

Change of IR spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals at the low-temperature phase transition

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IR absorption spectra of semiconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals ($x=0, 0.07, 0.17$) were recorded in the vicinity of band edge at temperature ranging from 6 to 490 K. The measurements reveal a sharp anomaly in the behavior of the material near $T_a=65-75$ K. At this temperature the band gap in all investigated specimens narrows inducing a steplike decrease of IR transmittance. The difference in transmittance above and below T_a depends on x and for $x=0.17$ compound exceeds one order of magnitude. Recorded changes are associated with the low-temperature structural phase transition in the substance. They resemble a switching phenomenon controlled by the transformation of crystallographic symmetry in the system with a substantial electronic instability. [S0163-1829(97)07843-0]

I. INTRODUCTION

Compounds of family $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ are known to possess both superconductivity with $T_c \approx 30$ K (for $x \approx 0.4$) and an exotic insulating state (for $x < 0.3$). The solid alloy has a complicated structural phase diagram.¹ With the decrease of potassium concentration simple cubic perovskite lattice of the superconducting composition transforms first into orthorhombic ($Ibmm$, $x \leq 0.3$) and then to body-centered monoclinic ($I2/m$ at room temperature, $x < 0.1$) structure. The lowering of crystallographic symmetry in the material was explained by tilting and breathing-mode distortions of BiO_6 octahedra.¹ Small deviations from ideal cubic structure enhanced by the valence instability of Bi ions (negative- U correlations²⁻⁵) are widely believed to result in the charge disproportionation of Bi^{4+} to $\text{Bi}^{3+}/\text{Bi}^{5+}$. Partial ordering of two crystallographically inequivalent Bi sites causes formation of a charge-density wave (CDW) gap probably on Peierls scenario. Different phase modifications of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ exhibit a great diversity of physical properties. Variation of the properties with the substitution of K for Ba, the origin of the insulator to metal transition at $x \sim 0.3$, and the nature of superconducting state in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ were studied by numerous groups.^{6-9,11-21} Their results evidence considerable progress in the understanding of the matter. In contrast to this, very little work has been done on the investigation of phase transitions in semiconducting compositions of the alloy ($x < 0.3$), which can be induced by the alteration of temperature.¹ Structural changes at the transitions were characterized with electron and powder neutron diffraction measurements;¹ however, to date no systematic studies of their influence on physical properties of the substances were reported.

Because of small electrical conductivity at low temperature and lack of magnetic ordering, transport or magnetic measurements of the semiconducting species meet significant difficulties and optical investigation would be an alternative source of information. In order to check this possibility we recorded midinfrared (IR) absorption spectra of several semiconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals ($x=0, 0.07, 0.17$) in the broad temperature range. It was found that the behavior of all investigated specimens exhibit a sharp

anomaly near $T_a=65-75$ K. At this temperature band gap in the substances narrows inducing a steplike decrease of IR transmittance. The difference in transmittance above and below T_a depends on x and for $x=0.17$ compound exceeds one order of magnitude. Observed spectral changes are associated with the low-temperature structural phase transition in the material.

II. EXPERIMENT

The BaBiO_3 crystal was prepared by the standard melt process; crystals of $\text{Ba}_{0.93}\text{K}_{0.07}\text{BiO}_3$ and $\text{Ba}_{0.83}\text{K}_{0.17}\text{BiO}_3$ were grown by an electrochemical method from a Ba-rich solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and Bi_2O_3 in KOH.^{8,9} Potassium concentration was evaluated by electron-probe microanalysis. Synthesized substances were characterized with powder x-ray diffraction measurements (Rigaku MJ diffractometer, Cu $K\alpha$ radiation); pseudocubic lattice parameters a_p were evaluated using d spacings of eight strongest peaks calibrated against Si powder. a_p in the compounds increased with decreasing potassium concentration in excellent agreement with the linear relationship in Ref. 1. Simultaneously distortion of cubic lattice evidenced by several weak reflections in recorded patterns showed trend to rise. According to the phase diagram¹ the distortion should result in body-centered monoclinic ($I2/m$) and orthorhombic ($Ibmm$) structures in $x=0,0.07$ and $x=0.17$ compounds, respectively.

