INFLUENCE OF PRESSURE ON FERROELASTIC PHASE TRANSITION IN Cu_6PS_5Br AND Cu_6PS_5I CRYSTALS

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Abstract. The temperature dependences of birefringence, dielectric permittivity and dielectric conductivity (1 MHz) at various hydrostatic pressures (up to 400 MPa) were studied. The measurements enabled the ferroelastic phase transition (PT) temperatures to be determined at various pressure values and the p,T-phase diagrams to be constructed. The ferroelastic PT temperatures appeared to shift linearly with pressure towards higher temperatures for Cu_6PS_5Br ($dT_c/dp=21\cdot10^{-9}$ K/Pa) and Cu_6PS_5I ($dT_c/dp=7.8\cdot10^{-9}$ K/Pa) crystals.

INTRODUCTION

Cu_6PS_5Hal (Hal = Br, I) single crystals belong to the argyrodite-structure compounds [1]. This class of crystals is characterized by high concentrations of disordered vacancies for copper cations, this resulting in relatively high ionic conductivity at room temperatures. In these crystals two successive low-temperature phase transitions (PTs) have been observed, one of them being superionic (T_s = 166–180 K for Cu_6PS_5Br and T_s = 165–175 K for Cu_6PS_5I), the other – ferroelastic (T_c= 268±2 K for Cu_6PS_5Br and T_c= 269±2 K for Cu_6PS_5I) [2]. At room temperature ($T > T_c$) the crystals belong to the cubic syngony (space group $F43m$) and at $T < T_s$ – to the monoclinic syngony (space group C_c) [3]. While the effect of temperature upon the physical properties of these crystals has already been the object of investigation, the influence of pressure has just begun to be studied. This paper is aimed at studying the hydrostatic pressure effect on the ferroelastic PT and to construct p,T-phase diagrams of these crystals.

EXPERIMENTAL

Pure Cu_6PS_5Hal (Hal = Br, I) single crystals were obtained by chemical vapour transport [2]. The crystals were grown from the mixture enriched by $CuHal + Cu_2S$. The temperature of the hot end of the vessel was kept at 650 to 750 °C, and that of the cool one – at 550 to 650 °C, depending on the crystal composition. Thus grown crystals had the shape of plane-parallel plates (5×5×2 mm^3) or distorted tetrahedrons (4×4×4 mm^3).

The crystals birefringence was studied by Senarmont technique (λ = 632.8 nm). Dielectric permittivity was measured at 1 MHz using the conventional technique. The birefringence studies were carried out for the samples oriented in the cubic phase, the light beam propagating along [100] crystallographic direction. The dielectric permittivity was also measured along this direction.

The temperature studies of birefringence under hydrostatic pressure (up to 400 MPa) were carried out in a three-window high-pressure chamber, the pressure being provided by purified petrol, whose optical properties within the studied pressure range remained unchanged. The optical windows were made of monocrystalline sapphire. The pressure was measured by mechanical and manganine pressure gauges within ±2.5 MPa. The temperature studies of the dielectric permittivity and dielectric conductivity under hydrostatic pressure were carried out in a high-pressure chamber designed for the electrical measurements. For the low-temperature studies the chambers were put into a thermostat and cooled by liquid nitrogen. The sample temperature was conrolled within ±0.5 K.

RESULTS AND DISCUSSION.

In Cu_6PS_5Br crystals the second-order ferroelastic PT from the cubic paraelastic phase to the anisotropic ferroelastic one is known to be accompanied by the appearance of birefringence [2]. We studied the birefringence, arising at $T < T_c$, along the [100] axis at various hydrostatic pressures (up to 400 MPa) (See Fig. 1).

The sample under investigations was the same as in [2]. With the pressure increase the ferroelastic PT temperature shift towards higher temperatures, as well as the birefringence value Δn increase; are observed. The similar results were obtained for Cu_6PS_5I crystal.

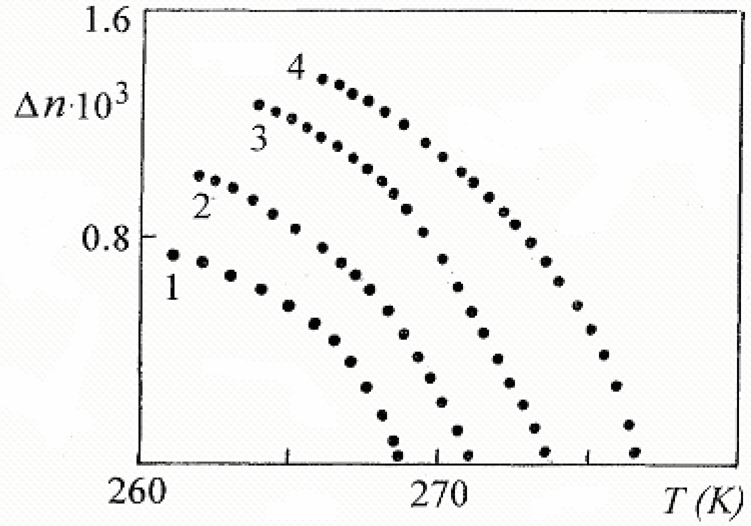

Fig.1. Temperature dependences of birefringence in Cu_6PS_5Br crystal at various hydrostatic pressure values: 10 MPa (1), 140 MPa (2), 280 MPa (3), 400 MPa (4).

