

DOI: 10.17516/1997-1397-2022-15-1-5-12

УДК 541.122: 538.214

NEXAFS and FTIR Spectroscopy of Co-doped $\text{SrBi}_2\text{Nb}_2\text{O}_9$

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Received 26.04.2021, received in revised form 20.08.2021, accepted 22.10.2021

Abstract. The solid-phase ceramic method was used to synthesize cobalt-containing solid solutions based on $\text{SrBi}_2\text{Nb}_2\text{O}_9$. NEXAFS (Near Edge X-ray Absorption Fine Structure) and IR spectroscopy were used to study the electronic state of cobalt atoms in solid cross-links with a layered perovskite-like structure. It was found that cobalt atoms are in high-spin states of Co(III) and, mainly, Co(II) in an octahedral oxygen environment.

Keywords: Aurivillius phases, IR spectroscopy, NEXAFS, cobalt.

Citation: N.A. Zhuk, E.U. Ipatova, B.A. Makeev, S.V. Nekipelov, D.S. Beznosikov, L.V. Rychkova, NEXAFS and FTIR Spectroscopy of Co-doped $\text{SrBi}_2\text{Nb}_2\text{O}_9$, J. Sib. Fed. Univ. Math. Phys., 2022, 15(1), 5–12. DOI: 10.17516/1997-1397-2022-15-1-5-12.

Strontium-bismuth niobate belongs to the well-known family of Aurivillius phases [1]. Aurivillius phases are characterized by high Curie temperatures, low degradation rates of residual polarization and piezoelectric properties when exposed to unipolar electric fields, high dielectric constant, which determines their use as components of composite film systems for processing and

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long-term storage of information (FRAM), as well as manufacturing for they are based on piezoelectric and pyroelectric transducers [2–5]. In the crystal structure of the Aurivillius phases, described by the general formula $A_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}$, fluorite-like $[\text{Bi}_2\text{O}_2]^{2+}$ and perovskite-like $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ layers alternate in which cationic sites A with large cubic octahedral surroundings are occupied by (Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Bi^{3+} , and octahedral positions of B contain highly charged cations with a small radius (Cr^{3+} , Ga^{3+} , Fe^{3+} , Co^{3+} , Ti^{4+} , Mn^{4+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+}) [6–9]. The parameter m corresponds to the number of layers $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ in the perovskite-like block. In the crystal structure of bismuth-strontium niobate $\text{Bi}_2\text{SrNb}_2\text{O}_9$ (gr. $A2_1am$, $a = 0.55189(3)$, $b = 0.55154(3)$ and $c = 2.51124(9)$ [10–12]), bismuth-oxygen layers alternate with perovskite-like blocks two niobium oxygen octahedrons thick. Bismuth-strontium niobate $\text{Bi}_2\text{SrNb}_2\text{O}_9$ belongs to relaxor ferroelectrics ($T_c = 420 - 440$ °C) [13]. Partial substitution of Bi(III) ions in fluorite-like layers by Sr(II) ions leads to smearing of the phase transition and the relaxation nature of the dielectric polarization. The dimensional mismatch of the cuboctahedral voids of perovskite-like blocks and strontium atoms causes geometric distortions of the structure, which are manifested in the asymmetry and angular inclination of niobium-oxygen octahedra [10–13]. The present work shows the results of a study of the electronic state of cobalt atoms in solid solutions of strontium bismuth niobate by vibrational (IR) and NEXAFS spectroscopy.

