OPTICAL AND ULTRASONIC INVESTIGATIONS OF PHASE TRANSITIONS IN FERROELECTRIC $RbHSeO_4$ SINGLE CRYSTAL

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Birefringence and ultrasonic measurements were done for ferroelectric $RbHSeO_4$ crystal. Influences of both stresses (σ_i) and pressure on the properties and phase transition were studied as well. The observed dependence of $\delta(\Delta n_b) = f(\sigma_5)$ shows hysteresis loop characteristic of ferroelectric phase whereas the dependence of $\delta(\Delta n_c) = f(\sigma_6)$ shows hysteresis loop characteristic of ferroelastic phase. Birefringence measurements prove the phase transition to ferroelectric phase at 373 K. Additionally, the phase transition was found at 398 K. The new phase may be regarded as an incommensurate one. On the grounds of the stresses influence the phase diagram is constructed in coordinates T, σ_5. The linear decrease in T_c with increase in pressure is observed in ultrasonic studies and it is similar to the results obtained in DSC measurements.

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1. Introduction

Rubidium hydrogen selenate $RbHSeO_4$ is known as hydrogen-bonded ferroelectric crystal with $T_c \approx 371$ K [1]. In this crystal, simultaneously ferroelectric and ferroelastic domain structure with the walls parallel to (001) plane exists below T_c. The observed domain structure pattern may be changed by application of electric field along the b-axis or mechanical stress (σ_5) to the b-45° cut samples [2]. Occasionally, ferroelastic domain structure with the walls parallel to the plane (100) exists both below and above T_c. This kind of domain structure may be changed by the mechanical stress (σ_6) applied to the c-45° cut samples. The aim of our work is to obtain some additional information related to the phase transitions diagram, domain structure and piezooptic properties on the grounds of birefringence and ultrasonic measurements. The birefringence measurements were also used to check on the possibility of incommensurate phase existence in $RbHSeO_4$ crystal.

2. Experimental

Single crystal of $RbHSeO_4$ of optical quality were grown by slow evaporation of an aqueous solution containing stoichiometric quantities of Rb_2SeO_4 and H_2SeO_4 at the temperature of 301 K. The temperature dependences of birefringence and piezooptic coefficients were measured by Senormonth's method (λ = 633 nm) using Faraday modulator cell. The accuracy of $\delta(\Delta n)$ measurements is equal to 10^{-7}. The temperature was kept and measured with the accuracy of 0.01 K. The accuracy of piezooptic coefficients is estimated as equal to about 10%. The shear ultrasonic wave (USW) velocities v_4 ($q \parallel b$, $E \parallel b$) and v_5 ($q \parallel c$, $E \parallel a$), where q is a USW wave vector, E — polarization, were measured by the pulse-echo overlap method [3] at the frequency f = 10 MHz with the accuracy of 10^{-4}–10^{-5}. Acoustic investigations under hydrostatic pressure were performed in the range of 0.1 to 500 MPa and 300–400 K using a high-pressure camera.

3. Results and conclusions

An influence of internal stresses σ_i on the birefringence of $RbHSeO_4$ crystal is shown in Figs. 1–5.

The mechanical stress σ_5 applied to the sample at room temperature gives a decrease in $\delta(\Delta n_b)$ for the stresses $\sigma_5 < 0.70 \times 10^6$ N/m^2. For the stresses

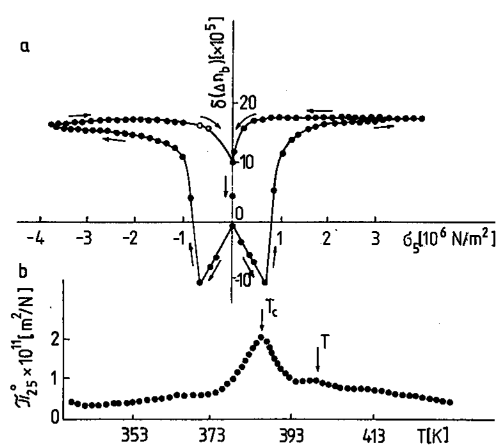


Fig. 1. (a) Dependence of $\delta(\Delta n_b)$ versus σ_5 at room temperature; (b) temperature dependence of piezooptic coefficient Π^0_{25}; (a) and (b) for $RbHSeO_4$ crystal.

