

Phase transition in $\text{Cs}_3\text{Bi}_2\text{I}_9$ ferroelastic: investigation by Raman scattering technique

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Raman scattering in unpolarized light has been studied for the first time for $\text{Cs}_3\text{Bi}_2\text{I}_9$ layered ferroelastic at temperatures from 5 to 300 K in the heating mode. Neither soft mode nor frequency softening was observed. For the low-frequency lines 37.0, 45.0, 61.4, 68.3 and 97.4 cm^{-1} , the doublets were detected. Those may be due to Davydov splitting or splitting of degenerate vibrations of E -symmetry. The intensity equalization effect has been found for 114.8 and 125.3 cm^{-1} lines in the phase transition region. It is shown that the 150.6 and 131.2 cm^{-1} lines can be explained by vibrations of Bi-I bonds in the $[\text{BiI}_6]^{3-}$ octahedrons. The Raman spectra in $z(y,y)z$ and $z(y,x)z$ polarizations taken at 100 K were found to be similar to those in unpolarized light. An analysis of both known and our results enabled us to conclude that the ferroelastic phase transition at $T_c = 220$ K belongs to those of the first order but close to the second one.

Впервые в неполяризованном свете изучено комбинационное рассеяние (КР) в слоистом сегнетоэластике $\text{Cs}_3\text{Bi}_2\text{I}_9$ при температурах 5–300 К в режиме нагревания. Не обнаружено ни мягкой моды, ни смягчения частот. Зарегистрированы дублеты у низкочастотных линий 37,0, 45,0, 61,4, 68,3 и 97,4 см^{-1} , обусловленных давидовским расщеплением, либо расщеплением вырожденных колебаний симметрии E . Обнаружен эффект выравнивания интенсивностей линий 114,8 и 125,3 см^{-1} в области фазового перехода. Показано, что линии 150,6 и 131,2 см^{-1} можно объяснить колебаниями связей Bi-I в октаэдрах $[\text{BiI}_6]^{3-}$. Установлено, что при 100 К спектры КР в поляризации света $z(y,y)z$ и $z(y,x)z$ подобны спектрам КР в неполяризованном свете. На основе анализа известных и полученных нами данных сделан вывод о принадлежности сегнетоэластичного фазового перехода при $T_c = 220$ К к фазовым переходам первого рода, близких ко второму.

The layered semiconductor $\text{Cs}_3\text{Bi}_2\text{I}_9$ belongs to ferroelastic crystals being of interest for investigation [1]. At room temperature, $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystals are hexagonal and belong to the space symmetry group $D_{6h}^4(P6_3/mmc)$, with lattice parameters $a = 8.409(1)$ and $c = 21.243(5)$ Å [2]. At temperature $T_c = 220$ K, they undergo ferroelastic phase transition [2–7], with reversible change of symmetry from centrally symmetric hexagonal ($6/mmm$) to centrally symmetric monoclinic ($2/m$). Taking into account the measured temperature depend-

ence of birefringence [4], elasticity modulus [3, 5], linear and cubical expansion coefficients [4]; nuclear quadrupole resonance [27] [3, 5] and X-ray powder diffraction [2, 5], the above phase transition is believed to be the second order one. On the other hand, such facts (found recently in [7]) as temperature hysteresis in expansion of the crystal lattice along the C -axis, a low value (79 J/kg) of latent heat Q and presence of a transition heterostructure region where the ferroelastic and paraelastic phases coexist in the temperature range 183–221 K, indi-

cate that the phase transition at $T_c = 220$ K belongs to those of the first order close to the second one.

The Raman scattering technique is an effective method for investigation of phase transitions [8, 9]. There are some data on the Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ at 300 K [10]. However, the temperature dependence of these spectra has not been studied to date. Here we present the results of our attempt to obtain additional information on the phase transitions in $\text{Cs}_3\text{Bi}_2\text{I}_9$ layered crystals basing on investigations of temperature dependence of their Raman spectra in unpolarized light.

