Journal of Siberian Federal University. Mathematics & Physics 2024, 17(5), 559–569

EDN: COUDXV
УДК 541.122: 538.214

Conversion of Cr(III) and Co(III) During the Synthesis of Co/Cr Codoped Bismuth Niobate Pyrochlore According to NEXAFS Data

Ksenia A. Badanina[*]
Pitirim Sorokin Syktyvkar State University
Syktyvkar, Russian Federation
Sergey V. Nekipelov[†]
Institute of Physics and Mathematics of the Komi Science Center UB RAS
Syktyvkar, Russian Federation
Alexey M. Lebedev[‡]
National Research Center – Kurchatov Institute
Moscow, Russian Federation
Nadezhda A. Zhuk[§]
Pitirim Sorokin Syktyvkar State University
Syktyvkar, Russian Federation
Dmitriy S. Beznosikov[¶]
Federal State Unitary Enterprise «General Radio Frequency Centre»
Syktyvkar, Russian Federation

Received 10.04.2024, received in revised form 29.05.2024, accepted 04.07.2024

Abstract. Cubic pyrochlore of the composition $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ (sp. gr. Fd-3m, a = 10.4838(8) Å) was synthesized in several stages using a solid-phase reaction from oxide precursors at a final temperature of 1050 °C. Using NEXAFS spectroscopy data, the electronic state of cobalt and chromium ions during the synthesis process was studied. It has been established that before the formation of phase-pure pyrochlore, Cr(III) ions are converted to Cr(VI), and then again to Cr(III); Cobalt ions Co(III) are reduced to Co(II). NEXAFS Cr2p spectra of ceramics synthesized at 650 °C, according to the main characteristics of the spectrum, coincide with the spectrum of $K_2Cr_2O_7$ and indicate the chromium content in the oxide ceramics in the form of tetrahedral CrO_4^{2-} ions, and according to the nature of the Co2p spectrum, cobalt ions are in the Co(II) state and Co(III). In the composition of pyrochlore $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$, synthesized at 1050 °C, cobalt and chromium appear predominantly in the form of Co(II) and Cr(III) ions. Analysis of phase transformations showed that changes in the oxidation state of transition element ions and the color of ceramics are associated with the formation of intermediate synthesis products.

Keywords: pyrochlore, bismuth niobate, NEXAFS, cobalt.

Citation: K.A. Badanina, S.V. Nekipelov, A.M. Lebedev, N.A. Zhuk, D.S. Beznosikov, Conversion of Cr(III) and Co(III) During the Synthesis of Co/Cr Codoped Bismuth Niobate Pyrochlore According to NEXAFS Data, J. Sib. Fed. Univ. Math. Phys., 2024, 17(5), 559–569. EDN: COUDXV.

---

[*] badanina-ksenia@mail.ru
[†] nekipelovsv@mail.ru
[‡] lebedev.alex.m@gmail.com
[§] nzhuck@mail.ru
[¶] uvn71p3@gmail.com

Introduction

Currently, pyrochlores based on bismuth niobate are being actively studied due to their promising dielectric properties [1,2]. Exhibiting low values of dielectric losses and high dielectric constant, tunable temperature coefficient of capacitance, chemical inertness with respect to low-melting conductors, materials based on oxide pyrochlores are promising as multilayer ceramic capacitors and tunable microwave dielectric components [3]. The crystal structure of pyrochlores $A_2B_2O_6O'$ is formed by two interpenetrating cationic sublattices A_2O' and B_2O_6 [4]. Octahedral positions B are occupied by relatively small cations (Nb^{+5}), larger ions (Bi^{+3}) are distributed in eight-coordinated positions A. A feature of bismuth-containing pyrochlores is the partial vacancy of the bismuth sublattice and the distribution of dopants - ions of transition 3d elements (Co, Cu, Zn , Mn) in both cation sublattices of bismuth and niobium, causing relaxation processes in ceramics [5,6]. New studies of pyrochlores based on bismuth niobate doped with transition 3d ions (Cr, Mn, Fe, Co, Ni, Cu, Zn) [5–11] have shown that low-porosity ceramics with low dielectric losses and high values of dielectric constant are formed. The possibility of solid-phase synthesis of multielement pyrochlores containing various combinations of atoms of 3d elements was shown in [12]. A study of the phase formation of a representative of mixed pyrochlores $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ showed [13] that during the synthesis (at 650 °C) the color of the ceramics strikingly and reversibly changes from green to brown, and the synthesis of phase-pure pyrochlore occurs at a temperature not lower than 1050 °C. It has been established that the formation of the pyrochlore phase occurs through the reaction of solid-phase interaction of orthorhombic bismuth niobate (α-$BiNbO_4$) with oxides of transition elements. In the presented work, based on X-ray spectroscopy data, the oxidation states of cobalt and chromium ions in ceramics are analyzed and the reason for the change in the color of ceramics is established. The phase composition of $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ ceramics at intermediate stages of solid-phase synthesis was studied in detail. The data obtained contribute to a deep understanding of the processes occurring during high-temperature processing of materials.