$\sigma_5 > 0.70 \times 10^6$ N/m^2 a sharp increase in $\delta(\Delta n_b)$ is observed and then its saturated value is reached. When the mechanical stress is removed, $\delta(\Delta n_b)$ slightly

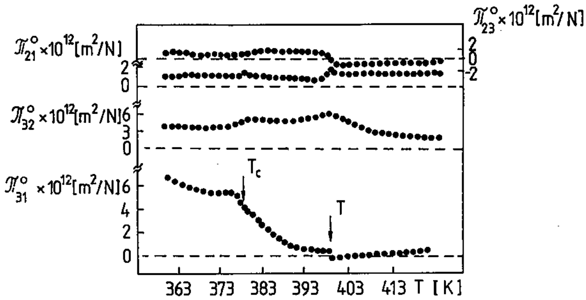


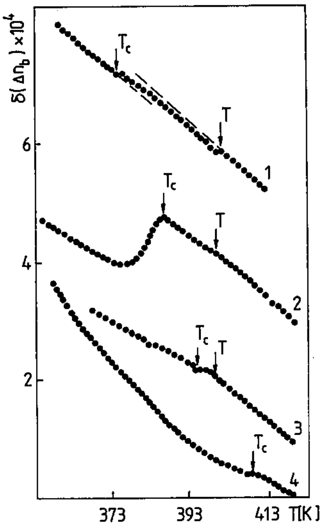
Fig. 2. Temperature dependences of some piezooptic coefficients Π^0_{ik} for $RbHSeO_4$ crystal.

decreases and after that the relaxation process is observed and nearly initial value for $\delta(\Delta n_b)$ is reached in some time (see the right side of Fig. 1a). If the sample is turned by 90° around the b-direction, the observed dependence of $\delta(\Delta n_b)$ on σ_5 is shown in the left side of Fig. 1a. The dependence of $\delta(\Delta n_b) = f(\sigma_5)$ (hysteresis loop) presented in Fig. 1a is similar to the dependence of $\delta(\Delta n)$ on E observed in ferroelectric phases. $RbHSeO_4$ crystal is simultaneously ferroelectric and ferroelastic and mechanical stress influence also gives histeresis loop. At room temperature the value of coercive stress $(\sigma_5)_c$ for $RbHSeO_4$ is equal to about 0.75×10^6 N/m^2. Figure 1b also shows the temperature dependence of piezooptic coefficient Π^0_{25} obtained for $\sigma_5 > (\sigma_5)_c$. As can be seen in Fig. 1b, a big anomaly at $T = 385$ K and a kink at $T_i \approx 398$ K on the curve $\Pi^0_{25} = f(T)$ are found. The observed anomaly at 385 K corresponds to the phase transition at $T_c = 373$ K (the value obtained in this work) shifted to higher temperature by application of external stress.

To explain the observed kink at T_i the dependences of $\delta(\Delta n_i) = f(T)$ and $\Pi^0_{ik} = f(T)$ were measured. According to the dependences of $\delta(\Delta n_b) = f(T)$ and $\delta(\Delta n_c) = f(T)$ the crystal undergoes the first- and second-order phase transitions at T_c and T_i, respectively. The first-order phase transition had been found earlier in dielectric [1] and birefringence measurements [4]. Temperature dependences of Π^0_{ik} are shown in Fig. 2. The anomalies of Π^0_{21}, Π^0_{23} and Π^0_{31} were found at T_c and T_i. They also give evidences for the phase transitions at these temperatures.

Temperature dependence of $\delta(\Delta n_b)$ at various values of σ_5 is shown in Fig. 3. As can be seen in Fig. 3 the difference $T_i - T_c$ decreases with increase in σ_5 whereas one diffused phase transition for $\sigma_5 \geq 3.6 \times 10^6$ N/m^2 is observed. For $\sigma_5 > 5 \times 10^6$ N/m^2 this transition is hardly distinguished. The similar shift of T_c versus σ_5 was observed in dielectric measurements [5].