The $\text{Cs}_3\text{Bi}_2\text{I}_9$ layered crystals were grown from the melt using the Bridgman-Stockbarger oriented crystallization technique (for the features of this technology, see [11]). The 5–7 mm thick samples were obtained from a boule by splitting along the cleavage plane in air. The optical axis C was perpendicular to the cleavage plane. The Raman spectra were measured in the frequency range 10–250 cm^{-1} in the heating mode at temperatures from 5 to 300 K. The measuring setup was assembled on the basis of an automated DFS-24 spectrometer and worked in the back-scattering configuration. The spectral slit width was 1–1.5 cm^{-1} . The determination error of the line spectral positions was below 0.2 cm^{-1} . The radiation line $\lambda = 632.8$ nm of a He-Ne laser (50 mW power) was used for excitation (λ_{exc}). The samples were studied in an optical cryostat in helium vapor. The temperature variations did not exceed ± 0.1 K. The signals were registered using a cooled photomultiplier tube FEU-136 in the photon counting mode. The line contours were approximated with Lorentzians. The integral line intensities were normalized to that of the highest-frequency line that was clearly pronounced in the Raman spectra over the whole temperature range used.

The hexagonal packing of the unit cell of $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystal contains 28 atoms (two formula units). Those belong to two translation-nonequivalent layer packets [2, 4]. 81 optical modes can appear in the vibrational spectrum. These modes are characterized by the following irreducible representations [10]:

$$\Gamma_{opt} = 5A_1^+ + A_1^- + 6A_2^+ + 2A_2^- + 2A_3^+ + 5A_3^- + A_4^+ + 5A_4^- + 8E_1^+ + 6E_1^- + 6E_2^+ + 7E_2^-, \quad (1)$$

19 modes ($5A_3^-$ and $7E_2^-$) are active in IR absorption, 33 modes ($5A_1^+$, $8E_1^+$ and $6E_2^+$) are active in

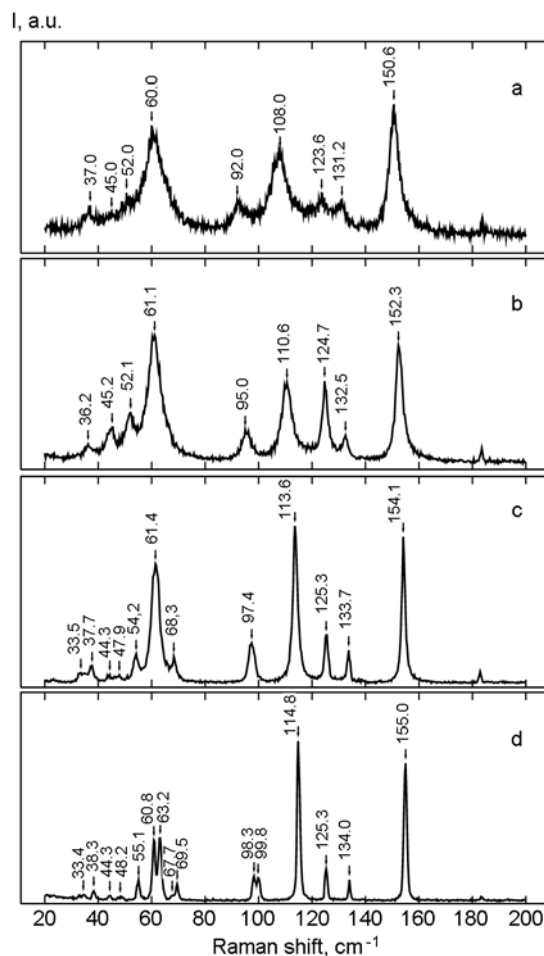


Fig. 1. Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ layered crystals taken in unpolarized light at temperatures 300 (a), 220 (b), 80 (c) and 5 K (d).

Raman scattering, and 29 modes (A_1^- , $6E_2^+$, $2A_2^-$, $2A_3^+$, A_4^+ , $5A_4^-$ and $6A_2^+$) are "dummy", i.e., inactive in both IR absorption and Raman scattering. Thus, 19 lines in Raman spectra can appear, of which 14 lines ($8E_1^+$ and $6E_2^+$) are doubly degenerate. In addition, the vibrational bands are expected to be split into the Davydov doublets [12] due to presence of two translation-nonequivalent layer packets in the unit cell, with van der Waals interaction between them. Because of the alternative exclusion, only one of the doublet components may be allowed in the Raman spectra, while another is allowed in the IR absorption spectra only, and vice versa. There is no developed mirror surface at the layer crystal butt. This fact makes it impossible to carry out the polarization investigations at $T = 300$ K, correlate the experimental results with those of group theory

analysis and determine the phonon symmetry.