1. Materials and methods

The samples of the bismuth barium niobate solid solutions were synthesized by the standard ceramic method from the "special purity grade" bismuth (III), niobium (V) and cobalt (II) oxides by the staged calcination at 650, 850, 950 and 1050 °C. The phase composition of the studied samples was controlled by X-ray phase analysis (DRON-4-13, $\text{CuK}\alpha$ -radiation) and electron scanning microscopy (a scanning electron microscope Tescan MIRA 3LMN, an energy dispersive spectrometer Oxford Instruments X-Act), the unit cell parameters of the solid solutions were calculated using the CSD software package [14]. Fourier transform infrared (FTIR) spectra were recorded on an IRPrestige-21 Shimadzu (Japan) spectrophotometer equipped with DLATGS detector in the wavenumber range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . Before analysis, the samples were mixed and grinding with KBr (2 % of a sample by weight). The transmission spectra were obtained using the diffuse reflection mode. The data were processed using Shimadzu software. Samples of cobalt-doped bismuth niobate were studied by NEXAFS spectroscopy using synchrotron radiation from a BESSY II Storage Ring (Berlin, Germany). NEXAFS spectra were obtained by recording the total electron yield (Total electron yield, TEY) [15].

2. Results and discussion

Cobalt-containing solid solutions $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ were obtained in a limited concentration range at $x \leq 0.06$. The single-phase nature of the preparations obtained was established by the methods of electron scanning microscopy and X-ray phase analysis (Fig. 1). The unit cell parameters of dilute solid solutions are practically unchanged and are close to the parameters of the $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$: $a=0.55124$ nm, $b=0.55131$ nm, $c=2.50882$ nm ($x = 0.005$) and $a=0.55161$ nm, $b=0.55195$ nm, $c=2.51254$ nm ($x = 0.06$), which is associated with isomorphic substitution of niobium (V) close in size cobalt atoms in the charge state of Co(II) and Co(III)

($R(\text{Nb(V)})_{c.n=6}=0.064$ nm; $R(\text{Co(III)})_{c.n=6(h.s)}=0.0545$ nm; $R(\text{Co(III)})_{c.n=6(l.s)}=0.061$ nm; $R(\text{Co(II)})_{c.n=6(h.s)}=0.065$ nm; $R(\text{Co(II)})_{c.n=6(l.s)}=0.0745$ nm) [16].

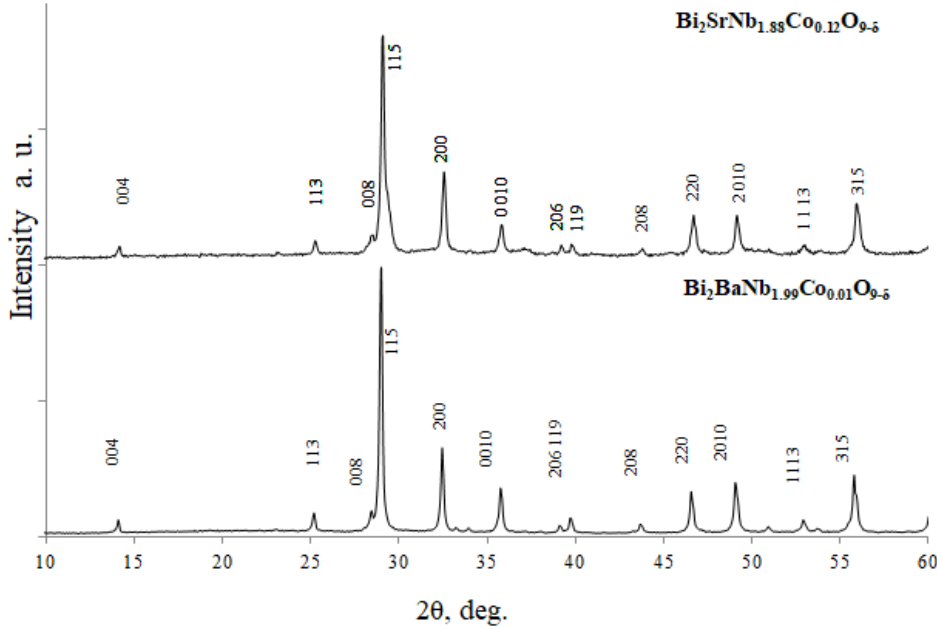


Fig. 1. X-ray diffraction patterns of the solid solutions $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$

Photographs of the crystalline powders of the synthesized preparations are presented in Fig. 2 [17]. The color of the samples varies from pink-orange to brown with a predominance of a pink tint, which may indicate the presence of cobalt (III) atoms in solid solutions.

