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A Raman Study of Hydrostatic Pressure Induced Phase Transitions in Rb_2KInF_6 Crystals

A. N. Vtyurin[a, *], A. S. Krylov[a], S. V. Goryainov[b], S. N. Krylova[a], A. S. Oreshonkov[a], and V. N. Voronov[a]

[a] *Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*

* *e-mail: slanky@iph.krasn.ru*

[b] *Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia*

Abstract—The Raman spectra of the elpasolite (Rb_2KInF_6) crystal have been studied in the pressure range from 0 to 5.3 GPa at a temperature of 295 K. A phase transition at a pressure of approximately 0.9 GPa has been found. An analysis of the variations in the spectral parameters has led to the conclusion that the phase transition to a distorted phase is accompanied by the doubling of the volume of the primitive cell of the initial cubic phase. Numerical calculations of the lattice dynamics in the Rb_2KInF_6 crystal have been performed. The numerical simulation has established that the phase transition at a pressure of 0.9 GPa is associated with condensation of the F_{lg} mode. A probable high-pressure phase is the phase with space group $C2/m$. 10.1134/S1063783412050472

1. INTRODUCTION

The Rb_2KInF_6 crystal belongs to the family of perovskite-like crystals with the elpasolite structure $A_2B^{(1)}B^{(2)}X_6$, where A and B are metal cations or more complex molecular ions and X stands for oxygen or halogen anions [1]. The phase transitions in this type of crystals are under an active study [2–5]. The structure of the unit cell (space group $Fm3m$, $Z = 4$) is shown in Fig. 1.

With a decrease in temperature at normal pressure, the Rb_2KInF_6 crystal successively undergoes two phase transitions: at $T_1 = 252$ K, from the cubic phase to the tetragonal phase (space group $I114/m$, $Z = 2$), and, at $T_3 = 223$ K, to the monoclinic phase with the doubling of the cell volume (space group $P12_1/n1$, $Z = 2$) [6, 7]. The ab initio calculation [8] of the static and dynamic properties of the Rb_2KInF_6 crystal in the cubic phase has shown that, in the cubic phase, unstable vibration modes in the lattice vibration spectrum occupy the phase space in the entire Brillouin zone. The eigenvectors of the most unstable mode at the center of the Brillouin zone of the cubic phase are connected with displacements of fluorine ions and correspond to rotation of the InF_6 octahedron. For this crystal, the influence of hydrostatic pressure on the phase transition temperatures in the region of pressures up to 0.6 GPa [9] was studied and it was shown that, in this range, the hydrostatic pressure increases the temperature of the phase transition from the cubic phase and expands the region of stability of the tetragonal phase, but the cubic phase remains stable at room temperature. At pressures above 0.6 GPa, the phase transitions in this crystal were not studied. In the isostructural Rb_2KScF_6 crystal, a phase transition at a pressure of approximately 1 GPa has been found using the Raman light scattering method [10]. In this work, in order to study the influence of hydrostatic pressure on structural distortions of the Rb_2KInF_6 crystal, the Raman spectra at a temperature of 295 K

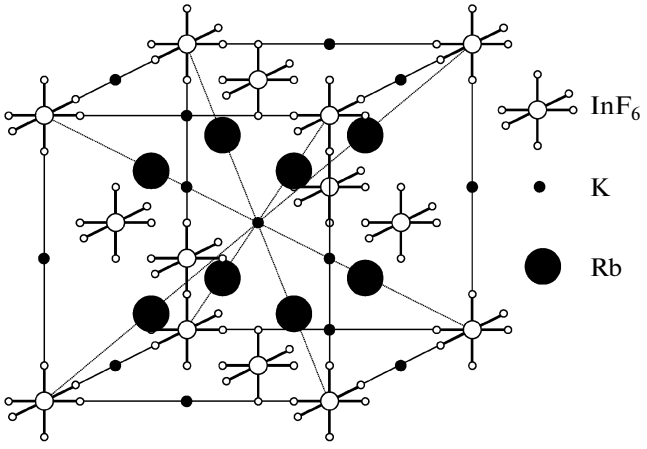

Fig. 1. Structure of the cubic phase of the Rb_2KInF_6 crystal under normal conditions.

and pressures up to 5.3 GPa were studied and comparative analysis with numerical results was carried out.

2. EXPERIMENTAL AND DATA PROCESSING TECHNIQUES

Transparent colorless single crystals with a diameter of 9–10 mm and length of 10–15 mm were grown by the Bridgman method in evacuated and sealed platinum ampoules. The X-ray powder diffraction analysis has shown the absence of extra phases both in the initial components and in the grown crystal. The samples under study were optically transparent and did not contain colored defects or inclusions visible in a microscope [5].