The typical Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ taken in the low-frequency region at 300, 220, 80, and 5 K are presented in Fig. 1. One can see that these spectra are rich indeed. Of 19 lines predicted by the group theory analysis, only 9 lines (at 37.0, 45.0, 52.6, 60.0, 92.0, 108.0, 123.6, 131.2, and 150.6 cm^{-1}) are observed at 300 K (Fig. 1a). Their number and frequencies coincide with those registered before in [10]. The different numbers of Raman lines in the experimental and theoretically predicted spectra can be related to the fact that the frequencies of some predicted lines are close to each other and cannot be resolved by a spectrometer. In this case, it is to note low intensities of the three lower-frequency lines (37.0, 45.0, and 50.6 cm^{-1}), as well as relatively high intensities of three lines (60.0, 108.0, and 150.6 cm^{-1}) at shorter wavelengths. Temperature lowering down to the phase transition point ($T_c = 220$ K) (Fig. 1b) makes the Raman spectrum clearer. The intensity of the 123.6 cm^{-1} line becomes the same as that of the 110.6 cm^{-1} one. At 80 K, the Raman spectrum is modified essentially (Fig. 1c). The 36.2 and 45.2 cm^{-1} lines appear as doublets (33.5–37.7) and (44.3–47.9) cm^{-1} , respectively. The peak intensity of the 113.6 cm^{-1} line becomes about three times as high as that of the 125.3 cm^{-1} one. In addition, a new weak line at 68.3 cm^{-1} appears at the high-frequency edge of the 61.4 cm^{-1} one.

As temperature decreases further down to 5 K (Fig. 1d), the above doublets remain weak but become more pronounced. In this case, on the one hand, the intensity ratio between the 113.6 and 125.3 cm^{-1} lines increases; on the other hand, the lines 61.4, 68.3, and 97.4 cm^{-1} are split into doublets (60.8–63.2), (67.7–69.5) and (98.3–99.8) cm^{-1} , respectively. It should be noted that the higher is the Raman line frequency, the smaller is doublet splitting. For instance, this splitting is 4.6 and 1.5 cm^{-1} for the lines 45.0 and 92.0 cm^{-1} , respectively. To reveal the so-called soft mode (i.e., vibrations with anomalous frequency decrease near the phase transition point; this is characteristic of the second order phase transitions [13–16]), we studied the temperature-induced changes in spectral positions of the above lines. The results of our measurements are presented in Fig. 2. The following three items are to be noted: (i) there is no line among those considered

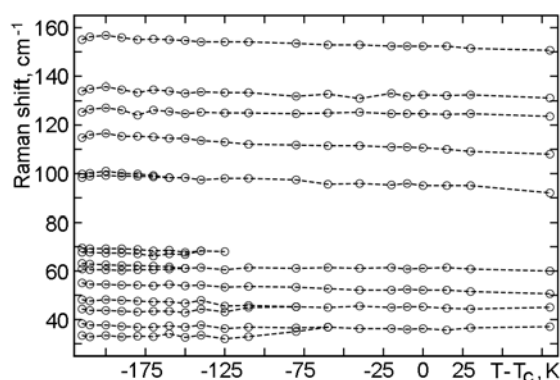


Fig. 2. Temperature dependences of the position of low-frequency lines 34.4, 38.3, 44.3, 48.2, 55.1, 60.8, 63.2, 67.7, 69.5, 98.3, 99.8, 114.8, 125.3, 134.0 and 155.0 cm^{-1} in the Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ layered crystals taken in unpolarized light. $\lambda_{exc} = 632.8$ nm.

with frequency tending to zero or decreasing considerably at $T_c = 220$ K; (ii) the line frequencies remain practically the same at phase transition from the high-symmetry hexagonal phase to the low-symmetry monoclinic one; (iii) the doublet structure of the lines in the Raman spectra begins to appear below (by about 70 K) the phase transition point, in the temperature region where the monoclinic phase exists.

Shown in Fig. 3 are temperature dependences of the reduced integral intensities (Fig. 3a) and half-widths (Fig. 3b) of two lines (114.8 and 125.3 cm^{-1}). These lines respond to thermal actions in a most pronounced way. To illustrate, the reduced integral intensity I_2 of the 125.3 cm^{-1} line (dots) first increases with temperature (peaking at the phase transition point) and then goes down. In contrast, the reduced integral intensity I_1 of the 114.8 cm^{-1} line (triangles) approaches a minimum at the same point and further remains practically at the same level (Fig. 3a). The observed variations of these line intensities indicate a strong interaction between their modes. The evolution of the reduced integral intensities of the 114.8 cm^{-1} (Fig. 3a, curve 1) and 125.3 cm^{-1} (Fig. 3a, curve 2) lines with temperature is approximated well by the following expressions:

$$I_1 = 1.11 - 1.96 \cdot 10^{-3}T^1 + 1.51 \cdot 10^{-5}T^2 - 8.70 \cdot 10^{-8}T^3 + 1.79 \cdot 10^{-10}T^4, \quad (2)$$

$$I_2 = 0.14 + 9.63 \cdot 10^{-3}T^1 - 1.13 \cdot 10^{-4}T^2 + 5.69 \cdot 10^{-7}T^3 - 9.78 \cdot 10^{-10}T^4. \quad (3)$$