1. Materials and methods

For the solid-phase synthesis of the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ sample, oxides of bismuth (III), niobium (V), chromium (III) and cobalt (II,III) of analytical grade taken in stoichiometric quantities were used. The stoichiometric mixture of oxides was thoroughly homogenized in an agate mortar for one hour, then pressed into disk shapes. The main stages of pyrochlore phase formation were studied using X-ray phase analysis of samples sequentially calcined at temperatures of 650, 850, 950, 1000 and 1050 °C for 15 hours at each stage of heat treatment. After each calcination step, the sample was carefully homogenized and pressed back into disk shape to ensure tight contact of the ceramic grains. X-ray data were obtained using a Shimadzu 6000 X-ray diffractometer (CuKα radiation; $2\theta = 10 - 80°$; scanning speed 2.0 °/min). The study of the microstructure and elemental mapping of the surface of the samples was carried out using scanning electron microscopy and energy-dispersive X-ray spectroscopy (Tescan VEGA 3LMN scanning electron microscope, INCA Energy 450 energy-dispersive spectrometer). The unit cell parameters of pyrochlores were calculated using the CSD software package [14]. Research using NEXAFS spectroscopy was carried out at the NanoFES station of the KISI synchrotron source at the Kurchatov Institute (Moscow). NEXAFS spectra were obtained by recording the total electron yield (TEY) with an energy resolution of 0.5 eV and 0.7 eV in the region of the Cr2p and Co2p absorption edges, respectively.

2. Results and discussion

As a review of the literature shows [12,13,15], the solid-phase synthesis of mixed pyrochlores based on bismuth niobate is a multi-step process, which is associated with the low reactivity of niobium (V) oxides and some transition elements, which include CoO, NiO [12,16]. In addition, the features of the solid-phase synthesis method are the duration of calcination and the multi-stage heat treatment process with intermediate remixing of the reaction mixture, which are necessary to accelerate the reaction and obtain a homogeneous synthesis product [17]. It was previously established that a sample of the composition $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ during ceramic synthesis reversibly changes its color in the temperature range of 500–650 °C from green to brown. In order to investigate the unusual thermal behavior of the complex oxide, the charge state of transition element ions in ceramics was studied using NEXAFS spectroscopy and the phase composition of samples calcined at 650, 850, 950, 1000 and 1050 °C. According to X-ray phase analysis of a sample calcined at 650 °C, the X-ray diffraction pattern shows reflections of intermediate products of the interaction of bismuth (III) oxide with chromium (III) and niobium (V) oxides - bismuth chromate $Bi_6Cr_2O_{15}$ (sp.gr. *Ccc2*), bismuth niobates $Bi_5Nb_3O_{15}$ (sp.gr. *P4/mmm*) and $BiNbO_4$ (sp.gr. *Pnna*), monoclinic β-Nb_2O_5 (sp.gr. *P2/m*) and pyrochlore (sp.gr. *Fd-3m*) [5,18–23]. Noteworthy is the formation of bismuth chromate, which has its own intense red-orange color due to electronic transitions with charge transfer [20,21]. The fact is that chromium (III) oxide does not oxidize under these synthesis conditions; this requires an oxygen atmosphere, a long duration and temperature of calcination. Meanwhile, the formation of chromium (VI) compounds can be indirectly indicated by the orange-brown color of the ceramics (Fig. 2) synthesized at 650 °C.

In order to establish or refute the presence of chromium (VI) ions in the sample, NEXAFS studies of the charge state of the ions were carried out. NEXAFS spectra of chromium ions in the composition of $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ ceramics synthesized at 650 °C are presented in Fig. 1. As the figure shows, the spectra have a rich structure; in particular, absorption bands at 578, 580.5 and 589 eV can be clearly distinguished in the $Cr2p_{3/2}$ and $Cr2p_{1/2}$ spectra of the sample. Comparison of the spectra of the samples with the spectra of the oxides CrO_3, CrO_2, Cr_2O_3 and potassium dichromate $K_2Cr_2O_7$ [24–27] shows that the low-energy bands in the spectrum coincide in the energy position of the peaks with the spectra of CrO_3 and $K_2Cr_2O_7$, which indicates that chromium ions in the composition of the samples have charge state of Cr(VI) and are in a tetrahedral environment in the form of CrO_4^{2-} ions, similar to $K_2Cr_2O_7$, which is consistent with the results of X-ray phase analysis. It is interesting to note that the spectra of chromium change significantly with increasing temperature: in the low-temperature sample (650 °C) they practically coincide with the NEXAFS Cr2p spectrum of $K_2Cr_2O_7$, and those calcined at high temperature (1050 °C) — with the spectra of Cr_2O_3.

