

# Valence state of Mn/Cr/Co/Cu cations in multi-element pyrochlores

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Three-component single-phase cubic pyrochlores  $\text{Bi}_{2-x}\text{Cr}_{1/3}\text{Mn}_{1/3}(\text{Co/Cu})_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  (sp. gr.  $Fd-3m$ ) were synthesized for the first time by the solid-phase reaction method. The unit cell parameter, depending on the chemical composition, changes from 10.4546(2) to 10.4832(2) Å. The chemical state of transition element cations in pyrochlores was characterized by X-ray photoelectron spectroscopy (XPS). The parameters of the XPS spectra of  $\text{Bi}4f$ ,  $\text{Nb}3d$ ,  $\text{Co}2p$ ,  $\text{Cu}2p$ ,  $\text{Mn}2p$ ,  $\text{Cr}2p$  for mixed pyrochlores are compared with the parameters of transition element oxides in different oxidation states. For complex pyrochlores, a characteristic shift of  $\text{Bi}4f$  and  $\text{Nb}3d$  spectra to lower energies by 0.1–0.2 and 0.6–0.65 eV, respectively, is observed. According to XPS and NEXAFS spectra, chromium, cobalt and copper atoms are in the charge state of  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ , and manganese atoms are in the mixed charge state of  $\text{Mn}^{2+}/\text{Mn}^{3+}$ .

**Keywords:** synthesis, pyrochlore, XPS, 3d elements, oxidation state.

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## Introduction

Inexhaustible interest in synthetic oxide pyrochlores is aroused by their wide range of unique and useful properties such as ferromagnetism and ferrimagnetism, spin glass state, photocatalytic, superconducting and dielectric properties [1–5]. Bismuth-containing pyrochlores draw close attention of researchers due to their outstanding dielectric properties: moderate and thermostable permeability, low dielectric loss, low sintering temperature and chemical inertness to low-melting copper electrodes. Combination of practically significant properties of pyrochlores underlies their future use in multilayer ceramic capacitors, phase shifters and tunable oscillators [5–9]. Due to their structural flexibility, synthetic pyrochlores feature a wide homogeneity range and diversity of chemical composition defining physical and chemical properties of pyrochlores [10–13]. Oxide pyrochlores are traditionally described by the formula:  $\text{A}_2\text{B}_2\text{O}_7$ . A basis substructure — a tetrahedral frame formed by vortex-bound regular  $\text{BO}_6$  octahedra arranged around diamond grid points, and containing large cations A in its voids, is distinguished in the cubic crystal structure of cubic pyrochlore ( $Fd-3m$ ). Relatively small five- or four-valent cations B ( $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ti}^{4+}$ , 3d-element cations) are coordinated in the octahedra, and large two- or three-valent ions A ( $\text{Ca}^{2+}$ ,  $\text{Bi}^{3+}$ ) are located in a distorted octahedron formed by oxygen atoms of both  $\text{A}_2\text{O}$  and  $\text{B}_2\text{O}_6$  sublattices [14,15]. Classical two-component stoichiometric oxide pyrochlores are formed by combination of cations with oxidation numbers of +3/ +4 or +2/ +5 in equimolar ratio. Structural stability of such pyrochlores can be predicted by the tolerance factor [15]. Besides

traditional pyrochlores, mixed stoichiometric pyrochlores,  $\text{A}_2(\text{BB}')_2\text{O}_7$ , are known where the  $\text{B}_2\text{O}_6$  cation octahedral sublattice is filled by cations that have different chemical nature and valence (B and B'), but are six-coordinated and have a mean oxidation number of +4 or +5. Mixed non-stoichiometric pyrochlores are known and have been studied, for example,  $\text{A}_{4/3}^{3+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})_2\text{O}_6$ , formed by 3d-element cation monodoping ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ) [16,17]. Such pyrochlores feature mixed arrangement of transition element cations in two  $\text{A}_2\text{O}$  and  $\text{B}_2\text{O}_6$  pyrochlore sublattices with explicit preference to the octahedral sublattice. Multi-element pyrochlores simultaneously doped with several 3d transition elements or magnesium cations [18] are currently extensively investigated. Such pyrochlores are interesting in terms of structural stability and cross-effect of transition element cations on each other and on ceramic properties generally.

This work describes the results of a charge state study of 3d element cations in phase-pure multielement pyrochlores containing equimolar amounts of Cr, Mn, Co and Cu ions using the X-ray photoelectron spectroscopy (XPS). These elements are interesting in that they feature a wide variety of oxidation numbers in an oxidized condition. They occur in pyrochlores in rare oxidation numbers such as Cr (VI) or Cu (I), the cause of which has not been conclusively established.

## Experimental part

Pyrochlores such as  $\text{Bi}_{2-x}\text{Cr}_{1/3}\text{Mn}_{1/3}(\text{Co/Cu})_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  and  $\text{Bi}_{2-x}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  have been chosen as the