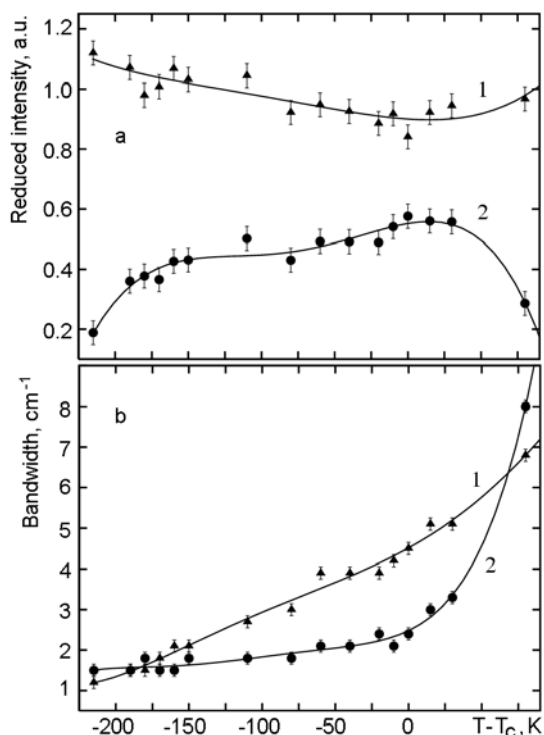


Fig. 3. Temperature dependences of the reduced integral intensities (a) and half-widths (b) of the lines 114.8 (curve 1) and 125.3 cm⁻¹ (curve 2) in the Raman spectra of Cs₃Bi₂I₉ layered crystals taken in unpolarized light ($\lambda_{exc} = 632.8$ nm): dots and triangles — experiment, full curves — extrapolation according to Eqs.(2) and (3) and Eqs.(4) and (5), respectively.

Thus, at $T_c = 220$ K the intensities of the 114.8 and 125.3 cm⁻¹ lines become equal to each other, without any peculiarities in behavior of the line frequencies.

The half-widths of the above lines depend on temperature in different ways, too (Fig. 3b). At $T \leq T_c$, the 114.8 cm⁻¹ line becomes broader considerably, while broadening of the 125.3 cm⁻¹ line is insignificant. At $T > T_c$, the latter line broadening is more pronounced. As a result, its half-width at 300 K exceeds that of the former line. Evolution of the half-widths of the 114.8 cm⁻¹ (Fig. 3b, curve 1) and 125.3 cm⁻¹ (Fig. 3b, curve 2) lines with temperature may be presented as

$$\Delta H_1 = 1.16 + 5.63 \cdot 10^{-3}T^1 + 2.06 \cdot 10^{-4}T^2 - 1.63 \cdot 10^{-6}T^3 + 5.23 \cdot 10^{-9}T^4 - 5.32 \cdot 10^{-12}T^5, \quad (4)$$

$$\Delta H_2 = 1.48 + 6.623 \cdot 10^{-3}T^1 - 1.81 \cdot 10^{-4}T^2 + 2.49 \cdot 10^{-6}T^3 - 1.34 \cdot 10^{-8}T^4 + 2.57 \cdot 10^{-11}T^5. \quad (5)$$

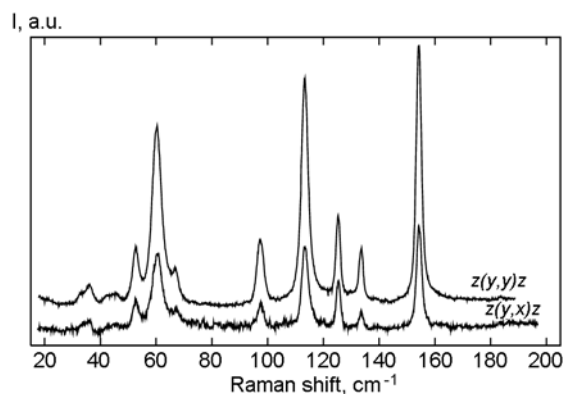


Fig. 4. Raman spectra of Cs₃Bi₂I₉ layered crystals taken at polarization $z(y,y)z$ and $z(y,x)z$. $\lambda_{exc} = 632.8$ nm, $T = 100$ K.