Indeed, signals appear at 577 eV and 578 eV, and in the region of 586-588 eV, characteristic of Cr(III) ions in an octahedral environment [27]. This allows us to assert that the charge state of chromium ions changes with increasing temperature of heat treatment of the sample from Cr(VI) to Cr(III). As X-ray phase analysis shows, the reason for the change in the charge state of chromium ions is the formation of an intermediate synthesis product — bismuth (VI) chromate, which is stable in a given temperature range and gives the ceramic a brown color. Apparently, with an increase in the synthesis temperature, bismuth chromate thermally dissociates with the formation of oxygen and oxide compounds of chromium (III), as evidenced by the disappearance of its reflections in the X-ray diffraction pattern of the sample synthesized at a temperature

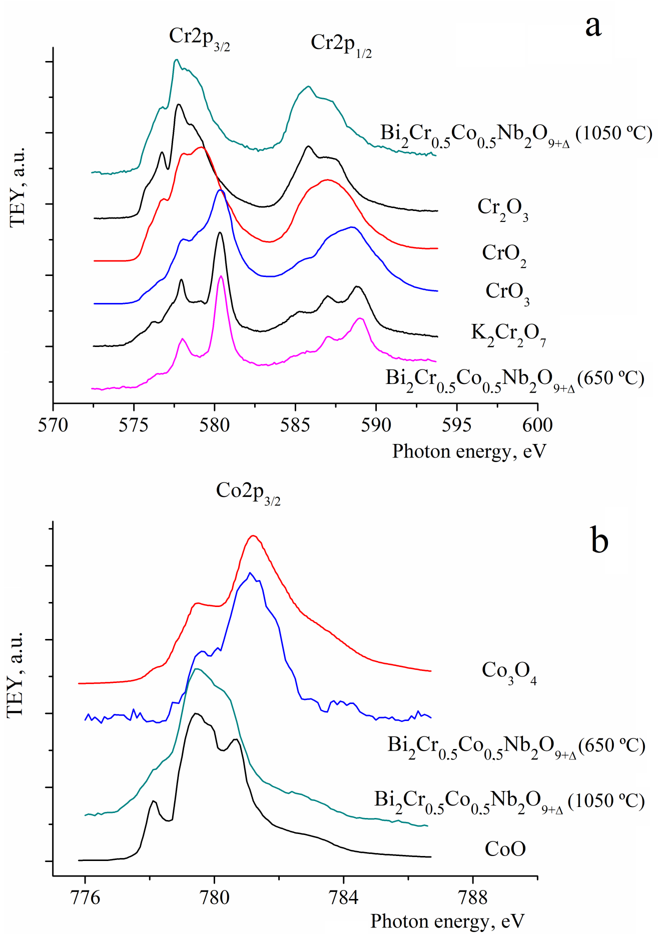

Fig. 1. NEXAFS Cr2p-spectra (a) and Co2p-spectra (b) of the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$, synthesized at 650 and 1050 °C, oxides Cr_2O_3, CrO_2, CrO_3, CoO, Co_3O_4 and potassium dichromate $K_2Cr_2O_7$

of 850 °C. The dissociation products interact with precursors to form a pyrochlore phase at 1050 °C, in which chromium ions are predominantly in the form of Cr(III) ions, as evidenced by NEXAFS data. According to X-ray diffraction data, active interaction of precursors is detected at temperatures above 650 °C. Reflections of niobium (V) oxide are not detected in the X-ray diffraction patterns of samples synthesized at 850 °C and above; bismuth chromate $Bi_6Cr_2O_{15}$ is practically not detected at 750 °C, and $Bi_5Nb_3O_{15}$ — at 900 °C. The pyrochlore phase appears in noticeable quantities in samples obtained at a temperature of 750 °C. At this temperature, the concentrations of Nb_2O_5 and $Bi_6Cr_2O_{15}$ decrease significantly. Apparently, low-temperature synthesis of pyrochlore is difficult due to the chemical inertness of Nb_2O_5. It is interesting to note that the intermediate phase in the synthesis of pyrochlore is $Bi_5Nb_3O_{15}$, while the analogue in the synthesis of pyrochlores based on bismuth tantalate is Bi_3TaO_7 (sp.gr. *Fm-3m*) [28]. This is partly due to the fact that the compound $Bi_5Ta_3O_{15}$ is unknown.

For other reasons, it can be assumed that the reactivity of chromium (III) oxide is higher than that of niobium (V), so bismuth oxide reacts with Cr_2O_3 first and in significant quantities. Its maximum relative content is recorded at 750 °C, then its share in the sample rapidly decreases.