The experiments in conditions of high hydrostatic pressure (up to 5.3 GPa) were performed on a facility with diamond anvils similar to [11, 12] at a temperature of 295 K. The diameter of the chamber with the sample was 0.25 mm, and its height was 0.1 mm. The pressure was determined with an error within 0.05 GPa from the shift in the luminescence band of ruby [13, 14], a microcrystal of which was placed near a nonoriented sample with a size of 50–70 μm. The pressure transmitting medium was a well dehydrated mixture of ethanol and methanol. The excitation source for obtaining the Raman spectra was the polarized radiation of 514.5 nm Ar^+-laser (Spectra-Physics Stabilite 2017) with the power of 100 mV (20 mV on the sample). The spectra in the 180° geometry were obtained on a Horiba Jobin Yvon T64000 spectrometer in the frequency range from 20 to 1200 cm^{-1}. Simultaneously, the domain structure and birefringence in the sample were observed by means of a polarization microscope. In order to obtain the parameters of spectral lines, the experimental data were processes by the OriginPro 8.0 program package, using the dispersion form of the contour.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In the high-symmetry cubic phase, the vibrational representation at the center of the Brillouin zone is expanded as

$$\Gamma(Fm3m) = A_{1g}(xx, yy, zz) + E_g(xx, yy, zz) + 2F_{2g}(xz, yz, xy) + F_{1g} + 5F_{1u} + F_{2u}. \quad (1)$$

The parentheses contain the components of the Raman tensor in which the corresponding vibrations are active. The transformation of the spectra with increasing pressure is shown in Fig. 2a. The Raman spectra in the range of pressures from 0 to 0.9 GPa have the form typical for the cubic phase of the crystal. At higher pressures, an additional line appears in the spectra in Fig. 2a in the vicinity of 500 cm^{-1}. The only vibration observed in this region in the cubic phase corresponds to the nondegenerate internal mode of

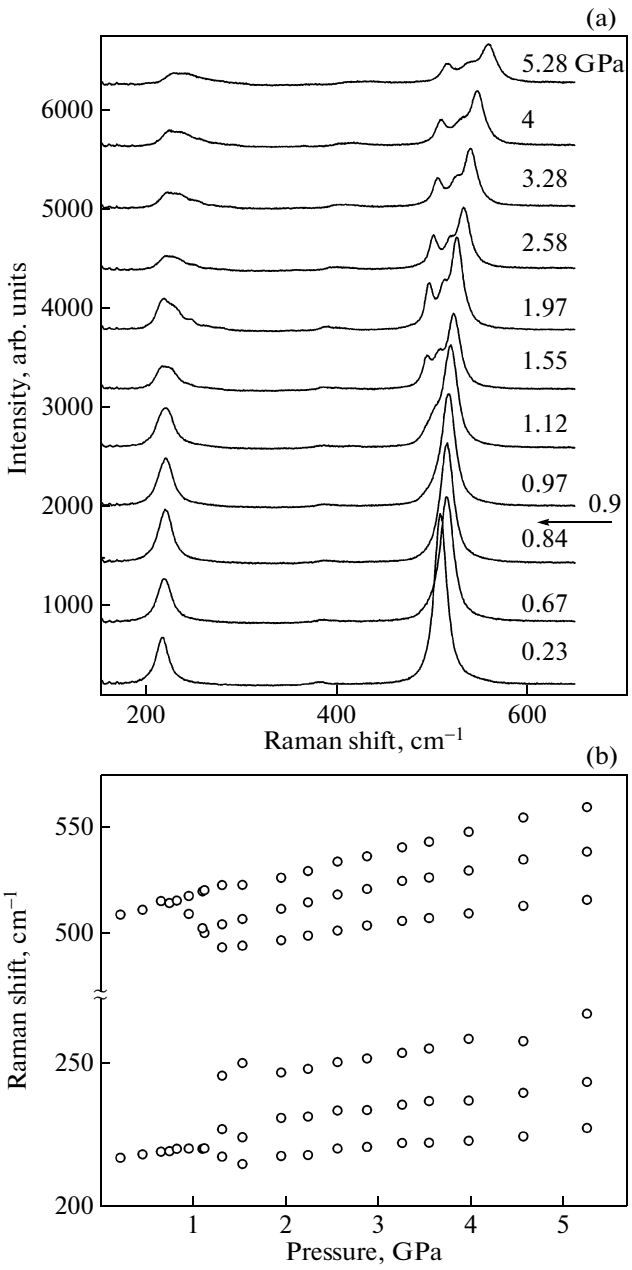

Fig. 2. (a) Transformation of the Raman spectra with increasing pressure at a temperature of 295 K and (b) pressure dependence of the frequencies of the Raman lines.

the octahedral InF_6 ion (A_{1g}, see (1)), and the emergence of an additional line here cannon be explained by removal of degeneracy. The emergence of this line may be associated only with an increase in the volume of the primitive cell of the cubic phase. The dependence of the frequency of observed vibrations on pressure is shown in Fig. 2b. At pressures above 1.3 GPa, additional lines emerge. In the present work, the lattice vibration spectrum was calculated using of the LADY software [15]. The interionic interactions were calculated by means of the rather simple but widely

used rigid ion model [16]. In the framework of this model, we succeeded in attaining a good agreement of the results of theoretical calculations with experimental values of the frequencies. It has been established that the phase transition at 0.9 GPa is connected with the condensation of the F_{1g} mode. In this case, the possible distorted phases are $I4/m$, $R\bar{3}$, $C2/m$, and $P\bar{1}$. The comparison of the calculated and experimental spectra of the high-pressure phase shows that the most probable phase is that with the space group $C2/m$.

4. CONCLUSIONS

The experimental measurements of the Raman spectra of the Rb_2KInF_6 crystal at a temperature of 295 K and a pressure of up to 5.3 GPa have revealed a phase transition at a pressure of approximately 0.9 GPa. The studied phase transition from the cubic phase to a lower-symmetry distorted phase is accompanied by an increase (probably, doubling) of the volume of the primitive cell of the initial phase. The calculated lattice vibration spectra are in a good agreement with experimental results. It has been established that the phase transition at 0.9 GPa is associated with rotation of the octahedral groups of InF_6. In this case, the most probable high-pressure phase is that with the space group $C2/m$.

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