For optical measurements, freshly prepared large bulk crystals were mechanically polished into thin plates, first with a sand paper and then with $0.3-0.05 \mu\text{m}$ abrasives. Typical dimensions of the plates were about $3 \times 3 \times 0.1 \text{ mm}^3$. In order to stabilize oxygen content and prevent degradation, prepared specimens were exposed to oxygen at slightly elevated temperature. Infrared absorption spectra in the range $7000-400 \text{ cm}^{-1}$ were recorded using a Bruker IFS-66v Fourier transform spectrometer equipped with an Oxford CF 1104 He-flow cryostat and a temperature controller. Collection time was about 10 min per spectrum recorded with the resolution of 2 cm^{-1} and the highest available sensitivity. The spectra were taken with the precise thermal stabilization of the sample space in cryostat. In order to characterize fast

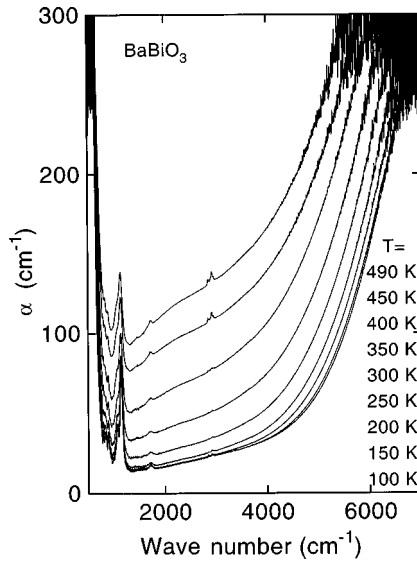


FIG. 1. The temperature dependence of IR absorption spectra of BaBiO_3 crystal in the range 100–490 K. Note the sensitivity of the spectrometer limited maximal available absorption coefficient.

temperature changes in IR transmittance, which were observed in investigated substances below 100 K, we independently recorded temperature dependencies of intensity I of a center burst (the most intense peak at the origin) in interferograms. This magnitude is known to be proportional to the integral intensity of light transmitted by specimens in measured frequency range.¹⁰ In our spectrometer the range 7000–400 cm^{-1} was limited by characteristics of global, KBr beamsplitter and DTGS detector. Without Fourier transformation and storing interferograms, magnitudes I could be recorded at every scan of moving mirror, i.e., quite rapidly, in about 5 sec. The data were taken on slow heating of specimens in cryostat from liquid-He temperature. In figures they are shown in the form $I(T)/I_{\text{max}}$ obtained after the normalization with the maximal for each specimen magnitude. For comparison similar values were calculated using numerical integration of recorded spectra. They are presented in the same normalized form.

III. RESULTS AND DISCUSSION

All recorded spectra are divided into two parts. Those taken above 100 K ($x=0, 0.07$ compounds) and 80 K ($x=0.17$ compound) are shown in Figs. 1–3; below these temperatures, in Fig. 4. Room temperature data for BaBiO_3 crystal are in agreement with previous measurements¹¹ and substantially deviate from powder spectra of similar substances recorded as KBr pellets.¹² In the latter case particle size probably influenced the shape of absorption curves. The low- and high-energy ends of recorded spectra (Figs. 1–4) are limited by the TO_1 phonon at about 500 cm^{-1} and the intense interband transition, respectively.⁶ Sharp peaks at 1146 cm^{-1} (with the side band at 1072 cm^{-1}) and 1729 cm^{-1} in BaBiO_3 can be related to the second and third overtones of phonon at 575 cm^{-1} , see Ref. 11. The frequency of the phonon is very close to the position of the strongest Raman band (569 cm^{-1} in BaBiO_3), which was assigned to the breathing mode.⁷ Similar peaks in spectra of

