

PHASE TRANSITIONS, CRITICAL PHENOMENA,  
AND THE STRUCTURE AND DYNAMICS  
OF CRYSTAL LATTICES

**Raman Spectroscopic Study of the Phase Transitions Induced  
by Hydrostatic Pressure in a  $\text{Rb}_2\text{KScF}_6$  Crystal**

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**Abstract**—The Raman spectra of  $\text{Rb}_2\text{KScF}_6$  elpasolite crystals are studied in the pressure range up to 7 GPa. A phase transition is revealed at a pressure of approximately 1 GPa. Analysis of the changes in the spectral parameters shows that the phase transition is accompanied by a doubling of the volume of the primitive cell in the initial cubic phase. Judging from the character of the variations in the pressure dependences of the frequency of the observed vibrations, there can exist another transition to the phase with a lower symmetry at a pressure of approximately 2.1 GPa.

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## 1. INTRODUCTION

The  $\text{Rb}_2\text{KScF}_6$  compound belongs to the family of perovskite-like fluorides with an elpasolite structure of the general formula  $A_2B^{(1)}B^{(2)}X_6$ , where  $A$  and  $B$  are metal cations or more complex molecular ions and  $X$  is an oxygen or halogen anion [1].

Flerov et al. [2] investigated the effect of hydrostatic pressure on the phase transition temperatures for  $\text{Rb}_2\text{KScF}_6$  crystals in the pressure range up to 0.6 GPa [2]. It was demonstrated that, under hydrostatic pressure in this range, the temperature of the phase transition from the cubic phase increases and the stability region of the tetragonal phase becomes wider. However, at room temperature, the cubic phase remains stable. At pressures higher than 0.6 GPa, the phase transitions in this crystal have not been investigated.

In this work, we investigated the effect of hydrostatic pressure on the Raman spectrum of a  $\text{Rb}_2\text{KScF}_6$  crystal.

## 2. STRUCTURE AND SYMMETRY OF THE CRYSTAL

The unit cell of the  $\text{Rb}_2\text{KScF}_6$  crystal has a cubic structure (space group  $Fm\bar{3}m$ ,  $Z = 4$ ). As the temperature decreases under normal pressure, the  $\text{Rb}_2\text{KScF}_6$  crystal sequentially undergoes two structural phase transitions [3]: (i) at a temperature  $T_1 = 252$  K, the crystal undergoes a transition from the cubic phase to the tetragonal phase (space phase  $I114/m$ ,  $Z = 2$ ); and (ii) at a temperature  $T_2 = 223$  K, the crystal transforms into the monoclinic phase with a doubling of the volume of

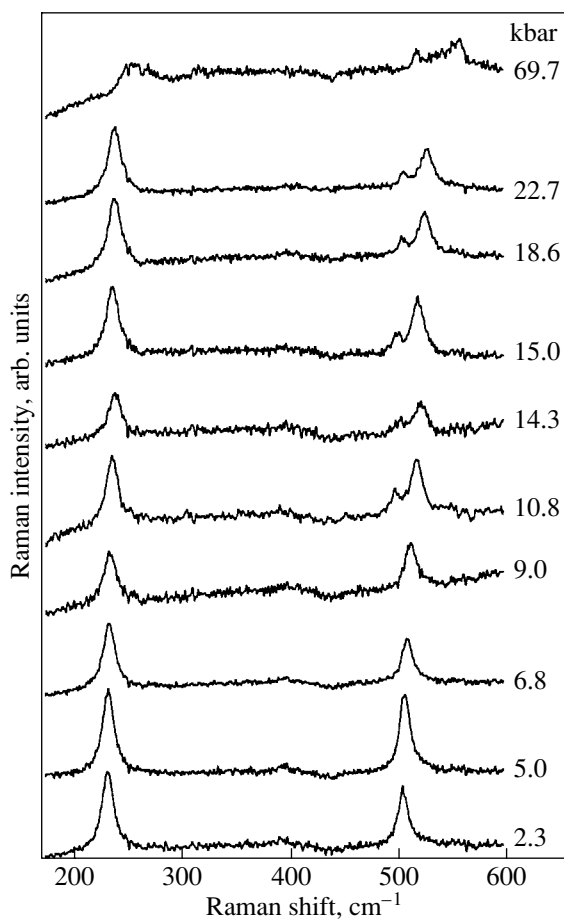
the primitive cell (space group  $P12_1/n1$ ,  $Z = 2$ ). In the high-symmetry cubic phase, the expansion of the vibrational representation at the center of the Brillouin zone has the following form:

$$\Gamma(Fm\bar{3}m) = A_{1g}(xx, yy, zz) + E_g(xx, yy, zz) + 2F_{2g}(xz, yz, xy) + F_{1g} + 5F_{1u} + F_{2u}. \quad (1)$$

The components of the Raman scattering tensor in which the corresponding vibrations are active are enclosed in parentheses.

