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Magnetic Behavior and NEXAFS-spectroscopy of $\text{Bi}_2\text{BaNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$

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The samples of solid solutions of $\text{Bi}_2\text{BaNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ composition at $x \leq 0.04$ were synthesized by the solid-phase method. The electron state and the nature of the exchange interactions of cobalt atoms in the samples were studied by the measurements of magnetic susceptibility and NEXAFS-spectroscopy. The NEXAFS spectra of the solid solutions and the cobalt oxides CoO , Co_3O_4 were recorded. According to the data of X-ray spectroscopy and magnetic susceptibility, the charge states of cobalt atoms in the solid solutions were identified as Co(II) and Co(III) in the forms of monomers and exchange-bound aggregates with the antiferromagnetic type of exchange.

Keywords: cobalt, clusters, exchange interactions, NEXAFS-spectroscopy.

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Introduction

The bismuth-containing layered perovskite-like oxides with structure of the Aurivillius phases draw the interest of researchers due to the discovery of their ferroelectric properties [1]. Particular attention was paid to a thorough analysis of structure and structural features, to technologies of synthesis of nanoscale materials and to the search for new compounds of this type. Studies related to the effect of dopants on the physicochemical properties of these compounds are also very relevant [2–4]. Crystal structure of complex oxides of this type is described by the general formula $A_{m-1}Bi_2B_mO_{3m+3}$, where the positions A are occupied by large cations (Bi(III), Ba(II), Pb(II), Na(I)), and the positions B inside the oxygen octahedra are occupied by cations with a smaller radius and a higher charge (Mo(VI), Nb(V), Ti(IV), Fe(III)). The parameter m determines the number of the perovskite-like layers of $[A_{m-1}B_mO_{3m+1}]^{2-}$ between the layers of $[Bi_2O_2]^{2+}$, and it has a half-integer or integer values in the range from 1 to 5 [1–4]. In the present paper, the electronic state and the character of interatomic interactions of cobalt atoms in the solid solutions of bismuth barium niobate $Bi_2BaNb_{2-2x}Co_{2x}O_{9-\delta}$ were studied using the methods of NEXAFS and magnetic susceptibility. The crystal structure of the bismuth barium niobate was described by the space group A21am ($a = b = 0.5567$ nm and $c = 2.5634$ nm) and was characterized by the alternation of bismuth-oxygen layers with perovskite-like blocks with a thickness of two layers of niobium-oxygen octahedra [5].

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, $CuK\alpha$ -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 [6].

The magnetic susceptibility of the solid solutions was measured by the Faraday method in the temperature interval of 77÷400 K at 16 points of temperatures and magnetic field strengths of 7240, 6330, 5230 and 3640 Oe. The accuracy of the measurements was 2 %. The samples of cobalt-doped solid solutions were studied by X-ray absorption spectroscopy (NEXAFS – Near Edge X-ray Absorption Fine Structure) using synchrotron radiation at BESSY II (Berlin, Germany). The NEXAFS spectra were obtained by the total electron yield method (TEY).

2. Results and discussion

The cobalt containing solid solutions $Bi_2BaNb_{2-2x}Co_{2x}O_{9-\delta}$ were synthesized in the concentration range $x \leq 0.04$. Electron scanning microscopy and X-ray phase analysis confirmed the single-phase nature of the samples (Fig.1).

The lattice parameters of the dilute solid solutions were almost unchanged and close to the parameters of bismuth barium niobate: $a = 0.5540$ nm, $b = 2.5621$ nm, $c = 0.5535$ nm ($Bi_2BaNb_{1.92}Co_{0.08}O_{9-\delta}$), which was associated with the isomorphic replacement of niobium (V) with close in size atoms of cobalt with the charge states of Co(II) and Co(III) [7]. The micrographs of the samples with higher content of the dopant ($x = 0.06$) showed inclusions of cobalt (II) that

were unevenly distributed in the material. It should be noted that the concentration range of the cobalt-doped solid solutions is more narrow than that of iron-doped solid solutions [8,9], which may be due to the lower degree of covalence of the cobalt-oxygen bond compared to the iron-oxygen bond.

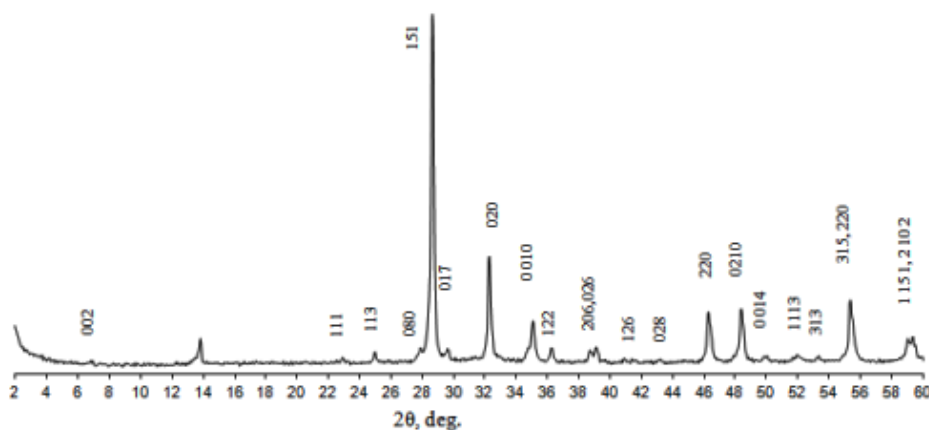


Fig. 1. X-Ray pattern for $\text{Bi}_2\text{BaNb}_{1.92}\text{Co}_{0.08}\text{O}_{4-\delta}$