The presented above measurements allowed us to construct the phase diagram in coordinates T and σ_5 which is shown in Fig. 4. To explain the obtained diagram one can assume that the phase existing in the temperature range $T_i - T_c$ is an incommensurate one. Thus, T_c is the temperature of phase transition to the ferroelectric phase and T_i is the phase transition temperature to the incommensurate one. The incommensurate phase existence was proved in an isomorphous ammonium hydrogen selenate (NH_4HSeO_4) crystal [6–8], as it is shown in Fig. 4.



← Fig. 3

Fig. 4

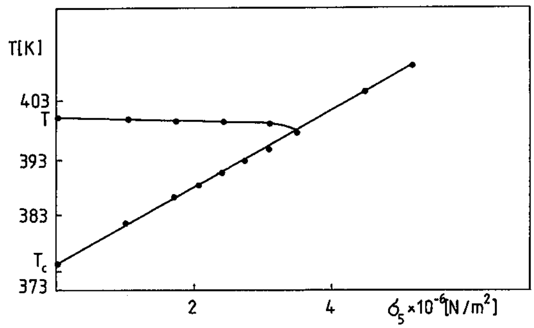


Fig. 3. Temperature dependences of $\delta(\Delta n_b)$ for $RbHSeO_4$ crystals at various σ_5 [$\times 10^{-6}$ N/m]: 1 — 0, 2 — 1.7, 3 — 3.1, 4 — 5.

Fig. 4. Phase diagram for $RbHSeO_4$ crystal; dependences of phase transition temperatures versus σ_5.

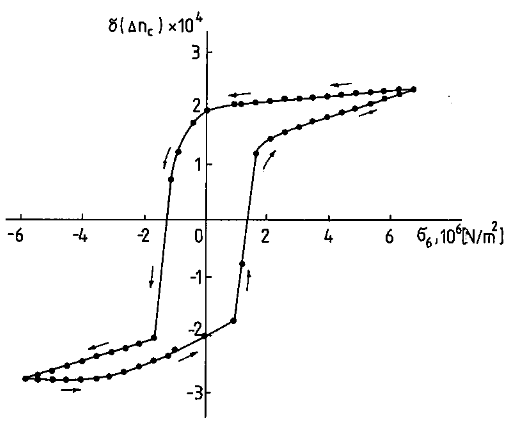


Fig. 5. Dependence of $\delta(\Delta n_c)$ versus σ_6 for $RbHSeO_4$ crystal.

The dependence of T_i on σ_5 is linear and diminishes very slightly with increase in σ_5. The dependence of T_c on σ_5 is also linear up to 5×10^6 N/m^2 with the rate of $\Delta T_c/\Delta\sigma_5 \approx 7.5\times10^6$ K$\cdot$ m^2/N. The dependence of T_c versus σ_5 is characteristic of proper ferroelectrics with the first-order phase transition without incommensurate phase. Both dependences (straight lines) meet at about 3.6×10^6 N/m^2 and this value is a limit of the incommensurate phase existence. Thus, the phase diagram contains triple point in which the incommensurate phase disappears. For stresses higher than 3.6×10^6 N/m^2 we deal with the direct transition from ferroelectric to paraelectric phase. For stresses higher than 5×10^6 N/m^2 the ferroelectric commensurate phase and the normal phase are indistinguishable.

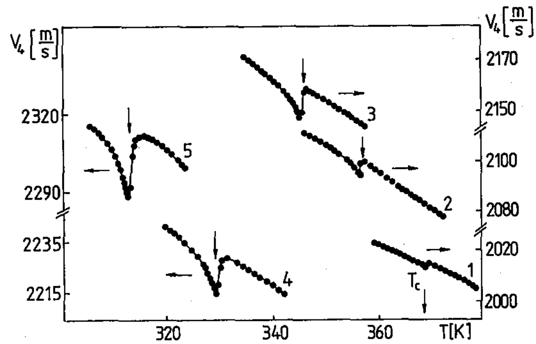


Fig. 6. Temperature dependence of the shear velocity v_4 for various p [MPa] ($RbHSeO_4$ crystal): 1 — 0.1, 2 — 95, 3 — 185, 4 — 325, 5 — 475.