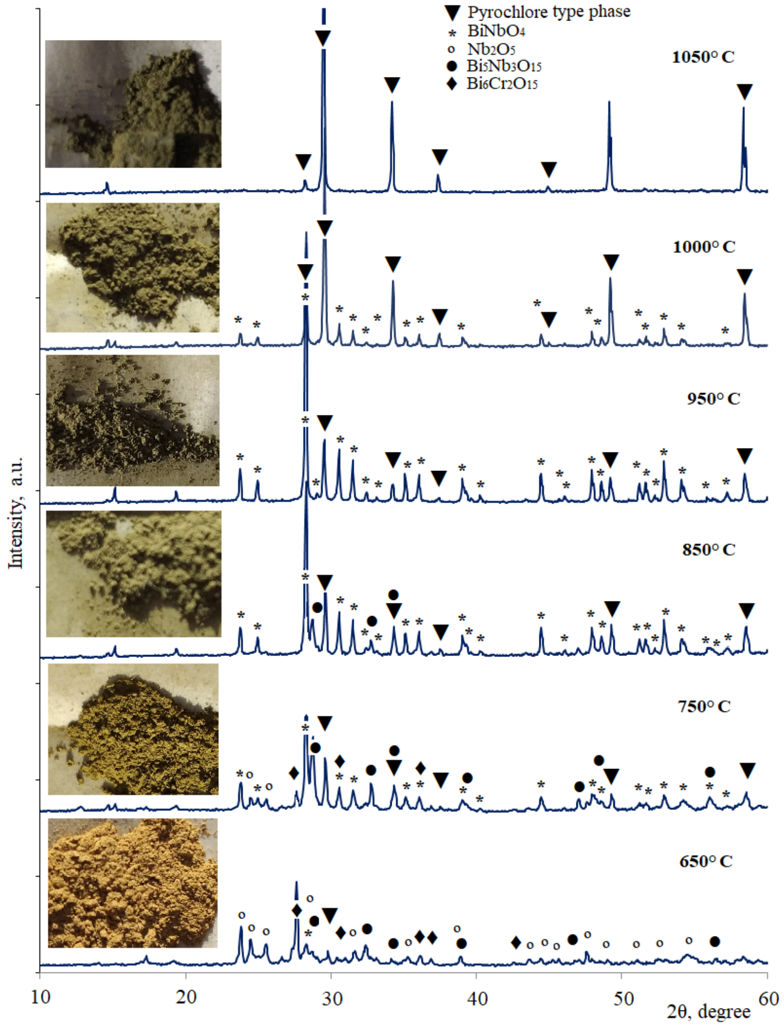

Fig. 2. X-ray diffraction patterns and photographs of $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ samples sequentially calcined at temperatures of 650, 850, 950, 1000 and 1050 °C

$Bi_5Nb_3O_{15}$ is replaced by α-$BiNbO_4$, which, interacting with oxides of transition elements, forms a pyrochlore phase of a given composition. In the temperature range of 900–1000 °C, reflections of the pyrochlore and α-$BiNbO_4$ phases are clearly observed.

The precursors oxides Cr_2O_3 and Co_3O_4 do not appear on the X-ray diffraction patterns of the samples due to their low content in the initial charge and the high reactivity of chromium (III) oxide. It is interesting to note that, according to NEXAFS spectroscopy, cobalt (II,III) oxide in ceramics synthesized at 650 °C is present as an independent impurity phase. Indeed, as the NEXAFS Co2p spectra of the sample show, the spectrum of the composite in terms of the shape of the spectrum and the energy position of the spectral details is similar to the spectrum of Co_3O_4 oxide, in which cobalt ions are found in the form of octahedrally coordinated Co(II) and Co(III) ions [29]. Meanwhile, as the heat treatment temperature of the sample increases, the charge state of cobalt changes and cobalt ions are detected in ceramics synthesized at 1050 °C, mainly in the form of Co(II) ions. Taking into account that a temperature of 1050 °C corresponds

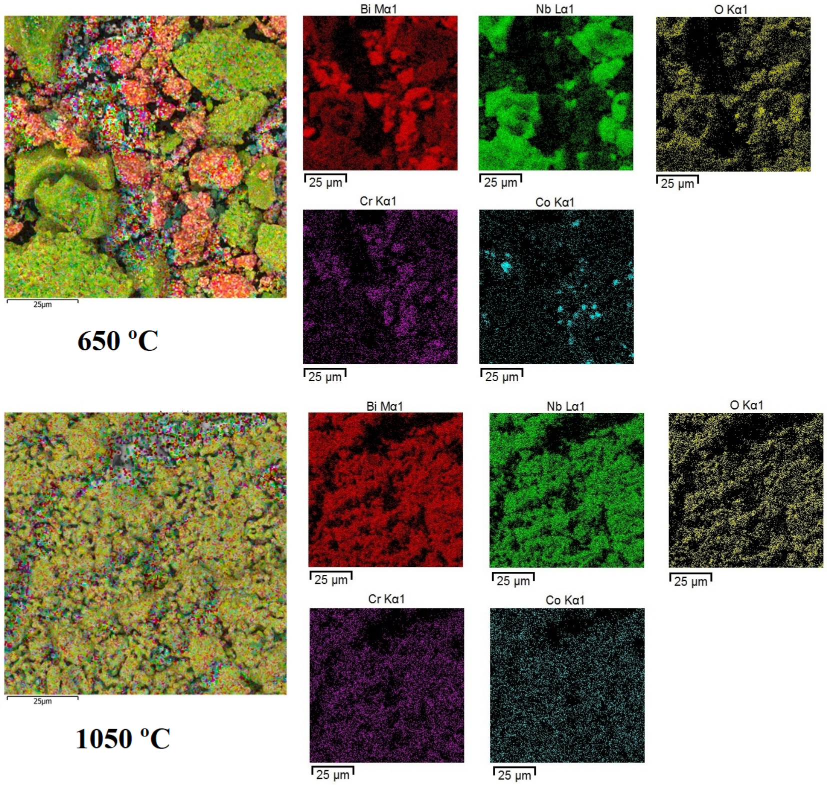

Fig. 3. Element maps of $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ samples synthesized at 650 °C and 1050 °C

to the production of phase-pure pyrochlore, it can be stated that cobalt ions in the composition of pyrochlore are mainly in the Co(II) state, which is confirmed in the work devoted to the study of cobalt-containing pyrochlores in the ternary system Bi_2O_3-Nb_2O_5-CoO [30]. The change in the oxidation state of cobalt during high-temperature treatment of the sample may be associated with the process of thermal dissociation of Co_3O_4 at a temperature of 920 °C into CoO and oxygen [31].