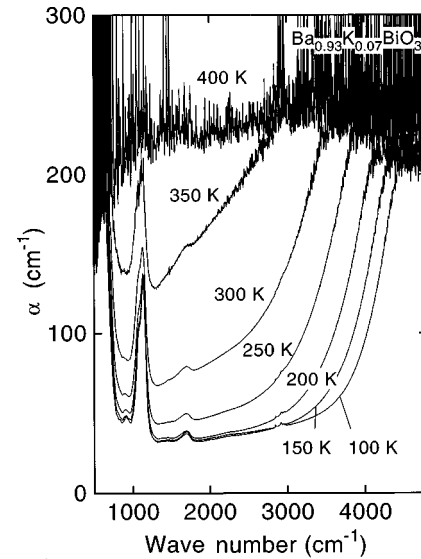


FIG. 2. The temperature dependence of IR absorption spectra of $\text{Ba}_{0.93}\text{K}_{0.07}\text{BiO}_3$ crystal in the range 100–400 K. Note the sensitivity of the spectrometer limited maximal available absorption coefficient.

$x=0.07$ and 0.17 compounds are located respectively at 1134, 1702, and 1090, 1635 cm^{-1} (with the side band at 1464 cm^{-1}). Energies of the peaks are almost temperature independent.

Numerous reflectivity studies^{6,13–15} showed that the maximum of the interband transition in BaBiO_3 is located near 16000 cm^{-1} and shifts down to 7000–8000 cm^{-1} in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with increasing x up to $x\sim 0.3$ when the material transforms into metal. The transition was associated with a direct charge excitation across CDW gap. It is known also¹¹ that the band gap deduced from transport measurements of BaBiO_3 (Ref. 16) is about 4000 cm^{-1} (twice of activation energy $E_a=0.24$ eV). Both optical and transport data seem to be in agreement with electronic structure

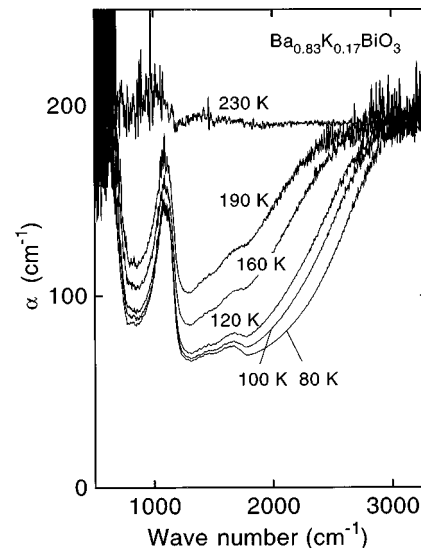


FIG. 3. The temperature dependence of IR absorption spectra of $\text{Ba}_{0.83}\text{K}_{0.17}\text{BiO}_3$ crystal in the range 80–230 K. Note the sensitivity of the spectrometer limited maximal available absorption coefficient.

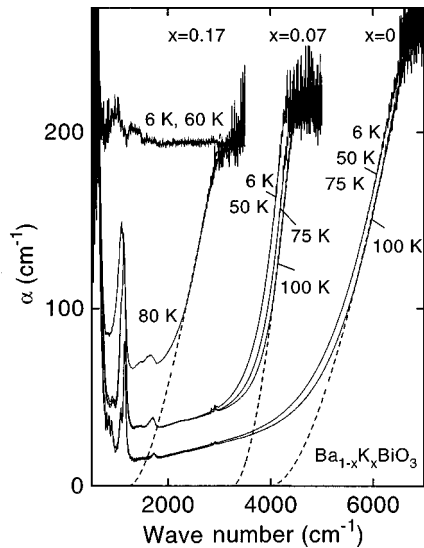


FIG. 4. The temperature dependencies of IR absorption spectra of three $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals in the range 6–100 K ($x=0,0.07$ compounds) and 6–80 K ($x=0.17$ compound). The spectra within 6–75 K ($x=0$), 6–50 K ($x=0.07$), and 6–60 K ($x=0.17$) almost coincide. Dashed lines represent the fit of the experimental data with the expression $\alpha\hbar\omega \sim (\hbar\omega - E_g)^2$ in the vicinity of the band edge. Note the sensitivity of the spectrometer limited region of maximal available absorption coefficient.