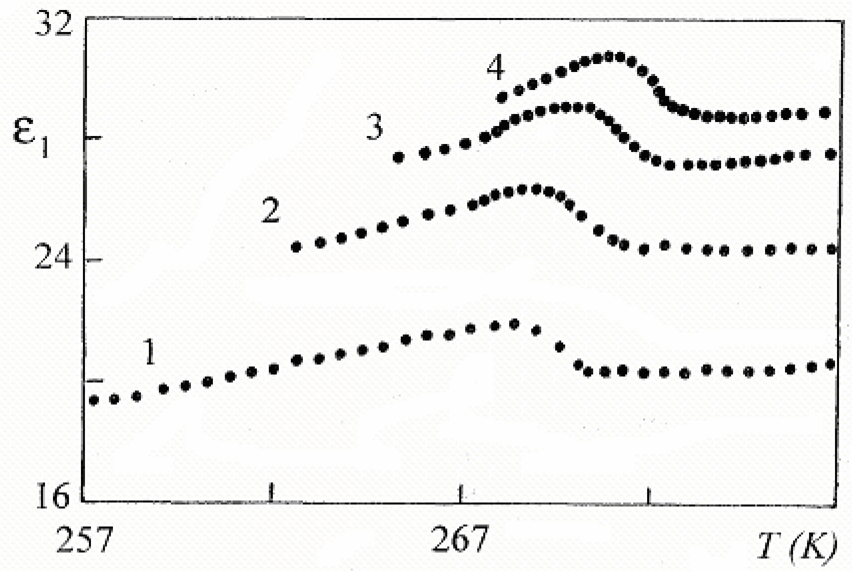

Fig.2. Temperature dependences of Cu_6PS_5I crystal dielectric permittivity at various hydrostatic pressure values: 0.1 MPa (1), 25 MPa (2), 150 MPa (3), 250 MPa (4).

In Fig. 2 the temperature dependences of the Cu_6PS_5I crystal dielectric permittivity at various hydrostatic pressure values are presented. In the range of the ferroelastic PT an ε_1 anomaly, typical for the PTs of such kind, is observed (See [4]). The pressure increase leads to the ε_1 increase and the PT temperature shift towards higher temperatures. Simultaneously with ε_1 the dielectric conductivity was measured, whose value at 295 K ($0.7 \cdot 10^{-3}\ \Omega^{-1}\,cm^{-1}$) correlates well with the results of [5]. Besides, in the ferroelastic PT range a knee in the $\lg\sigma(T) = f(1/T)$ plots is observed, what also confirms the results of [5]. The similar results were obtained for Cu_6PS_5Br crystal.

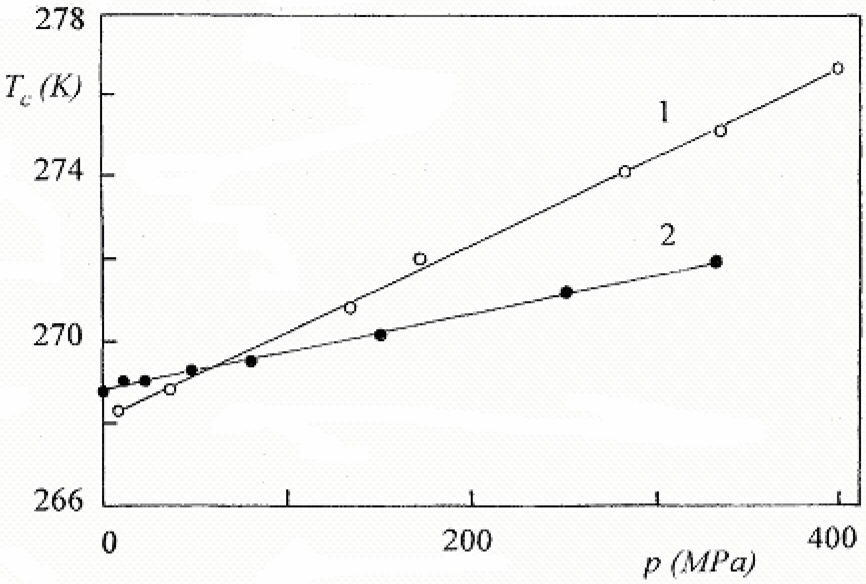

Fig.3. The p,T-phase diagrams of Cu_6PS_5Br (1) and Cu_6PS_5I (2) crystals.

Thus, these measurements enabled the ferroelastic PT temperature to be determined at various pressure values and the *p,T*-phase diagram to be constructed (See Fig. 3). The ferroelastic PT temperatures appeared to shift linearly with pressure towards higher temperatures for Cu_6PS_5Br (dT_c/dp=21·10^{-9} K/Pa) and Cu_6PS_5I (dT_c/dp=7.8·10^{-9} K/Pa) crystals.

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ВПЛИВ ТИСКУ НА СЕГНЕТОЕЛАСТИЧНИЙ ФАЗОВИЙ ПЕРЕХІД В КРИСТАЛАХ Cu_6PS_5Br ТА Cu_6PS_5I

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Вивчені температурні поведінки двопроменезаломлення, діелектричної проникності та діелектричної провідності кристалів Cu_6PS_5Br та Cu_6PS_5I при різних значенях гідростатичного тиску (до 400 МПа). По результатам досліджень побудована фазова *p,T*-діаграма. Виявлено, що із підвищенням гідростатичного тиску температура сегнетоеластичного фазового переходу в кристалах Cu_6PS_5Br (dT_c/dp=21·10^{-9} К/Па) та Cu_6PS_5I (dT_c/dp=7.8·10^{-9} К/Па) зростає.