As shown by elemental mapping of a sample (Fig. 4) synthesized at temperatures below 1050 °C, cobalt atoms are unevenly distributed on the surface of the sample, which indicates that cobalt atoms are not part of the pyrochlore, but represent an impurity phase, which may be Co_3O_4 oxide, which was subsequently subjected to thermal decomposition. Thus, cobalt enters into a high-temperature reaction with bismuth orthoniobate in the form of CoO oxide. This may be the reason that cobalt ions in pyrochlore are predominantly in the Co(II) state.

Microphotographs of the surface of the synthesized samples at temperatures of 650, 850, 950, 1000 and 1050 °C are shown in Fig. 4. A heterogeneous microstructure with heterogeneous grains and inclusions of impurity phases is characteristic of samples calcined at a temperature of 650-1000 °C. A low-porosity, dense microstructure was formed in the sample synthesized at a temperature of 1050 °C. On the surface of the ceramic, both individual small grains and partially fused grains with the formation of large agglomerates are observed, which contributes to the formation of a monolithic microstructure. The average crystallite size determined by X-ray diffraction using the Scherrer formula is ∼58 nm (1050 °C), while larger crystallites in the range of 2-10 μm (1050 °C) were determined using a scanning electron microscope (SEM). Apparently, the

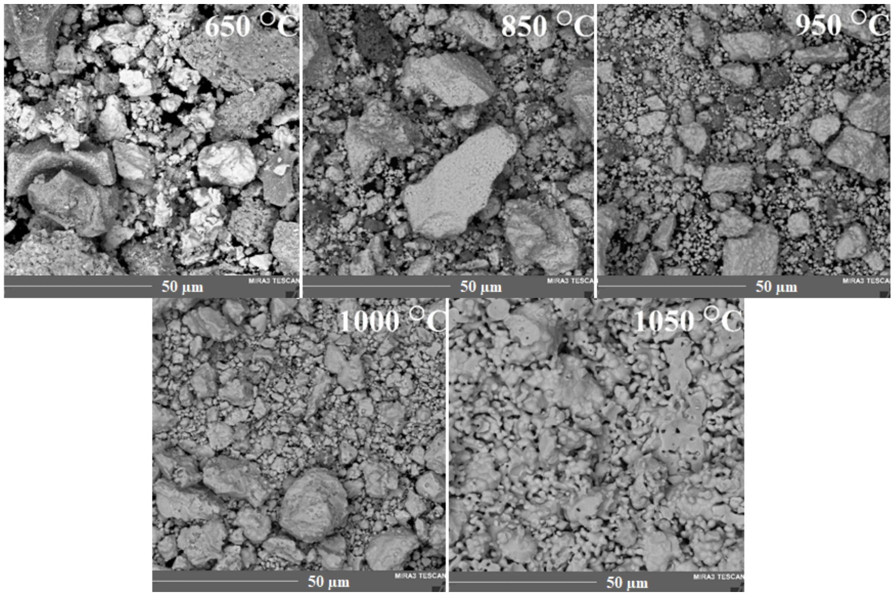

Fig. 4. Microphotographs of the surface of $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ samples synthesized at temperatures of 650, 850, 950, 1000 and 1050 °C

crystallites in the micrographs are aggregated ceramic grains of much smaller sizes. Full-profile analysis by the Rietveld method showed that the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ sample synthesized at 1050 °C is single-phase [13].