calculations¹⁷ which demonstrated that Bi 6s bands in BaBiO_3 form a direct gap of ~ 1.3 eV and indirect one of ~ 0.3 eV. The magnitudes correlate well with the results of optical and transport experiments. The same conclusion was made in Ref. 18 on the basis of photoemission and x-ray-absorption spectroscopy investigations. It was reported also that potassium doping changes band filling in semiconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and systematically reduces CDW gap energy without significantly altering the band structure of the material.^{19,20}

For these reasons spectra in Figs. 1–4 should be related to the region of an indirect band-to-band transition. If exciton formation is neglected, the band edge in semiconductors with the indirect gap can be described by the expression $\alpha\hbar\omega \sim (\hbar\omega - E_g)^2$.²² In pure crystalline solids E_g should include the energy of phonons that have to be emitted or absorbed at the transition in order to conserve momentum. In heavily doped or disordered systems the requirement of momentum conservation at nonvertical transitions can be fulfilled by scattering process involving free carriers, impurities, and defects.²³ The quadratic frequency dependence of the absorption coefficient near E_g is also valid for many disordered and amorphous materials.²² We found that similar law can satisfactorily approximate absorption edge (region of steep increase of absorption coefficient) in low-temperature spectra of all investigated compounds (see Fig. 4). Fitting parameter E_g , which may be used to define the indirect gap, for specimens with $x=0, 0.07$ and 0.17 is equal to 3979 cm^{-1} (at 100 K), 3246 cm^{-1} (at 100 K), and 1220 cm^{-1} (at 80 K), respectively. Variation of E_g with potassium concentration in investigated substances forms almost linear dependence (Fig. 5, open symbols), which may be extrapolated to the region of metallic composition ($E_g=0$ when $x=0.25$). Related downshift of the interband transition

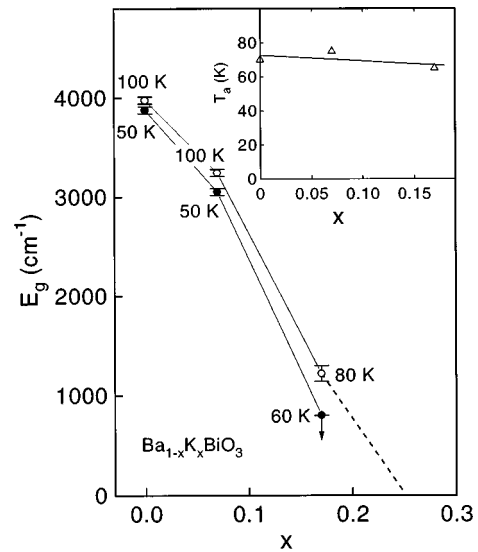


FIG. 5. The energy gap E_g vs potassium concentration x in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ deduced from spectra in Fig. 4 and extrapolated to the region of metallic composition. Open and solid symbols stand for data recorded just above and below $T_a = 65\text{--}75$ K, respectively. Note that E_g for the $x=0.17$ compound at $T=60$ K was evaluated only approximately. The inset shows T_a defined according to Fig. 6 vs x in investigated specimens.

with increasing x and occurrence of metallic phase near $x \sim 0.3$ was reported by many authors.^{13–15} This fact along with the excellent agreement of E_g for BaBiO_3 with results of transport measurements¹⁶ can be regarded as additional arguments in favor of validity of the analysis.

Below the band-edge spectra of all investigated substances reveal a residual absorption that is quite substantial even in undoped compound. In usual semiconductors such absorption is normally ascribed to the contamination of material with some impurities or intraband transition due to free carriers.^{22,23} The latter frequently obeys λ^2 law and has intensity proportional to the number of free carriers. A long-wave exponential tail is typical for disordered and amorphous materials as well. Origin of substantial residual absorption in BaBiO_3 is not clear for us at the moment. Beside the common sources, it can be associated with the electron-hole interaction^{11,21} or peculiar bipolaron excitation.¹⁵ It is obvious, however, that the residual absorption increases in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with increasing x . This correlates with the composition-induced band-gap narrowing (Fig. 5) and the rise of reflectivity and optical conductivity in IR region of similar compounds reported in Refs. 13–15. The effect can be related to the reduction of band filling at K substitution,^{19,20} which probably results in strengthening of the intraband contribution.

