chemical constitution was first indicated by single-crystal x-ray data and a density measurement, and was confirmed by chemical analysis. The cell is monoclinic, with $a=9.96$ A, $b=8.53$ A, $c=6.86$ A, $\beta=107\pm0.5°$. The space group is $P2_1$. A density determination by the flotation method at 20°C gave 1.875_0 g/cc. There are two formula groups per unit cell. These data give a measured formula weight of 314.9; the calculated molecular weight for $(NH_2CH_2COOH)_2 \cdot MnCl_2 \cdot 2H_2O$ is 312.0. A structure analysis is in progress. This suggests the existence of a complex ion involving short Mn—Cl bonding, as found in the structure of the $MnCl_2$-hexamethylenetetramine dihydrate complex as reported by Tang and Sturdivant.[14]

The ferroelectric direction is that of the monoclinic axis.[15] The coercive field is 5.6 kv/cm and the spontaneous polarization is 1.3×10^{-6} coulomb/cm^2, both at room temperature. Variations of these quantities with temperature are shown in Figs. 1 and 2, respectively. Figure 3 shows the variation of ϵ_b with temperature. The dielectric constants at room temperature are $\epsilon_a=6.6$, $\epsilon_b=8.1$, and $\epsilon_c=7.4$. These decrease very slightly and linearly as the temperature falls to 77°K. The value of ϵ_b climbs sharply just below 55°C, and the rise is not attributable to increased conductivity. The dielectric constant cannot be measured above that temperature; nor do the crystals show ferroelectricity when the temperature is again lowered below 55°C. Observations on the heating stage of a polarizing microscope reveal the gradual and irreversible nucleation of a new phase, at the crystal surfaces, at temperatures above 72°C; this no doubt involves loss of water molecules. Below this temperature the crystals must be protected from dehydration. Storage in kerosene at room temperature is one adequate means to such protection. The dehydration interferes with calorimetric measurement above 35°C.

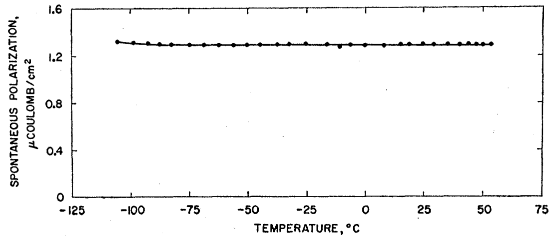

FIG. 2. $(CH_2NH_2COOH)_2 \cdot MnCl_2 \cdot 2H_2O$: spontaneous polarization *vs* temperature.

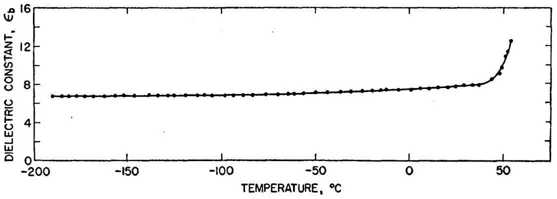

FIG. 3. $(CH_2NH_2COOH)_2 \cdot MnCl_2 \cdot 2H_2O$: dielectric constant *vs* temperature.

It has not as yet been possible to observe domain structure, even with application of strong electric fields, with the polarizing microscope.

No isomorphous compound has as yet been found. Manganous bromide forms a neutral-salt complex with glycine, but this proves to be a tri-hydrate, $(glycine)_2 \cdot MnBr_2 \cdot 3H_2O$. The cell of this complex is monoclinic, space group $P2_1/c$, $a=11.10$ A, $b=6.12$ A, $c=9.05$ A, $\beta=91°$, density$=2.23$ g/cc, and two molecules per cell. The observed formula weight is 416, and the calculated weight for the tri-hydrate is 418. It has not as yet been possible to substitute any other metal in place of manganese and maintain isomorphism.

III. COMPARISON WITH GASH AND G_3S

As in the case of GASH,[1] no Curie point is attainable for G_2MCD. GASH shows ferroelectric behavior right

TABLE I. Comparison of room-temperature values of P_s and E_c for GASH, GVSH, G_3S, G_3F, and G_2MCD.[a]

	P_s (10^{-6} coul/cm^2)	E_c (kv/cm)
GASH[b]	0.35	1.5
GVSH[c]	0.38	6.0
G_3S[d]	2.2	0.2
G_3F[e]	3.2	5.0
G_2MCD	1.3	5.6

[a] GASH = guanidinium aluminum sulfate hexahydrate; GVSH = guanidinium vanadium sulfate hexahydrate; $G_3S = (glycine)_3 \cdot H_2SO_4$; $G_3F = (glycine)_3 \cdot H_2BeF_4$; $G_2MCD = (glycine)_2MnCl_2 \cdot 2H_2O$.
[b] See reference 1.
[c] J. P. Remeika and W. J. Merz, Phys. Rev. 102, 295 (1956).
[d] See reference 8.
[e] See reference 13.