The unit cell parameter of the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ sample is 10.4838(8) Å and exceeds the cell constant of chromium-containing pyrochlore $Bi_2CrNb_2O_{9+y}$ (a = 10.459(2)) [32], which is explained by the large radius of Co(II) ions compared to Cr(III) ions (R(Cr(III)) = 0.615 Å, R(Co(II))c.n.-6 = 0.745 Å) [33]. Since the radii of Ta(V) and Nb(V) ions (R(Nb(V)/Ta(V))c.n.-6 = 0.064 nm) are equal, the lattice constants for pyrochlores based on bismuth niobate and bismuth tantalate can be comparable. Indeed, the unit cell parameter $Bi_2CrTa_2O_{9+\Delta}$ (a = 10.45523(3) Å) [34] which is due to the closeness of the ionic radii (R(Mg(II)) = 0.72 Å, R(Co(II))c.n.-6 = 0.745 Å). Unit cell parameter for cobalt-containing pyrochlores based on bismuth tantalate $Bi_{1.49}Co_{0.8}Ta_{1.6}O_{7.0}$ a = 10.54051(3) Å and for $Bi_{1.6}Co_{0.8}Ta_{1.6}O_{7\pm\Delta}$ a = 10.5526 (2) Å significantly exceeds the parameter of chromium-cobalt-containing pyrochlore, which is associated with a significant difference in the radii of chromium (III) and cobalt (II) ions (R(Cr(III)) = 0.615 Å, R(Co(II))c.n. 6 = 0.745 Å) [36, 37]. Local chemical analysis using energy-dispersive spectroscopy showed that the chemical composition of the synthesized $Bi_2Co_{0.51}Cr_{0.52}Nb_{2.05}O_{9+\Delta}$ sample is close to the nominal composition. Thus, the atypical thermal behavior of the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ sample is associated with the formation of an impurity phase of bismuth chromate, as shown by X-ray phase analysis and NEXAFS spectroscopy.

Conclusions

Using NEXAFS spectroscopy and X-ray phase analysis, it was determined that the change in the oxidation state of cobalt and chromium ions during the synthesis of the $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ sample is associated with the peculiarities of obtaining pyrochlore by the solid-phase method. It has been established that before the formation of phase-pure pyrochlore, Cr(III) ions are converted to Cr(VI) in the composition of bismuth chromate as an intermediate product of the synthesis, and then again to Cr(III) during the decomposition of bismuth chromate and the formation of pyrochlore; Cobalt ions Co(III) are reduced to Co(II) as a result of thermal dissociation of Co_3O_4. In the composition of pyrochlore $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$, synthesized at 1050 °C, cobalt and chromium appear predominantly in the form of Co(II) and Cr(III) ions. The process of phase formation of pyrochlore is a series of sequential solid-phase reactions involving precursors. A strategically important intermediate product of the synthesis is bismuth orthoniobate α-$BiNbO_4$ due to the fact that doping bismuth orthoniobate with atoms of transition elements leads to the formation of the pyrochlore phase.

The NEXAFS study was carried out within the framework of the topic 122040400069-8, as well as with the financial support of the Ministry of Science and Higher Education of Russia under agreement No. 075-15-2021-1351.

References

[1] C.C.Khaw, K.B.Tan, C.K.Lee, High temperature dielectric properties of cubic bismuth zinc tantalate, *Ceram. Intern.*, **35**(2009), 1473–1480.

[2] G.Giampaoli, T.Siritanon, B.Day, J.Li, M.A.Subramanian, Temperature independent low loss dielectrics based on quaternary pyrochlore oxides, *Prog. Solid State Chem.*, **50**(2018), 16–23.

[3] H.Du, X.Yao, Structural trends and dielectric properties of Bi-based pyrochlores, *J. Mater. Sci. Mater. Electron.*, **15**(2004), 613–616.

[4] M.A.Subramanian, G.Aravamudan, G.V.Subba Rao, Oxide pyrochlores - a review, *Prog. Solid State Chem.*, **15**(1983), 55–143.

[5] S.Kamba, V.Porokhonskyy, A.Pashkin and ets., Anomalous broad dielectric relaxation in $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ pyrochlore, *Phys. Rev. B.*, **66**(2002), 054106.

[6] M.Valant, Dielectric Relaxations in Bi_2O_3-Nb_2O_5-NiO Cubic Pyrochlores, *J. Am. Ceram. Soc.*, **92**(2009), 955–958.

[7] P.Y.Tan, K.B.Tan, C.C.Khaw, Z.Zainal, S.K.Chen, M.P.Chon, Phase equilibria and dielectric properties of $Bi_{3+(5/2)x}Mg_{2-x}Nb_{3-(3/2)x}O_{14-x}$ cubic pyrochlores, *Ceram. Intern.*, **40**(2014), 4237–4246.

[8] M.W.Lufaso, T.A.Vanderah, I.M.Pazos, I.Levin, R.S.Roth, J.C.Nino, V.Provenzano, P.K.Schenck, Phase formation, crystal chemistry, and properties in the system Bi_2O_3-Fe_2O_3-Nb_2O_5, *J. Sol. St. Chem.*, **179**(2006), 3900–3910.

[9] T.A.Vanderah, M.W.Lufaso, A.U.Adler, I.Levin, J.C.Nino, V.Provenzano, P.K.Schenck, Subsolidus phase equilibria and properties in the system Bi_2O_3:Mn_2O_3±x:Nb_2O_5, *J. Sol. St. Chem.*, **179**(2006), 3467–347. DOI: 10.1016/j.jssc.2006.07.014.

[10] I.Levin, T.G.Amos, J.C.Nino, T.A.Vanderah, C.A.Randall, M.T.Lanagan, Structural Study of an Unusual Cubic Pyrochlore $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$., *J. Sol. St. Chem.*, **168**(2002), 69–75.