Recorded spectra exhibit unusual temperature dependencies. With decreasing T down to 100 K for $x=0, 0.07$ and 80 K for $x=0.17$ compounds, the band edge shifts upward in energy (Figs. 1–3) as normally observed in ordinary semiconductors. Below 80–100 K the pattern changes; the band edge shifts in opposite way—to the low-energy end of spectra (Fig. 4). The anomalous shift downward occurs in the narrow temperature range 100–50 K, is quite small in BaBiO_3 and becomes larger in $\text{Ba}_{0.93}\text{K}_{0.07}\text{BiO}_3$. E_g values deduced from 50 K spectra of the two substances are equal,

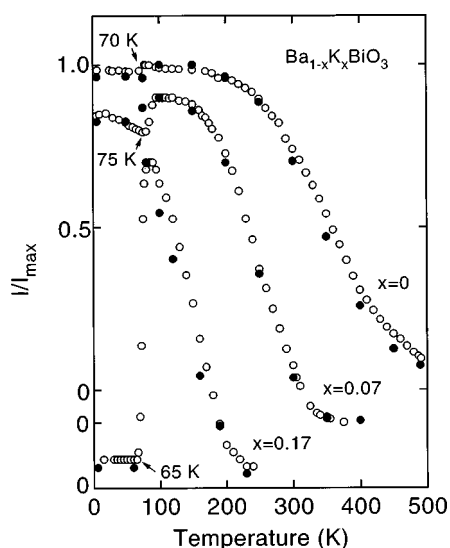


FIG. 6. The temperature dependencies of integral transmittance in the range $7000\text{--}400\text{ cm}^{-1}$ of three $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals normalized with the maximal for each specimen value. The magnitudes recorded as intensities of the center burst at interferograms and calculated using integration of spectra in Figs. 1–4 are shown with open and solid symbols, respectively. The temperature of the sharp anomaly T_a in the dependencies is marked. Note the sensitivity of the spectrometer limited signal for $x=0.17$ compound below 65 K and above 230 K.

respectively, to 3879 cm^{-1} and 3054 cm^{-1} , i.e., they decrease by 2.5% in $x=0$ compound and by 6% in $x=0.07$ compound as compared with 100-K data. The behavior of heavily doped $\text{Ba}_{0.83}\text{K}_{0.17}\text{BiO}_3$ crystal is very peculiar. Below 80 K its IR transmittance drops down to the magnitude when the recorded signal becomes smaller than the sensitivity of our spectrometer. The spectrum of the specimen at 60 K reveals only structureless noise (Fig. 4) and resembles data taken at 230 K (Fig. 3). Variation of E_g in $\text{Ba}_{0.83}\text{K}_{0.17}\text{BiO}_3$ with decreasing temperature from 80 to 60 K is difficult to evaluate exactly, though it should probably be comparable or larger than that in the range 80–230 K. Taking $E_g \sim 800\text{ cm}^{-1}$, the value derived from the 190-K spectrum, as the upper limit, we can conclude that the band gap in the crystal diminishes by more than 34% when temperature decreases from 80 to 60 K. Although E_g at $T < 80\text{ K}$ in the specimen is quite indefinite, the trend becomes obvious: in the critical temperature region the anomalous downshift of the band edge and corresponding narrowing of band gap develop with increasing potassium concentration. Variation of E_g deduced from the low-temperature spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with x is shown in Fig. 5 with solid symbols.