At last, since the anisotropy of Cs₃Bi₂I₉ crystal decreases considerably at low temperatures [19], we have managed to obtain (by chipping) a mirror butt surface of a sample in the monoclinic phase and to register the low-frequency Raman spectra in polarized light at 100 K. The results of our measurements for two configurations ($z(y,y)z$ and $z(y,x)z$) are presented in Fig. 4. It is seen that the same 9 lines appear in the spectra in both cases, with about the same intensity distributions between them. At present, it seems to be impossible to identify these lines with certain types of vibration modes, because there is no group theory analysis of the monoclinic Cs₃Bi₂I₉ lattice.

When interpreting the results obtained, it seems to be expedient to compare the Raman frequencies of Cs₃Bi₂I₉ crystals (where structure elements of the layer packets are the ions [Bi₂I₉]³⁻ formed by two octahedrons [BiI₆]³⁻ having a common face made by iodine atoms [2, 4]) to the known frequencies of related crystals Rb₃Bi₂I₉ [10] at 300 K. The corresponding data are presented in the Table. It is seen that the relation $\nu_{Cs_3Bi_2I_9} / \nu_{Rb_3Bi_2I_9} = 1$ is valid for all the compared frequencies of Cs₃Bi₂I₉ and Rb₃Bi₂I₉ considered in the Table. This relation confirms the equality of structure element masses in Cs₃Bi₂I₉ and Rb₃Bi₂I₉ and indicates the decisive role of vibrations of [Bi₂I₉]³⁻ molecular ions as a whole in formation of the low-frequency Raman spectra of both compounds. So the force constants remain practically the same when going from Cs₃Bi₂I₉ to Rb₃Bi₂I₉, as in the case of antimony and of bismuth triiodides [18].

The total Raman spectrum of Cs₃Bi₂I₉ may be separated arbitrarily into the following three portions, namely, low-fre-

Table. Line frequencies in the Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Rb}_3\text{Bi}_2\text{I}_9$ layered crystals and their ratios. $\lambda_{exc} = 632.8$ nm, $T = 300$ K

$\nu_{\text{Cs}_3\text{Bi}_2\text{I}_9}$, cm^{-1} [our results]	$\nu_{\text{Rb}_3\text{Bi}_2\text{I}_9}$, cm^{-1} [10]	$\nu_{\text{Cs}_3\text{Bi}_2\text{I}_9}/\nu_{\text{Rb}_3\text{Bi}_2\text{I}_9}$
–	24	–
37	37	1
45	45	1
52	52	1
60	62	0.97
–	67	–
–	76	–
92	–	–
108	–	–
124	–	–
131	131	1

quency ($\nu < 105$ cm^{-1}), middle-frequency ($105 < \nu < 130$ cm^{-1}) and high-frequency ($\nu > 130$ cm^{-1}) ones. A characteristic feature of the first portion is the presence of five doublets in the spectrum. Let us consider their origin in more detail. The doublet of the lowest frequency in the Raman spectra of layered crystals is related usually to the rigid layer vibrations [17] defined by weak van der Waals interaction between the layer packets. For $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystals, however, assigning the doublet (33.4–38.3) cm^{-1} to the rigid layer vibrations seems to be unlikely. First, the lines that correspond to such vibrations would appear at lower frequencies than those in the Raman spectra of the basic BiI_3 layered crystals (22–34 cm^{-1}) [18]. The reason is that the mass of molecular ion $[\text{Bi}_2\text{I}_9]^{3-}$ is bigger than the masses of Bi atoms which form the layer packets BiI_3 and are responsible for the low-frequency Raman spectra of BiI_3 . Another fact (which is of great importance) is that $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystal in its monoclinic phase loses the strong anisotropy of its chemical bond [19, 20] and demonstrates the physical properties that are inherent in classical semiconductors. In addition, the doublet components cannot be assigned to manifestation of single IR-active phonons. On the one hand, those are forbidden by the alternative exclusion rules for the vibrational spectra of the centrally symmetric monoclinic $\text{Cs}_3\text{Bi}_2\text{I}_9$ lattice. On the other hand, if this would be actually true, then the intensities of the corresponding lines would be weak and vary when

going from one sample to another, contrary to the experiment.