[11] H.B.Nguyen, L.Noren, Y.Liu, R.L.Withers, X.R.Wei, M.M.Elcombe, The disordered structures and low temperature dielectric relaxation properties of two misplaced-displacive cubic pyrochlores found in the Bi_2O_3-MO-Nb_2O_5 (M = Mg, Ni) systems, *J. Sol. St. Chem.*, **180**(2007), 2558–2565.

[12] E.P.Rylchenko, B.A.Makeev, D.V.Sivkov, R.I.Korolev, N.A.Zhuk, Features of phase formation of pyrochlore-type $Bi_2Cr_{1/6}Mn_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Cu_{1/6}Ta_2O_{9+\Delta}$, *Lett. Mater.*, **12**(2022), 486–492.

[13] N.A.Zhuk, K.A.Badanina, R.I.Korolev, B.A.Makeev, M.G.Krzhizhanovskaya, V.V.Kharton, Phase Formation of Co and Cr Co-Doped Bismuth Niobate with Pyrochlore Structure, *Inorganics*, **11**(2023), 288.

[14] L.G.Akselrud, Yu.N.Grin, P.Yu.Zavalij et al. CSD-universal program package for single crystal or powder structure data treatment, *Thes. Rep. XII Eur. Crystallogr. Meet.*, 1989, 155.

[15] J.C.Nino, M.T.Lanagan, C.A.Randa, Phase formation and reactions in the Bi_2O_3-ZnO-Nb_2O_5-Ag pyrochlore system, *J. Mater. Res.*, **16**(2001), 1460–1464.

[16] N.AZhuk., S.Yu.Kovalenko, R.I.Korolev, B.A.Makeev, M.G.Krzhizhanovskaya, D.V.Sivkov, S.V.Nekipelov, V.N.Sivkov, M.V.Yermolina, Features of Phase Formation of Pyrochlore-type Ceramics $Bi_2Mg(Zn)_{1-x}Ni_xTa_2O_9$, *ACS Omega*, **8**(2023), 11351–11363.

[17] K.N.Parshukova, E.P.Rylchenko, V.A.Muravyev, K.A.Badanina, B.A.Makeev, R.I.Korolev, N.A.Zhuk, Synthesis of multicomponent compounds with a pyrochlore structure, *Glass and ceramics*, **95**(2022), 34–39.

[18] J.A.Da Cruz, E.A.Volnistem, R.F.Ferreira, F D.B.reitas, A.J.M.Sales, L.C.Costa, M.P.F.Graca, Structural characterization of Brazilian niobium pentoxide and treatment to obtain the single phase (H-Nb_2O_5), *Thermal Sci. Engineering Progr.*, **25**(2021), 101015. DOI: 10.1016/j.tsep.2021.101015

[19] J.Gopalakrishnan, R A.amanan, C.N.R.Rao, D.A.Jefferson, J.Smith David, A homologous series of recurrent intergrowth structures of the type $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ formed by oxides of the aurivillius family, *Sol. St. Chem.*, **55**(1984), 101–105.

[20] J.Grins, S.Esmaeilzadeh, S.Hull, Structure and Ionic Conductivity of $Bi_6Cr_2O_{15}$, a New Structure Type Containing $(Bi_{12}O_{14})_{8n+n}$ Columns and CrO_4^{2-} Tetrahedra, *Journal of Solid State Chemistry*, **163**(2002), 144–150.

[21] Y.H.Liu, J.B.Li, J.K.Lianga, J.Luo, L.N.Ji, J.Y.Zhang, G.H.Rao, Phase diagram of the Bi_2O_3-Cr_2O_3 system, *Mater. Chem. Phys.*, **112**(2008), 239–243.

[22] R.S.Roth, J.L.Waring, Synthesis and stability of bismutotantalite, stibiotantalite and chemically similar ABO_4 compounds, *Am. Mineral.*, **48** (1963), 1348–1356.

[23] N.AZhuk., M.G.Krzhizhanovskaya, V.A.Belyy, B.A.Makeev, High-Temperature Crystal Chemistry of α-, β-, and γ-$BiNbO_4$ Polymorphs, *Inorg. Chem.*, **58**(2019), 1518–1526. DOI: 10.1021/acs.inorgchem.8b03024

[24] S.-Y.Jeong, J.-B.Lee, H.Na, T.-Y.Seong, Epitaxial growth of Cr_2O_3 thin film on Al_2O_3 (0001) substrate by radio frequency magnetron sputtering combined with rapid-thermal annealing, *Thin Solid Films*, **518**(2010), 4813–4816.

[25] H.A.Bullen, S.J.Garrett, CrO_2 by XPS: Comparison of CrO_2 Powder to CrO_2 Films on TiO_2 (110) Single Crystal Surfaces, *Surf. Sci. Spectra*, **8**(2001), 225–233.

[26] C.Theil, J.Van Elp, F.Folkmann, Ligand field parameters obtained from and chemical shifts observed at the Cr L2,3 edges, *Physical Review B*, **59**(1999), no. 12, 7931–7936.

[27] Y.Ito, T.Tochio, A.M.Vlaicu and ets., The contribution of the ligands around Cr to the resonant inelastic L X-ray emission spectra, *J. Electron Spectroscopy and Related Phenomena*, **101-103**(1999), 851–858.