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[14] Y. C. Tang and J. H. Sturdivant, Acta Cryst. 5, 174 (1952).

[15] This is true also for G_3S and isomorphs, and for GSN. It is *not* the case for ammonium monochloroacetate, however. The latter crystal has space-group $C2/c$ above its Curie temperature, but the ferroelectric axis is along the $[10\bar{1}]$ direction. [Unterleitner, Vedam, Okaya, and Pepinsky (to be published)]. The symmetry of the low-temperature phase is perhaps Cc.

up to its dehydration temperature, above 200°C. G_3S is entirely stable up to its Curie temperature,[8] 47°C; and G_3F is equally stable to its Curie temperature at 70°C.[9] G_2MCD alone among the three classes of compounds is unstable at room temperature, and increasingly less stable above.

A comparison of values of spontaneous polarizations and coercive fields for GASH and its vanadium analog, G_3S, G_3F, and G_2MCD, is given in Table I. G_3S is by far the most advantageous of the three. GASH has the disadvantage of unsymmetric hysteresis loops. The coercive field of G_2MCD is thirty times higher than that of G_3S, and the spontaneous polarization is half as high, but the hysteresis loops in both classes of crystals are nicely square and unbiased.

IV. ACKNOWLEDGMENTS

We are grateful to Mrs. Dora Diamant for assistance in growth of the crystals, and to Dr. S. Triebwasser of the IBM Research Laboratory, Poughkeepsie, New York, for helpful discussions.

PHYSICAL REVIEW VOLUME 110, NUMBER 6 JUNE 15, 1958

Ferromagnetic Resonance Line Width in Yttrium Iron Garnet Single Crystals

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(Received February 24, 1958)

A study of ferromagnetic resonance line width in polished, single-crystal spheres of yttrium iron garnet is described. Wave-guide cavity perturbation techniques are used with samples 0.013 in. to 0.020 in. in diameter. An extremely narrow line width of 520 millioersteds (the full width) is observed at 9300 Mc/sec along the hard axis [100]. It is believed this is the narrowest resonance line yet reported on ferromagnetic materials. The line width is shown to be strongly influenced by the sample surface, with the line narrowing by over a factor of twenty as the polishing proceeds.

The line width at 3000 Mc/sec on the same sample is 530 millioersteds. The approximate invariance of the line width for more than a three-to-one change in frequency is compared with the predictions of some recent theories of ferromagnetic resonance line width. The invariance of line width with frequency is also used to conclude that $\lambda\omega$ and T_2 in the Landau-Lifshitz and Bloch-Bloembergen equations of motion, respectively, are approximately constant over this frequency range.

A STUDY of ferromagnetic resonance in single crystals of yttrium iron garnet (YIG) has been made at 9300 Mc/sec and 3000 Mc/sec using cavity perturbation techniques. The samples are polished spheres 0.013 in. to 0.020 in. in diameter, the same samples being used at both frequencies. At 9300 Mc/sec the samples are placed in the center (away from all walls) of a tunable TE_{108} transmission cavity with inside dimensions of 0.8×0.9×7.16 in. At 3000 Mc/sec a tunable TE_{101} transmission cavity is used with inside dimensions of 0.7×2.74×2.74 in., the samples being placed approximately six diameters off the wall. In both cases the samples are placed in an essentially uniform rf magnetic field.

Standard cavity perturbation techniques are used,[1] with the value of μ'' being computed from the change in transmission through the cavity when the applied dc field is moved from a reference point considerably above resonance to the point being measured. One important change in the usual technique was introduced, however, because of the narrowness of the resonance line. In obtaining ΔH, the usual procedure of shifting the frequency of the microwave source at each of the $\frac{1}{2}\mu_{\max}''$ points, to counteract the detuning effect of the sample, was found to yield erroneously narrowed lines. Thus for the data in this paper the cavity is manually retuned by tuning screws at each of these points, and the frequency of the frequency-stabilized source is never varied.

LINE WIDTH AT 9300 Mc/sec

A line width of 2.3 oe at 9300 Mc/sec has been reported previously[2] on YIG crystals grown at this laboratory. In a later batch and with more refined polishing techniques, an extremely narrow line width ΔH of 520 millioersteds (moe) has been observed at 9300 Mc/sec with the dc field along the hard axis [100]. (Fig. 1.) (ΔH here is the full width between $\frac{1}{2}\mu_{\max}''$ points.) The line widths along the medium and easy axes are slightly higher. It is believed this is the narrowest resonance line yet reported on ferromagnetic materials.[3] The quantities $4\pi M_s$ and K_1/M_s have also

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[2] LeCraw, Spencer, and Porter, J. Appl. Phys. **29**, 326 (1958).

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