INVESTIGATION OF FERROELECTRIC PHASE TRANSITION IN NH_4HSeO_4 (AHSe) CRYSTALS BY THE PYROELECTRIC METHOD*

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Results of measurements of the pyroelectric properties of NH_4HSeO_4 (AHSe) crystals are presented. On the basis of these and the results of earlier investigations, the free energy development coefficient as well as the temperature and critical polarization were calculated. From observations of the piezoelectric phenomenon, it is evident that the crystal in the paraelectric phase does not have a centre of symmetry. Also some parameters of NH_4HSeO_4 and $RbHSeO_4$ crystals were compared. These crystals were found to constitute a new subfamily of ferroelectric substances.

1. Introduction

The ferroelectric properties of NH_4HSeO_4 (AHS) crystals were presented in paper [1]. These crystals in the paraelectric phase are isomorphous with $RbHSeO_4$ (RHSe) crystals and possess $I2$ [1–3] symmetry. The purpose of the present paper is to investigate the pyroelectric properties of AHSe crystals.

2. Process measurements — the results

An investigation of the pyroelectric properties was carried out by the quasistatic method [4]. Prior to the measurements, the crystals were polarized with an electric field of intensity of 5×10^5 V/m during the cooling process from the paraelectric to ferroelectric

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phase. The measurements were carried out in the direction of the ferroelectric axis only, that is axis a [1]. During the measurements, the crystal was heated at a constant velocity of 2×10^{-2} K/s. The pyroelectric signal from the $R = 10^6$ resistor was given at the Y input of the register X, Y. At the X terminal, an input voltage from a copper-constantan thermo-

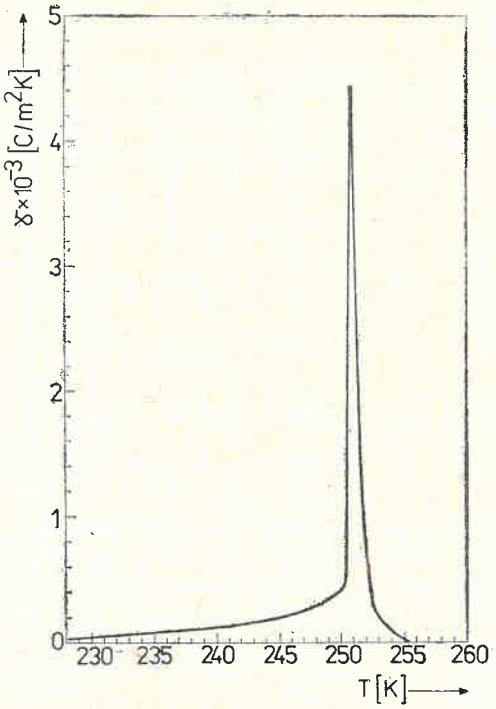

Fig. 1. Temperature dependence of the pyroelectric coefficient for AHSe crystals

couple was applied. From the diagram, the dependence of the pyroelectric coefficient on temperature was calculated, (Fig. 1).

This dependence is characteristic for the first type of phase transition and confirms the character of the phase transition, resulting from the spontaneous polarization measure-

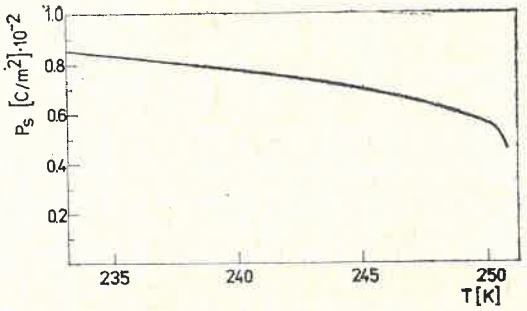

Fig. 2. Temperature dependence of the spontaneous polarization, obtained as a result of a graphical integration of the pyroelectric coefficient

ments and electric permeability [1]. The pyroelectric signal in the paraelectric phase is most likely caused by the space charge induced during the polarization of the crystal [5]. Figure 2 presents the spontaneous polarization vs temperature dependence obtained from graphical integration of the pyroelectric coefficient. This dependence is in agreement with the spontaneous polarization dependence obtained by the Sawyer-Tower method [1].