The changes in spectra of the heavily doped material take place quite rapidly making measurements within 80–60 K difficult. Small fluctuations of temperature at the thermal stabilization of the sample space in cryostat have a substantial influence on recorded data. In order to characterize spectral changes in this critical range we recorded temperature dependencies of integral intensity of light transmitted by our specimens in the IR region. Acquired as intensities of the center burst at interferograms¹⁰ (see above for details), the data can be taken quite rapidly on slow heating of the sample space from the liquid-He temperature. The magnitudes normalized

with the maximal for each specimen value are shown in Fig. 6 (open symbols). One can see an unusual steplike anomaly near $T_a = 65\text{--}75\text{ K}$ at all dependencies. Magnitudes of the steps in compounds with $x=0, 0.07$ and 0.17 are equal to 2%, 11%, and 91%, respectively. One should mention, however, that the latter values as well as the onset of the anomaly were sensitive to the heating rate and slightly varied at measurements. Besides, the signal in $\text{Ba}_{0.83}\text{K}_{0.17}\text{BiO}_3$ at low temperature was limited by the sensitivity of our spectrometer and could not be evaluated precisely. Temperatures of the sharp anomaly T_a in specimens with different x are shown in inset in Fig. 5.

Solid symbols in Fig. 6 represent integral transmittance calculated for comparison using integration of recorded spectra. Their agreement with values $I(T)/I_{\text{max}}$ acquired directly is good in the whole temperature range; the data in Figs. 1–4 and Fig. 6 are evidently consistent. We can conclude hence that the steplike anomaly near $T_a = 65\text{--}75\text{ K}$ in integral transmittance is provoked by the downshift of the band edge. A contribution from the rise of residual absorption in the critical temperature region may also be of importance for the narrow gap $x=0.17$ compound.

Peculiar behavior of investigated specimens can be understood taking into account the phase diagram of the material.¹ According to it, body-centered monoclinic $I2/m$ structure of BaBiO_3 transforms into primitive monoclinic, probably of $P2/m$ symmetry, at temperature below 150 K. The transition is evidenced by new reflections in neutron powder diffraction patterns. The lightly doped compound with $x=0.1$ has an orthorhombic $Ibmm$ lattice in the temperature range 300–200 K and is body-centered monoclinic at 10 K. In both instances crystallographic symmetry of the material reduces in a low-temperature phase. Structural data at $T < 295\text{ K}$ on compositions $0.1 < x < 0.3$ are not reported. We believe that the instability below 150 K is common for all $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ crystals with $x=0\text{--}0.17$ investigated by us and the transition from high- to low-temperature state is responsible for sharp changes in recorded IR spectra. In other words, T_a values in Fig. 6 should correspond to the phase transformation. Slightly higher temperature of the onset of the transition in BaBiO_3 according to Ref. 1 (about 100 K) than that in our study (70 K) was detected on ceramic specimens. An inhomogeneity and multiple grain boundaries typical of ceramics may be a reason for the discrepancy. Quite broad transition range in Ref. 1 is an indication of the possibility. It was mentioned also that oxygen content in the compounds (poorly controlled variable) is important for the occurrence of the phase transformation.¹ Our preliminary results obtained on $x=0.17$ crystal confirm the observation; annealing of the specimen in oxygen affected its T_a value. Finally doping of BaBiO_3 with potassium should influence T_a as well. However, lack of structural data on lightly doped $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ at $10\text{ K} < T < 200\text{ K}$ does not allow us to compare location of the phase boundary for it with our measurements (inset in Fig. 5).

It appears that the transition from high- to low-temperature phase is accompanied by the narrowing of energy gap in semiconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ specimens. This fact is quite surprising. Reduction of crystallographic symmetry in the sequence cubic–orthorhombic–body-centered monoclinic (at room temperature) can be induced by lower-

ing of potassium concentration. The two latter structures are related by a logical progression of first tilting and then breathing-mode distortions of the cubic lattice. The orthorhombic phase is highly conducting for $x=0.3$ but acquires semiconducting properties at smaller x . The energy gap develops further in substantially distorted body-centered monoclinic phase ($x < 0.1$). No deviation from the behavior was reported for compounds with $x \sim 0.1$ where the transformation from orthorhombic to body-centered monoclinic lattice takes place.¹ Although in this case the influence of the structural transition on properties of the compound may be smeared by the effect of doping. Lowering temperature down from 150 K seems to reduce crystallographic symmetry of $Ba_{1-x}K_xBiO_3$ in the same manner, i.e., from orthorhombic to body-centered monoclinic ($x \sim 0.1$) and from body-centered monoclinic to primitive monoclinic ($x < 0.1$).¹ However the band gap deduced from our spectroscopic measurements changes in opposite way, it unexpectedly decreases. As x is constant, the temperature-induced distortions of crystal lattice in the material should provoke a peculiar modification of its electronic structure. It is noteworthy also that the relative decrease of E_g in the critical temperature region becomes larger with increasing potassium concentration. Evidently doping promotes the band-structure alteration.