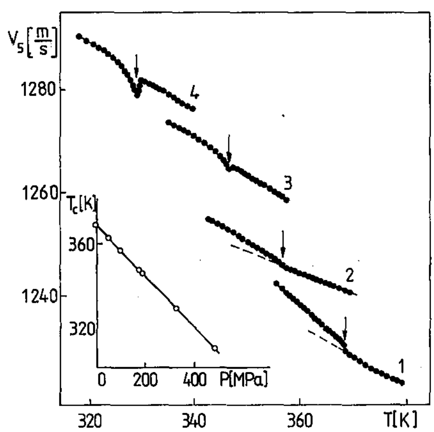


Fig. 7. Temperature dependence of the shear velocity v_5 for various p [MPa] ($RbHSeO_4$ crystal): 1 — 0.1, 2 — 95, 3 — 185, 4 — 325.

In connection with the existence of ferroelastic domain structure observed along the c-axis the dependence of $\delta(\Delta n_c)$ on mechanical stress σ_6 was studied. The hysteresis loop $\delta(\Delta n_c) = f(\sigma_6)$ obtained at room temperature phase is shown in Fig. 5. As can be seen in Fig. 5 the shape of the observed hysteresis loop is characteristic of ferroelastic crystals. The value of the coercive mechanical stress $(\sigma_6)_c$ is equal to about 1.3×10^6 N/m^2 at room temperature and the hysteresis loop may be regarded as symmetrical in respect to both coordinates.

The results of ultrasonic measurements are presented in Figs. 6 and 7.

Anomalies of shear USW velocities v_4 and v_5 were observed at T_c. At the pressure $p = 0.1$ MPa a small decrease in v_4 (Fig. 6) and a small jump of v_5 (Fig. 7) can be seen at the phase transition temperature T_c. Under applied hydrostatic pressure the phase transition temperature T_c shifts to lower temperatures with the rate equal to -0.126 K/MPa (-12.6 K/kbar). Simultaneously, an increase in the v_4 jump at $T = T_c$ is observed with increase in the value of applied pressure. In the case of v_5 the change of the anomaly character takes place (see Fig. 7). The shift of T_c is characteristic of hydrogen-bonded ferroelectrics (see the insert in Fig. 7) and is in good agreement to that observed from DSC measurements [9].

On the grounds of presented above investigations one can state that:

1. two different forms of $\delta(\Delta n_i) = f(\sigma_i)$ dependences are observed in $RbHSeO_4$ crystal: the dependence of $\delta(\Delta n_b) = f(\sigma_5)$ is characteristic of ferroelectric phase and the dependence of $\delta(\Delta n_c) = f(\sigma_6)$ is characteristic of ferroelastic one;

2. the existence of incommensurate phase is proposed and the phase diagram in coordinates "temperature" (T)–stress (σ_5) was constructed;

3. the influence of pressure on the phase transition at T_c characteristic of hydrogen-bonded crystals was confirmed.

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References

[1] Z. Czapla, T. Lis, L. Sobczyk, J. Mróz, R. Poprawski, *Ferroelectrics* **26**, 771 (1980).

[2] T. Tsukamoto, M. Komukae, S. Suzuki, H. Futama, M. Makita, *J. Phys. Soc. Jpn.* **52**, 3966 (1983).

[3] E.P. Papadakiz, *J. Acoust. Soc. Am.* **42**, 1045 (1967).

[4] A. Waśkowska, A.M. Glazer, *J. Phys. C, Solid State Phys.* **19**, 6221 (1992).

[5] R. Styrkowiec, private information.

[6] H. Pykacz, *Solid State Commun.* **66**, 567 (1988).

[7] J. Kroupa, J. Fousek, Z. Czapla, *Ferroelectrics* **79**, 291 (1988).

[8] F. Denoyer, A. Rozycki, K. Parliński, M. More, *Phys. Rev. B* **39**, 405 (1989).

[9] B. Baranowski, M. Friesel, A. Lunden, *Z. Naturforsch. A* **41**, 981 (1986).