The polarization jump at the transition point is $P_{s0} = 0.5 \times 10^{-2}$ C/m^2. Utilizing the electric permeability of the dependence on temperature [1] as well as the spontaneous polarization dependence obtained from the pyroelectric measurements and indicated by the coefficients α, β, γ of free development, one gets

$$\phi = \phi_0 + \alpha(T-\theta)P^2 - \beta P^4 + \gamma P^6, \tag{1}$$

where ϕ_0 is the free energy of the crystal in the paraelectric phase; T — temperature; θ — Curie temperature. For the coefficient calculations, the following relations were utilized [5]

$$\alpha = [2\kappa_{(T_K+)}(T-\theta)]^{-1}, \tag{2}$$

$$\beta = \frac{2\alpha(T_K-\theta)}{P_{s0}^4}, \tag{3}$$

$$\gamma = \frac{\alpha(T_K-\theta)}{P_{s0}^4}, \tag{4}$$

where $\kappa_{(T_K+)}$ is the electric flexibility at the phase transition temperature, which was extrapolated from the paraelectric phase; P_{s0} — polarization jump at the phase transition point.

Values of the calculated coefficients are: $\alpha = 1 \times 10^7$ Vm/CK, $\beta = 2.64 \times 10^{12}$ Vm^5/C^3, $\gamma = 5.3 \times 10^{16}$ Vm^9/C^5. They describe well the spontaneous polarization dependence on temperature. From observations of the double hysteresis loops in the paraelectric phase, the critical temperature was indicated. For comparison purposes the value of the critical temperature T_{cr}, as well as critical polarization P_{cr} were calculated using the following relations:

$$T_{cr} = \theta + \tfrac{2}{5}\frac{\beta^2}{\alpha\gamma} \tag{5}$$

and

$$P_{cr}^2 = -\tfrac{1}{5}\frac{\beta}{\gamma}. \tag{6}$$

Utilizing the free energy development coefficients, the critical polarization value $P_{cr} = 0.32 \times 10^{-2}$ C/m^2 was calculated. The value of the critical temperature, obtained from measurements, is 256.4 K, which is close to the calculated value, (255.8 K). The initial measurements indicated the presence of a piezoelectric effect in the paraelectric phase and dependence of some resonance frequencies on temperature. This confirms the fact that the paraelectric phase does not have a centre of symmetry. Such a conclusion for RHSe crystals

was drawn on the basis of observations of the domain structure in the ferroelectric phase using a polarizing microscope [7]. A detailed investigation of the piezoelectric effect will be the subject of a separate paper. Observation of the piezoelectric effect in the paraelectric phase of AHSe crystals gives evidence that AHSe and RHSe crystals are isomorphous in their paraelectric and ferroelectric phases. This was suggested in paper [1] from a consideration of certain crystallographic and physicochemical properties. Those properties, along with the parameters obtained in this work for AHSe crystals as well as the earlier indicated parameters for RHSe crystals, are compiled in Table I.

TABLE I

Crystals parameters \ Crystals	NH_4HSeO_4	$RbHSeO_4$
the symmetry of the paraelectric phase	$I2$ [1]	$I2$ [2, 3]
the symmetry of the ferroelectric phase	$P1$	$P1$ [2]
phase transition temperature	253.5 K [1]	367.5 K [8]
Curie constant	$C = 5.45 \times 10^3$ [1]	$C = 4.33 \times 10^5$ [6]
C/T_K	22 [1, *]	1.2×10^3 [6]
P_{s0} jump	0.5×10^{-2} C/m^2 [*]	2.2×10^{-2} C/m^2 [7]
development coefficient	$\alpha = 1 \times 10^7$ Vm/CK	$\alpha = 1.55 \times 10^5$ Vm/CK
	$\beta = 2.64 \times 10^{12}$ Vm^5/C^3	$\beta = 1.63 \times 10^{10}$ Vm^5/C^3
	$\gamma = 5.3 \times 10^{16}$ Vm^9/C^5	$\gamma = 3.37 \times 10^{13}$ Vm^9/C^5

[*] — present work.

A comparison of those properties gives proof that the crystals under examination are isomorphous despite the fact that some parameters indicate large differences, (T_C, ε, P_s). The relation between the Curie constant and Curie temperature for NH_4HSeO_4 crystals is equal to 22, and the Curie constant is of the order of 10^3. This indicates that the crystal is of the order-disorder type.

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