The nature of exchange interactions and the electronic state of cobalt atoms in solid solutions of bismuth barium niobate were studied via magnetic susceptibility measurements in the samples of triclinic and orthorhombic modifications. The results of the measurements allowed us to calculate the paramagnetic components of the magnetic susceptibility [$\chi^{\text{para}}(\text{Co})$](Fig. 2) and the values of effective magnetic moments [$\mu_{\text{eff}}(\text{Co})$](Fig. 3) of cobalt atoms at various temperatures and concentrations of the solid solutions. The diamagnetic corrections for the calculation of the paramagnetic component of the magnetic susceptibility were introduced taking into account the susceptibility of bismuth barium niobate measured in the same temperature range.

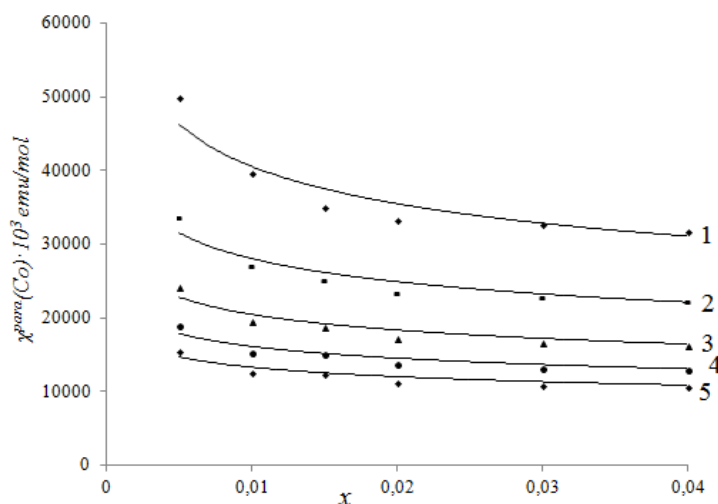


Fig. 2. Paramagnetic component isotherms of the magnetic susceptibility of cobalt in the solid solutions of $\text{Bi}_2\text{BaNb}_{1.92}\text{Co}_{0.08}\text{O}_{4-\delta}$ at 90 (1), 140 (2), 200 (3) and 320 K (4)

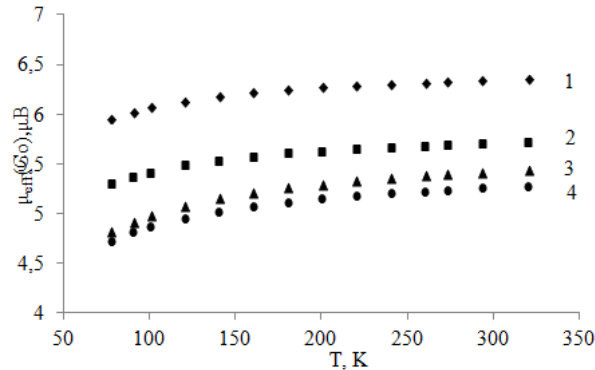


Fig. 3. Temperature dependencies of the effective magnetic moment of cobalt in the solid solutions of $\text{Bi}_2\text{BaNb}_{1.92}\text{Co}_{0.08}\text{O}_{4-\delta}$ at x 0.005 (1), 0.010 (2), 0.02 (3), 0.04 (4)

It was established that the dependence of the reciprocal paramagnetic component of the magnetic susceptibility per one mole of cobalt atoms on temperature obeys the Curie-Weiss law in all of the solid solutions in the studied temperature range. The negative values of the Weiss constant revealed the antiferromagnetic exchange interactions. The isotherms of the paramagnetic component of the magnetic susceptibility of cobalt atoms [$\chi^{para}(\text{Co})$] in the solid solutions were a characteristic of dilute antiferromagnets. The magnitude of the effective magnetic moment of cobalt atoms calculated by the extrapolation of the concentration dependences of [$\chi^{para}(\text{Co})$] to infinite dilution of solid solutions increased with increasing temperature from $\mu_{eff}(\text{Co})=6.29 \mu_B$ (90 K) to $6.79 \mu_B$ (260 K) and exceeded the pure spin values of the magnetic moments of high-spin cobalt atoms Co(II) ($\mu_{eff}=3.89 \mu_B$) and Co(III) ($\mu_{eff}=4.92 \mu_B$) [10]. The observed fact indicated the aggregation of paramagnetic cobalt atoms in the infinitely dilute solid solutions with the formation of clusters mainly with the antiferromagnetic type of exchange. The decrease in the paramagnetic component of the magnetic susceptibility of cobalt atoms with an increase in the concentration of solid solutions was associated with the predominance of antiferromagnetic interactions between cobalt atoms or their clusters. This assumption was also supported by the temperature dependences of the effective magnetic moment of cobalt atoms on the concentration of the solid solutions (Fig. 3).