It was reported¹⁵ that important features of $BaBiO_3$ band structure cannot be reproduced by calculations involving lattice distortions alone and strong correlation effects of Bi $6s$ electrons have to be taken into account. In order to describe the phase diagram of undoped and doped $BaBiO_3$, a model with negative Hubbard energy U on the Bi sites was employed by several authors.²⁻⁵ According to it, intraatomic electronic correlations and the underlying negative- U term are responsible for the valence instability of Bi ions and charge disproportionation of Bi^{4+} to Bi^{3+} and Bi^{5+} . The model can produce both the CDW and the superconducting ground state as a function of doping and the coupling strength. One may suggest that fine-structural changes induced by the low-temperature phase transition modify on-site pairing of electrons in Bi $6s$ states. It can take place either directly, as a result of the interplay of on-site attraction and intersite repulsion,^{4,5} or via coupling with phonons and a soft mode.^{2,3} Small variation of the charge disproportionation or related disordering of the CDW state should alter the electronic structure of the material and may be attributed to the band-gap narrowing detected in our spectroscopic study. If so, the band-structure modification is controlled by the electronic instability in the compound and triggered by lattice distortions at the phase transition. Although differences between band-structures of the semiconducting phases are unknown and we can only speculate on their origin, it is obvious that the inner instability of electronic system should be

taken into account at the assessment of the low-temperature state in such strongly correlated material as $Ba_{1-x}K_xBiO_3$.

The substitution of K on the Ba site decreases charge disproportionation and reduces band gap. Beside the effect of lattice expansion, it introduces an additional disorder in the cation site energies, changes band filling, and effectively screens CDW charge fluctuations.¹³⁻¹⁵ The influence of doping goes in line with the band structure alteration at the low-temperature phase transition. It should significantly affect properties of the heavily doped substance as observed in $Ba_{0.83}K_{0.17}BiO_3$, the compound located on the phase diagram close to the boundary with the metallic phase. The trend seems to be consistent with models.²⁻⁵

The changes of optical properties in $Ba_{0.83}K_{0.17}BiO_3$ at the phase transition resemble a switching phenomenon. The material has two stable states—transparent in IR and opaque with the variation of transmittance exceeding one order of magnitude. Switching between the states is triggered by fine-structural distortions that modify crystallographic symmetry of the material. An instability of its electronic system is responsible for the occurrence of the phenomenon. To some extent it looks similar to optical switching in organic photonic crystals, see, for instance, Ref. 24. The ability of reversible switching in organic media is expected to find application in information technology.

In summary, we report measurements of IR spectra of semiconducting $x=0, 0.07, 0.17$ crystals of $Ba_{1-x}K_xBiO_3$ in the band-edge region at temperature ranging from 6 to 490 K. It was found that the band gap in investigated specimens anomalously narrows at $T_a=65-75$ K, inducing a step-like decrease of IR transmittance. The difference in transmittance above and below T_a depends on potassium concentration and exceeds one order of magnitude in $Ba_{0.83}K_{0.17}BiO_3$. Observed spectral changes are associated with the low-temperature structural phase transition in the material. Fine lattice distortions probably cause an instability of its electronic system and trigger the band-structure alteration. The influence of the transition on optical properties of the substance can be enhanced by K substitution and becomes significant in the heavily doped narrow-gap material. The temperature-induced spectral changes in investigated compounds resemble a switching phenomenon controlled by the transformation of crystallographic symmetry in the system with a substantial electronic instability. Advanced study of the phenomenon is now under way.

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