## 3. EXPERIMENTAL TECHNIQUE

The experiments under high hydrostatic pressures (up to 7 GPa) at room temperature were performed on a setup equipped with diamond anvils (similar to that described in [4]). The diameter of the chamber containing the sample was equal to 0.25 mm, and the height of the chamber was 0.1 mm. The pressure was determined accurate to within 0.05 GPa from the shift of the ruby luminescence line. For this purpose, a ruby microcrystal was placed near an unoriented sample 50–70  $\mu\text{m}$  in size. A carefully dehydrated mixture of ethanol with methanol was used as a pressure-transmitting medium. The Raman spectra were excited by radiation from an  $\text{Ar}^+$  laser (514.5 nm, 500 mW) and recorded on a Dilor OMARS 89 multichannel Raman spectrometer. Because of the small sizes of the samples and the strong diffuse scattering, the Raman spectra could be recorded only in the high-frequency range (higher than 200  $\text{cm}^{-1}$ ). Simultaneously, the domain structure and the effects of bire-

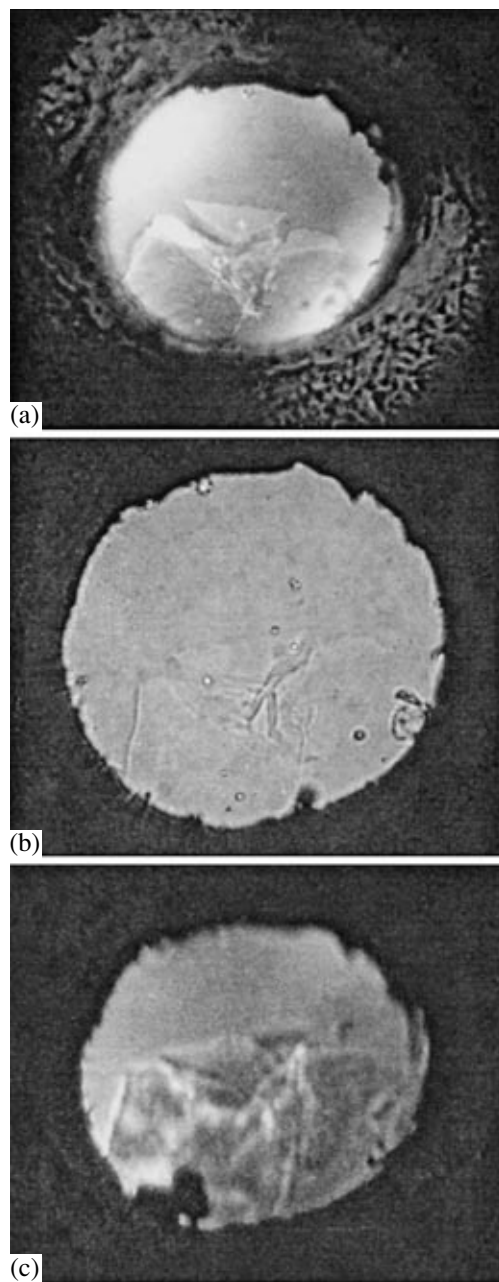


**Fig. 1.** Evolution of the Raman spectra with increasing pressure.

fringence in the sample were observed with a polarizing microscope.

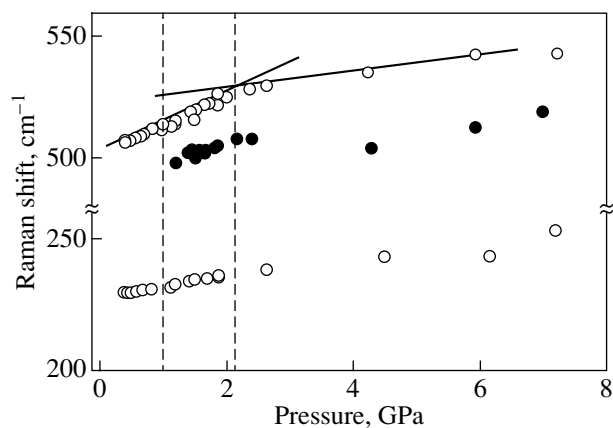
#### 4. RESULTS AND DISCUSSION

Figure 1 illustrates the evolution of the Raman spectra with increasing pressure. At pressures lower than 1 GPa and a temperature of 300 K, the sample is optically isotropic. A micrograph of the crystal under investigation at a pressure of 0.1 GPa is displayed in Fig. 2a. As the pressure increases to 0.6 GPa, the refractive index of the sample becomes equal to the refractive index of the medium. The corresponding micrograph is displayed in Fig. 2b. The Raman spectra in the range of pressures from 0 to 1 GPa have a shape characteristic of the cubic phase of the crystal. At higher pressures, the Raman spectra shown in Fig. 1 exhibit an additional line in the range of  $500\text{ cm}^{-1}$ . The single vibration observed in this range corresponds to the nondegenerate internal mode ( $A_{1g}$ ; see relationship (1)) of the  $\text{ScF}_6$  octahedral ion in the cubic phase, and the additional line in this case cannot be caused by the lifting of the degeneracy. The appearance of this line can be associated only with the increase in the volume of the primi-



**Fig. 2.** Micrographs of the sample at different pressures: (a) 0.1, (b) 0.6, and (c) 1.04 GPa.

tive cell in the cubic phase. The effects of birefringence in the sample are observed at a pressure of 1.04 GPa. A micrograph of the sample at this pressure is displayed in Fig. 2c. The shape of the spectra once more drastically changes when the pressure becomes higher than 2.1 GPa (the dependence of the frequency of the observed vibrations on the pressure is shown in Fig. 3). The lines are considerably broadened, and the rate of increase in the frequency changes. The observed spectral changes can be associated with yet another phase transition.



**Fig. 3.** Dependences of the frequencies of the Raman lines on the pressure.

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