[28] M.Struzik, X.Liu, I.Abrahams, F.Krok, M.Malys, J.R.Dygas, Defect structure and electrical conductivity in the pseudo-binary system Bi_3TaO_7-Bi_3NbO_7, *Solid State Ionics*, **218**(2012), 25–30.

[29] T.J.Regan, H.Ohldag, C.Stamm, F.Nolting, J.Luning, J.Stöhr, W R.L.hite, Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy, *Phys. Rev. B*, **64**(2001), 214422.

[30] T.A.Vanderah, T.Siegrist, M.W.Lufaso, M.C.Yeager, R.S.Roth, J.C.Nino, S.Yates, Phase Formation and Properties in the System Bi_2O_3:$2CoO_{1+x}$:Nb_2O_5, *Eur. J. Inorgan. Chem.*, **2006**(2006), 4908–4914.

[31] B.Bingyang, A.Hamidreza, L.Junhuaб Comparison of the performance for oxidation of formaldehyde on nano-Co_3O_4, 2D-Co_3O_4, and 3D-Co_3O_4 catalysts, *Applied Catalysis B: Environmental*, **142-143**(2013), 677–683.

[32] I.V.Piir, D.A.Prikhodko, S.V.Ignatchenko, A.V.Schukariov, Preparation and structural investigations of the mixed bismuth niobates, containing transition metals, *Sol. St. Ion.*, **101-103**(1997), 1141–1146.

[33] R.D.Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. A*, **32**(1976), 751–767.

[34] N.A.Zhuk, N.A.Sekushin, M.G.Krzhizhanovskaya and ets., Cr-doped bismuth tantalate pyrochlore: electrical and thermal properties, crystal structure and ESR, NEXAFS, XPS spectroscopy, *Mater. Res. Bull.*, **158**(2023), 112067.

[35] N.A.Zhuk, M.G.Krzhizhanovskaya, A.V.Koroleva and ets., Cr and Mg codoped bismuth tantalate pyrochlores: Thermal expansion and stability, crystal structure, electrical and optical properties, NEXAFS and XPS study, *J. Sol. St. Chem.*, **323**(2023), 124074.
DOI: 10.1016/j.jssc.2023.124074

[36] N.A.Zhuk, K M.G.rzhizhanovskaya, A.V.Koroleva and ets., Spectroscopic characterization of cobalt doped bismuth tantalate pyrochlore, *Sol. St. Sci.*, **125**(2022), 106820.

[37] N.A.Zhuk, M.G.Krzhizhanovskaya, N.A.Sekushin, D.V.Sivkov, I.EAbdurakhmanov, Crystal structure, dielectric and thermal properties of cobalt doped bismuth tantalate pyrochlore, *J. Mater. Res. Technol.*, **22**(2023), 1791–1799. DOI: 10.1016/j.jmrt.2022.12.059

Конверсия Cr(III) и Co(III) в процессе синтеза кобальт-хромсодержащего пирохлора на основе ниобата висмута по данным NEXAFS

Ксения А. Баданина
Сыктывкарский государственный университет имени Питирима Сорокина
Сыктывкар, Российская Федерация
Сергей В. Некипелов
Физико-математический институт Коми научного центра УрО РАН
Сыктывкар, Российская Федерация
Алексей М. Лебедев
Национальный исследовательский центр – Курчатовский институт
Москва, Российская Федерация
Надежда А. Жук
Сыктывкарский государственный университет имени Питирима Сорокина
Сыктывкар, Российская Федерация
Дмитрий С. Безносиков
Федеральное государственное унитарное предприятие «Главный радиочастотный центр»
Сыктывкар, Российская Федерация

Аннотация. Кубический пирохлор состава $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$ (пр.гр. Fd-3m, a = 10.4838(8) Å) синтезировали в несколько этапов методом твердофазной реакции из оксидных прекурсоров при финальной температуре 1050 °C. По данным NEXAFS-спектроскопии исследовано электронное состояние ионов кобальта и хрома в процессе синтеза. Установлено, что до формирования фазовочистого пирохлора ионы Cr(III) превращаются в Cr(VI), а затем снова в Cr(III); ионы кобальта Co(III) восстанавливаются до Co(II). NEXAFS Cr2p-спектры керамики, синтезированной при 650 °C, по основным характеристикам спектра совпадают со спектром $K_2Cr_2O_7$ и свидетельствуют о содержании хрома в оксидной керамике в виде тетраэдрических ионов CrO_4^{2-}, а по характеру Co2p-спектра ионы кобальта находятся в состоянии Co(II) и Co(III). В составе пирохлора $Bi_2Co_{0.5}Cr_{0.5}Nb_2O_{9+\Delta}$, синтезированного при 1050 °C, кобальт и хром проявляются преимущественно в виде ионов Co(II) и Cr(III). Анализ фазовых превращений показал, что изменение степени окисления ионов переходных элементов и цвета керамики связано с образованием промежуточных продуктов синтеза.

Ключевые слова: пирохлор, ниобат висмута, NEXAFS, кобальт.