The doublet line structure may be related to the Davydov doublets due to non-equivalent positions of molecular ions $[\text{Bi}_2\text{I}_9]^{3-}$ in monoclinic lattice. However, one should not exclude also that such a structure is related to splitting of the degenerate vibrations of E symmetry due to removal of degeneracy under spontaneous strain which appears when high-symmetry hexagonal crystal lattice becomes low-symmetry monoclinic by passing through the phase transition point.

The middle portion of the spectrum involves two lines (108.0 and 123.6 cm^{-1}). It is of the biggest interest, because both lines demonstrate the strongest temperature dependence. Their nature, however, is not quite clear. Nevertheless, a number of facts evidence convincingly that the above phase transition belongs to those of the first order close to the second one. These facts are as follows: (i) the registered temperature effect of intensity equalization of these lines near the phase transition point (accompanied by some peculiarities in behavior of the line half-widths); (ii) absence of the soft mode and frequency softening as well as of any peculiarities of the Raman spectra in polarized light; (iii) low latent heat value; (iv) the presence of temperature hysteresis in the crystal lattice expansion; and (v) the presence of a heterophase transition region where the ferroelastic and paraelastic phases coexist [7]. Two lines (150.6 and 131.2 cm^{-1}) of the last portion of the spectra demonstrate only a weak variation of their frequencies over the temperature range 5–300 K. They practically coincide with the lines in $\text{Rb}_3\text{Bi}_2\text{I}_9$ crystal (see Table). These facts enable us to assign these lines to the vibrations of Bi–I bonds in the $[\text{BiI}_6]^{3-}$ octahedrons.

To conclude, we measured the low-frequency Raman spectra in unpolarized light of layered ferroelastic $\text{Cs}_3\text{Bi}_2\text{I}_9$ in the heating mode over the temperature range 5–300 K (involving the ferroelastic phase transition point at $T_c = 220$ K). Neither soft mode nor frequency softening have been revealed. Doublets have been found for five lines (37.0, 45.0, 61.4, 68.3, and 97.4 cm^{-1}) of the lowest frequencies. The higher is the line frequency, the smaller is the line splitting. The above doublets are assumed to be due to the Davydov doublets (that appear due to nonequivalent positions of molecular ions $[\text{Bi}_2\text{I}_9]^{3-}$ in monoclinic lattice) or to the splitting of the E symmetry

degenerate vibrations due to removal of degeneracy under spontaneous strain which appears when high-symmetry hexagonal crystal lattice transits into low-symmetry monoclinic one. The intensity equalization of 114.8 and 125.3 cm^{-1} lines without appearance of any peculiarities in the line frequency behavior has been revealed in the phase transition region. It has been shown that the 150.6 and 131.2 cm^{-1} lines (which change their frequency with temperature only weakly) may be assigned to the vibrations of Bi-I bonds in the $[\text{Bi}_6]^{3-}$ octahedrons. It was found that the Raman spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystals taken in the $z(y,y)z$ and $z(y,x)z$ polarizations ($T = 100$ K) are similar to those taken in unpolarized light. The ferroelastic phase transition at $T_c = 220$ K belongs to those of the first order close to the second one.

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Фазовий перехід у сегнетоеластичку $\text{Cs}_3\text{Bi}_2\text{I}_9$: дослідження методом комбінаційного розсіювання світла

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Вперше у неполяризованому світлі вивчено комбінаційне розсіювання (КР) у шаруватому сегнетоеластичку $\text{Cs}_3\text{Bi}_2\text{I}_9$ при температурах 5–300 К у режимі нагрівання. Не виявлено ані м'якої моди, ані пом'якшення частот. Зареєстровано дублети у низькочастотних ліній 37,0, 45,0, 61,4, 68,3 і 97,4 cm^{-1} , обумовлених давидівським розщепленням, або ж розщепленням вироджених коливань симетрії E . Виявлено ефект вирівнювання інтенсивностей ліній 114,8 і 125,3 cm^{-1} в області фазового переходу. Показано, що лінії 150,6 і 131,2 cm^{-1} можна пояснити коливаннями зв'язків Bi-I в октаедрах $[\text{Bi}_6]^{3-}$. Встановлено, що при 100 К спектри КР у поляризації світла $z(y,y)z$ та $z(y,x)z$ є подібними до спектрів КР у неполяризованому світлі. Проаналізовано відомі та отримані нами дані і зроблено висновок про належність сегнетоеластичного фазового переходу при $T_c = 220$ К до фазових переходів першого роду, що є близькими до другого.