NEW PHASE-TRANSITION LINE IN CRYSTALLINE TRIGLYCINE SELENATE AT HIGH PRESSURES

V. P. Mylov, I. N. Polandov, and B. A. Strukov
Chemistry Department, Moscow State University
Submitted 5 July 1966
ZhETF Pis'ma 4, No. 7, 255-258, 1 October 1966

The ferroelectric properties of triglycine selenate $(NH_2CHCOOH)_3H_2SeO_4$ were established by Matthias, Miller, and Remeika [1]. Hoshino, Mitsui, et al. [2] have shown that a second-order phase transition takes place in triglycine selenate, just as in triglycine sulfate. The Curie temperature is 22°C.

The crystal belongs to the space group $P2_1/M$ of the monoclinic system above the Curie temperature and to the space group $P2_1$ below the Curie temperature [3]. The ferroelectric properties are revealed in the direction of the twofold polar axis (monoclinic b axis). According to [4], at room temperature triglycine selenate has the following lattice parameters: a = 0.54 Å, b = 12.92 Å, c = 5.86 Å, and β = 110°.

The ferroelectric properties of triglycine sulfate and triglycine selenate crystals were investigated in [5,6]. Jona and Shirane [6] investigated triglycine selenate crystals at pressures up to 2700 kg/cm^2. They have shown that with increasing pressure the Curie temperature of triglycine selenate increases linearly like

$$T_C = T_C^0 + Kp,$$

where T_C^0 is the transition temperature at atmospheric pressure and K a quantity characterizing the rate of shift of the Curie temperature with change in pressure.

All the characteristics of the ferroelectric phase transition (the Curie-Weiss law, the magnitude of the spontaneous polarization, and the character of its variation) do not change relative to the new transition temperature at pressures up to 2700 kg/cm^2.

We investigated triglycine selenate crystals at hydrostatic pressures up to 8000 kg/cm^2. Measurements were made of the dielectric constant and the spontaneous polarization in the phase-transition region. It was found that the dielectric constant decreases at the Curie point with increasing pressure (Fig. 1). Thus, at 5000 kg/cm^2 the relative change in the dielectric constant at the Curie point is ~60%.

At temperatures up to 8000 kg/cm^2 the Curie temperature shifts linearly into the region of higher temperature at a rate 3.7×10^{-3} deg/kg/cm^2, which is in good agreement with the results obtained at pressures up to 2700 kg/cm^2 [6] We have marked this phase-transition line No. 1.

In measurements of the spontaneous polarization of triglycine selenate with the aid of a "hysteresograph" [7] it was noted that at room temperature and at a pressure near 6000 kg/cm^2 the triglycine selenate crystal goes over to the paraelectric state. When the temperature is raised at fixed pressure, the crystal again becomes ferroelectric, as manifest by the appearance of a hysteresis loop on the oscilloscope screen and by the readings of the hysteresograph. Further increase in temperature again makes the crystal paraelectric after

a phase transition.

We have thus found that at 6000 kg/cm^2 triglycine selenate goes through two ferroelectric phase transitions as the temperature is raised.

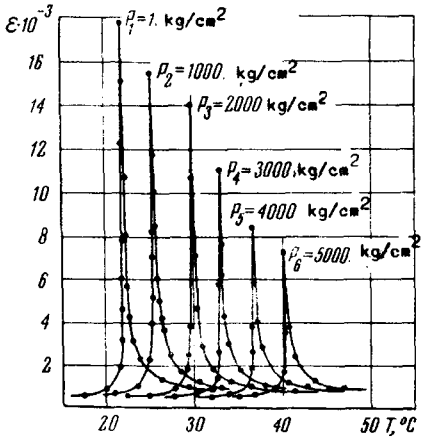

Fig. 1. Temperature dependence of the dielectric constant of triglycine selenate at different hydrostatic pressures.

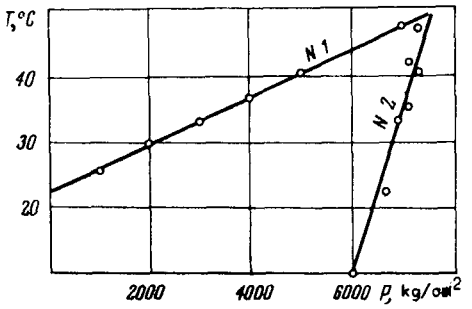

Fig. 2. Phase-transition lines in triglycine selenate at high pressures.

Further investigations were made with the pressure varied under isothermal conditions. During the course of the experiment, hysteresis loops were observed, and the transition temperature was established as the spontaneous polarization decreased to zero and the hysteresis loop disappeared.

The investigations show that in the temperature region 0 - 50°C, at pressures 5800 - 7500 kg/cm^2, there exists in the triglycine selenate crystal a new line of phase transitions (No. 2, Fig. 2). The phase-transition lines 1 and 2 limit the region of existence of the ferroelectric state of the triglycine selenate crystals.

It is our pleasant duty to express deep gratitude to the director of this work, Academician L. F. Vereshchagin, for continuous interest and help.

[1] B. Matthias, G. Miller, and I. Remeika, Phys. Rev. 104, 849 (1956).

[2] S. Hoshino, T. Mitsui, F. Jona, and R. Pepinsky, ibid. 107, 1255 (1957).

[3] E. Wood and A. Holden, Acta Cryst. 10, 145 (1957).

[4] R. Pepinsky, Y. Okaya, and F. Jona, Bull. Amer. Phys. Soc. 2, No. 4, 220 (1957).

[5] G. G. Leonidov and I. N. Polandov, FTT 4, 3337 (1962), Soviet Phys. Solid State 4, 2443 (1963).

[6] F. Jona and G. Shirane, Phys. Rev. 117, 139 (1960).

[7] B. A. Strukov, Izv. VUZov, Priborostoenie (Instrument Building) 3, 25 (1960).