The electronic state of cobalt atoms in samples of $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ solid solutions was studied using NEXAFS spectroscopy using a BESSY-II synchrotron source. All NEXAFS spectra were recorded in the total electron yield (TEY) mode [15].

Fig. 3 shows the absorption spectra of cobalt atoms in $\text{Bi}_2\text{MnNb}_2\text{O}_9$ (M-Sr,Ba) and in the oxides Co_3O_4 и CoO [18]. It can be seen from the spectra that the spectra of cobalt in these bismuth niobates are closest in intensity and energy position of the main peaks with the corresponding details of the $\text{Co}2p_{3/2}$ spectrum of CoO and are less similar to the spectra of Co_3O_4 . Considering this, we can conclude that in the compounds under consideration, the cobalt atoms are in the high-spin state of Co(II) like the cobalt atoms in CoO .

Meanwhile, the ratio of the band intensities at 781 eV and 779-780 eV in the cobalt spectrum does not exclude the possibility of the presence of Co(III) atoms. Due to the fact that the width of the $\text{Co}2p_{3/2}$ spectrum of $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ does not significantly differ from the CoO spectrum, then, according to the data of [19–21], we can speak of high-spin Co(III) . In view of the foregoing, the spectrum of cobalt atoms in bismuth niobate can be represented as a superposition of subspectra from high-spin cobalt atoms in oxidation states (II) and (III) with a lower content of the latter. CoO has a NaCl structure in which cobalt atoms have an octahedral environment of oxygen atoms. A similar polyhedral environment has niobium atoms in $\text{ABi}_2\text{Nb}_2\text{O}_9$ ($A = \text{Sr, Ba}$) [10], which suggests that cobalt atoms are introduced at the positions of niobium (V) cations.