The antiferromagnetic exchange usually occurs between isovalent atoms of cobalt (II) and (III) in the same spin state, e.g. $\text{Co(III)}_{s=2} - \text{Co(III)}_{s=2}$ or $\text{Co(II)}_{s=3/2} - \text{Co(II)}_{s=3/2}$ through the exchange channels $d_{x^2-y^2} \parallel p_x \parallel d_{x^2-y^2}$, $d_{x^2-y^2} \parallel p_y \parallel d_{x^2-y^2}$, $d_{xy} \mid p_y \mid d_{xy}$ and $d_{xz} \mid p_z \mid d_{xz}$. On the contrary, the ferromagnetic exchange is realized between cobalt atoms in equal oxidation states with different valences or different spines. No evidences of this type of exchange was observed in the solid solutions of bismuth barium niobate.

The charge state of cobalt atoms in the samples of $\text{Bi}_2\text{BaNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$ solid solutions was studied using NEXAFS spectroscopy at the synchrotron radiation source BESSY-II. The NEXAFS spectra were recorded in the total electron yield (TEY) mode [11]. Fig. 4 shows the absorption spectra of cobalt atoms in $\text{Bi}_2\text{BaNb}_2\text{O}_9$ and in oxides Co_3O_4 and CoO [12]. As can be seen, the spectra of cobalt in bismuth barium niobate are most similar in intensity and energy position of the major peaks to the Co $2p_{3/2}$ -spectrum of CoO and to a lesser extent to the spectra of Co_3O_4 . The cobalt atoms in CoO are divalent, i.e. they have a charge state of Co^{2+} , while in the mixed oxide, Co_3O_4 , cobalt atoms are present in the oxidation states (II) and (III). Meanwhile, the ratio of intensities of the bands at 781 eV and $779 \div 780$ eV in the broadband spectrum of cobalt in bismuth niobate allowed us to process this spectrum as a superposition

of subspectra of cobalt in oxidation states (II) and (III) with a lower content last one. The oxidation states (III) of cobalt atoms is not unexpected, as shown earlier for the solid solutions of heterovalent substitution of bismuth niobate [13, 14]. This was associated with the stabilizing effect of the structure of solid solutions.

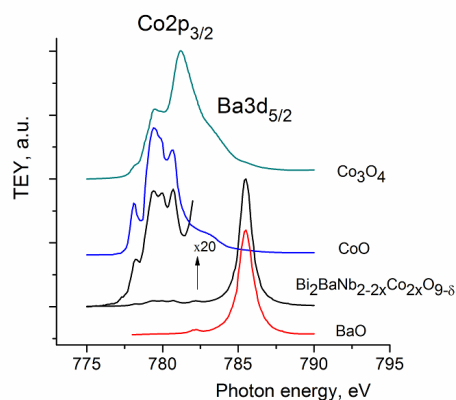


Fig. 4. NEXAFS Co $2p_{3/2}$ - spectra of the cobalt-doped $\text{Bi}_2\text{BaNb}_{1.92}\text{Co}_{0.08}\text{O}_{4-\delta}$

Conclusion

The cobalt-doped solid solutions of bismuth barium orthoniobate were synthesized by the solid phase method in a narrow concentration range ($x \leq 0.04$). The higher content of cobalt led to appearance of cobalt (II) oxide. According to the study of magnetic susceptibility, it was found that the infinitely dilute solid solutions contained Co(II) and Co(III) high-spin atoms and their aggregates with the antiferromagnetic type of exchange. The proportion of the aggregates increased with increasing cobalt concentration. According to NEXAFS spectroscopy, cobalt atoms in the solid solutions exhibited the charge states Co(III) and, mainly, Co(II).

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Магнитное поведение и NEXAFS-спектроскопия $\text{Bi}_2\text{BaNb}_{2-2x}\text{Co}_{2x}\text{O}_{9-\delta}$

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Твердофазным методом синтеза получены образцы твердых растворов состава $Bi_2BaNb_{2-2x}Co_{2x}O_{9-\delta}$ в ограниченном концентрационном интервале ($x \leq 0.04$). Методами магнитной восприимчивости и NEXAFS-спектроскопии исследовано электронное состояние и характер обменных взаимодействий атомов кобальта в образцах. Получены NEXAFS-спектры твердых растворов и оксидов кобальта CoO , Co_3O_4 . По данным рентгеновской спектроскопии и магнитной восприимчивости, атомы кобальта в твердых растворах находятся в зарядовом состоянии $Co(II)$ и $Co(III)$ в форме мономеров и обменносвязанных агрегатов с антиферромагнитным типом обмена.

Ключевые слова: кобальт, кластеры, обменные взаимодействия, NEXAFS-спектроскопия.