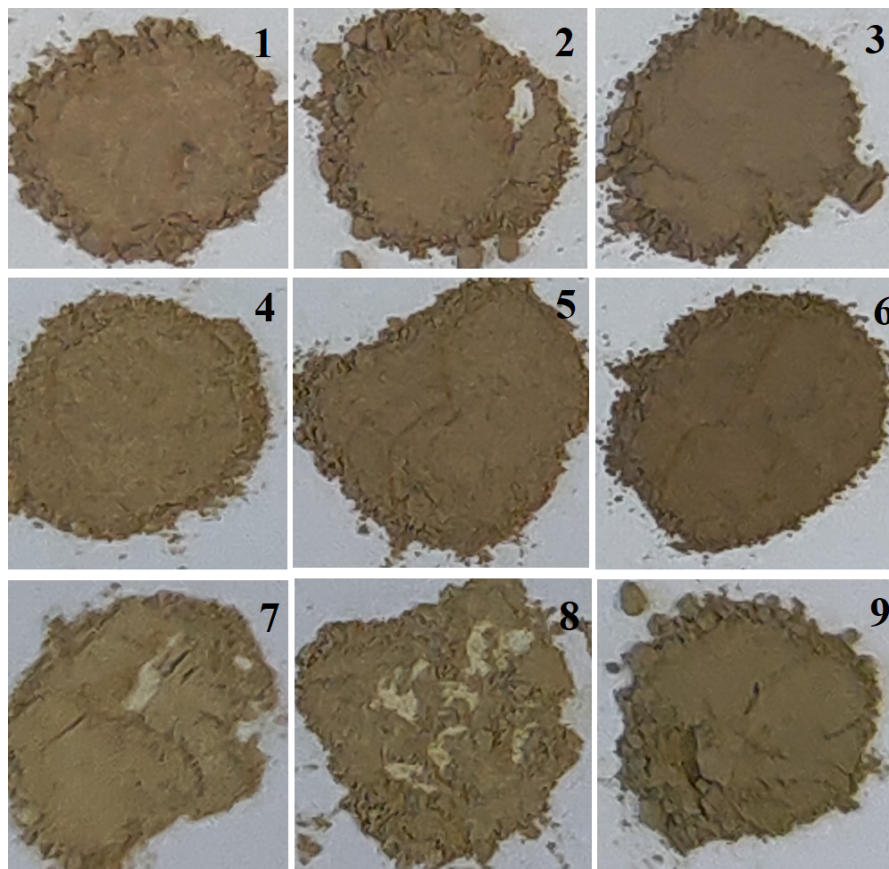


Fig. 2. Photographs of the series of the solid solutions $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ (1-3), $\text{Bi}_2\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ (4-6) and $\text{Bi}_2\text{BaNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ (7-9) at $x = 0.01(1,4,7)$, $0.02(2,5,8)$, $0.04(3,6,9)$

The Fig. 3 shows the 3d spectra of barium atoms in bismuth niobates, a comparison of which with the corresponding spectrum of barium oxide BaO indicates that the barium atom has a +2 charge state. The presence of Co(III) atoms in the $\text{Bi}_2\text{SrNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ ceramic is indirectly confirmed by the IR spectra of the samples. The samples were characterized using IR spectra with the Fourier transform, taken in the range of wave numbers $400\text{--}4000\text{ cm}^{-1}$. The figure shows fragments of the IR spectra of three samples of the composition $\text{Bi}_2\text{BaNb}_{1.92}\text{Co}_{0.08}\text{O}_{9-\delta}$, $\text{Bi}_2\text{SrNb}_{1.92}\text{Co}_{0.08}\text{O}_{9-\delta}$, $\text{Bi}_2\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Nb}_{1.92}\text{Co}_{0.08}\text{O}_{9-\delta}$. A characteristic feature of the spectra of the compounds is the presence of two diffuse absorption bands in the range of $650\text{--}1200\text{ cm}^{-1}$ и $400\text{--}600\text{ cm}^{-1}$, against the background of which the stretching vibration bands of the Nb-O, Bi-O, and Co-O in CoO_6 [22–26].

Co-O stretching vibrations are manifested in the spectral region of $400\text{--}600\text{ cm}^{-1}$. According to the literature, at $548\text{--}570\text{ cm}^{-1}$, the absorption band of the stretching vibrations of the Co(III)-O bond in the CoO_6 octahedron [22, 23] is fixed., and in the region of $653\text{--}663\text{ cm}^{-1}$, the band is responsible for vibrations of the Co(II)-O bond in tetrahedron CoO_4 [23]. In the spectra of the compounds, an absorption band at $\sim 575\text{ cm}^{-1}$ is observed, the presence of which indirectly indicates the presence of six-coordinated Co(III) atoms in the structure of solid solutions.

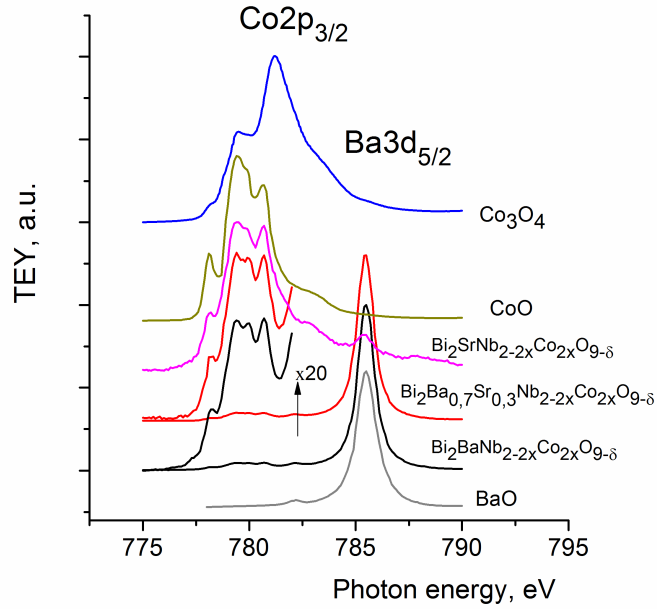


Fig. 3. NEXAFS Co₂p_{3/2} — spectra of the cobalt-doped bismuth niobates and spectra of CoO [18] and Co₃O₄

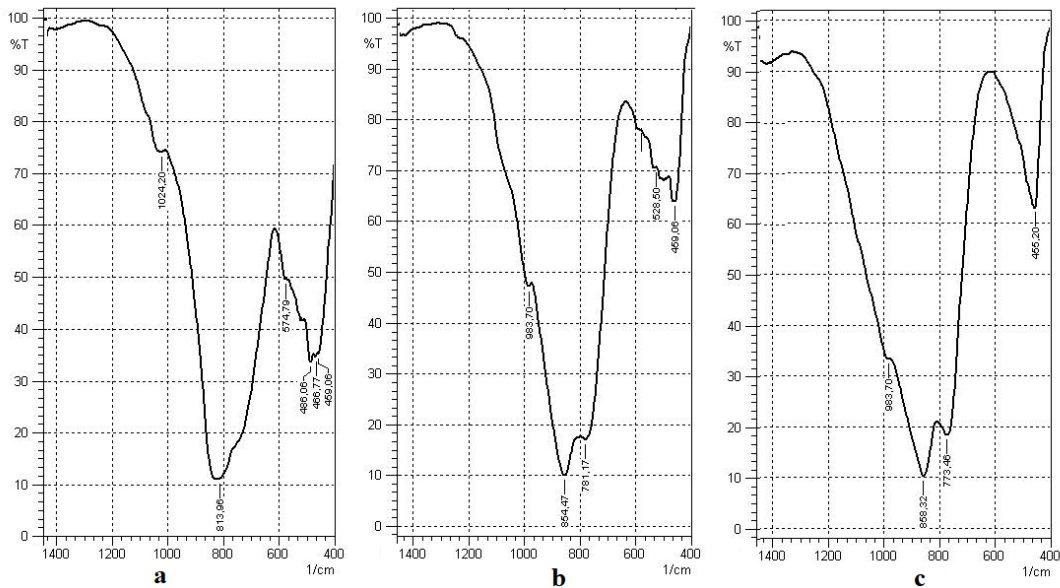


Fig. 4. Comparison of IR spectra of the Bi₂SrNb_{2-2x}Co_{2x}O_{9-δ} (a), Bi₂BaNb_{2-2x}Co_{2x}O_{9-δ} (b), Bi₂Sr_{0.3}Ba_{0.7}Nb_{2-2x}Co_{2x}O_{9-δ} (c) at $x = 0.04$

Conclusions

The solid-phase method was used to obtain cobalt-containing solid solutions of strontium-bismuth orthoniobate in a narrow concentration range ($x \leq 0.06$). According to NEXAFS

spectroscopy, cobalt atoms in solid solutions are in the high-spin state of Co(III) and, mainly, Co(II). Two broad absorption bands appear in the range of 650–1200 cm⁻¹ and 400–600 cm⁻¹, against the background of which stretching vibrations of the Nb-O, Bi-O, and Co-O in the IR spectra of solid solutions, in the area of fingerprints. The presence of an absorption band at ~575 cm⁻¹ in the spectra of compounds indirectly confirms the conclusion that six-coordinated Co(III) atoms are present in the structure of solid solutions.

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DOI: 10.5923/j.pc.20120206.01.

NEXAFS и ИК-спектроскопия Со-допированного SrBi₂Nb₂O₉

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Аннотация. Твердофазным керамическим методом синтезированы кобальтсодержащие твердые растворы на основе SrBi₂Nb₂O₉. Методами NEXAFS (Near Edge X-ray Absorption Fine Structure) и ИК-спектроскопии исследовано электронное состояние атомов кобальта в твердых растворах со слоистой перовскитоподобной структурой. Установлено, что атомы кобальта находятся в высокоспиновых состояниях Со(III) и преимущественно Со(II) в октаэдрическом кислородном окружении.

Ключевые слова: фазы Ауривилиллиуса, ИК-спектроскопия, NEXAFS, кобальт.