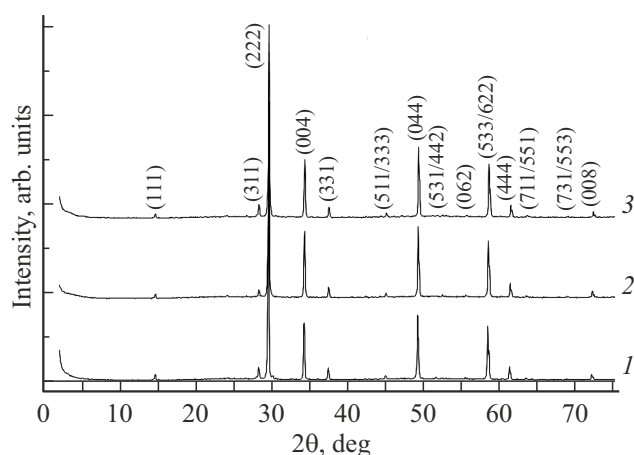


**Figure 1.** X-ray patterns: 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ .

subject of research. Bismuth(III), niobium(V), copper(II), cobalt(II,III), chromium(III), manganese(III) oxides, AR grade, in stoichiometric amounts were used as precursors for solid-phase synthesis. A mixture of oxides was blended and triturated in an agate mortar for 1 h, then the homogeneous mixture was disc-shaped and calcinated in four stages at 650, 850, 950, 1050 °C (15 h) to get single-phase samples. At each calcination stage, the reaction mixture was blended again and compacted for better contact between ceramic grains. Phase analysis of samples was performed using the Shimadzu 6000 diffractometer with  $\text{CuK}\alpha$  radiation in the  $2\theta$  range of 10–80° at a scanning rate of 2.0 grad/min. Surface morphology and local quantitative elemental analyses were performed by the scanning electron microscopy and energy-dispersive X-ray spectroscopy (TescanVEGA 3LMN scanning electron microscope, INCAEnergy 450 energy-dispersive spectrometer). XPS examination was performed using the Thermo Scientific ESCALAB 250Xi X-ray spectrometer. The  $\text{Al K}\alpha$  (1486.6 eV) X-ray tube was used as an ionising radiation source. An ion-electron charge compensation system was used for charge neutralization during experiments. All peaks were calibrated by the  $\text{C1s}$  peak at 284.6 eV. Test data were processed in ESCALAB 250 Xi.

## Results and discussion

$\text{Bi}_{2-x}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co/Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  and  $\text{Bi}_{2-x}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  were synthesized first at  $x = 0$ , but as shown by the X-ray diffraction analysis (XRD), all samples are mixed-phase and contain various amount of bismuth ortho-niobate impurity depending the chemical composition of pyrochlore. To synthesize single-phase preparations with the specified ratio of 3d transition elements, vacancies were created in the bismuth sublattice to a magnitude proportional to the content of  $\text{BiNbO}_4$  impurity in each sample. As a result, the samples have different stoichiometry

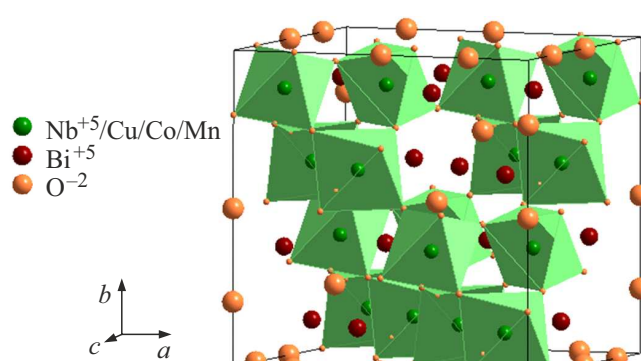


**Figure 2.** Cubic pyrochlore lattice cell.

by bismuth cations: 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ , and according to the XRD data, all samples are single-phase (Figure 1) and are crystallized as a cubic pyrochlore (space group  $Fd-3m$ ) (Figure 2). The given formula of the synthesized compounds:  $\text{Bi}_{2-x}\text{Cr}_{1/3}\text{Mn}_{1/3}(\text{Co/Cu})_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , formally doesn't correspond to the traditional pyrochlore formula, and shall be correctly written as  $\text{Bi}_{4/3-y}[\text{Cr}_{2/9}\text{Mn}_{2/9}(\text{Co/Cu})_{2/9}\text{Nb}_{4/3}]\text{O}_{6\pm\Delta} = \text{A}_{4/3-y}[\text{B}'_{2/3}\text{B}_{4/3}]\text{O}_{6\pm\Delta}$ . This formula shows that bismuth(III) cations play a role of cations A, and Cr(III), Mn(II,III), Nb(V) and Co(II,III)/Cu(II) ions fill the octahedral sublattice of cations B. Octahedral sublattice is fully filled, the fraction of 3d metal cations is 1/3 of the sublattice capacity. 3d metal dopant cations — Cr(III), Mn(II,III), Nb(V), Co(II,III)/Cu(II), serve as cations B'. Bismuth sublattice is partially vacant (the coefficient at bismuth is other than 2), moreover, large 3d metal cations such as Co(II), Cu(II) and Mn(II) are partially distributed in the bismuth position. Bismuth sublattice vacancy with 3d-doping is a necessary condition for pyrochlore crystal structure stabilization. In case when cation dopants are placed in the bismuth sublattice, „vacant positions“ shall be additionally created in the sublattice, otherwise the  $\text{BiNbO}_4$  impurity is formed. Coefficient y means that there are such additional vacant positions in the bismuth sublattice for 3d metal cations and they are created artificially — with a deficiency of precursor — bismuth(III) oxide.

Crushed synthesized samples have a form of dark-grey polycrystalline powders with faint shades of green and brown (Figure 3). As described in the experimental part, sintered samples consisted of disc-shaped compacts of ~ 12 mm in diameter and 3–4 mm in thickness, a disc weigh is 1.5–2 g.

A pyrochlore lattice cell parameter is 10.4832(2) Å for  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 10.4724(2) Å for  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  and 10.4546(2) Å for  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ . Pyrochlore lattice cell parameters in the samples differ significantly and are defined by the nature of dopants. Lattice cell

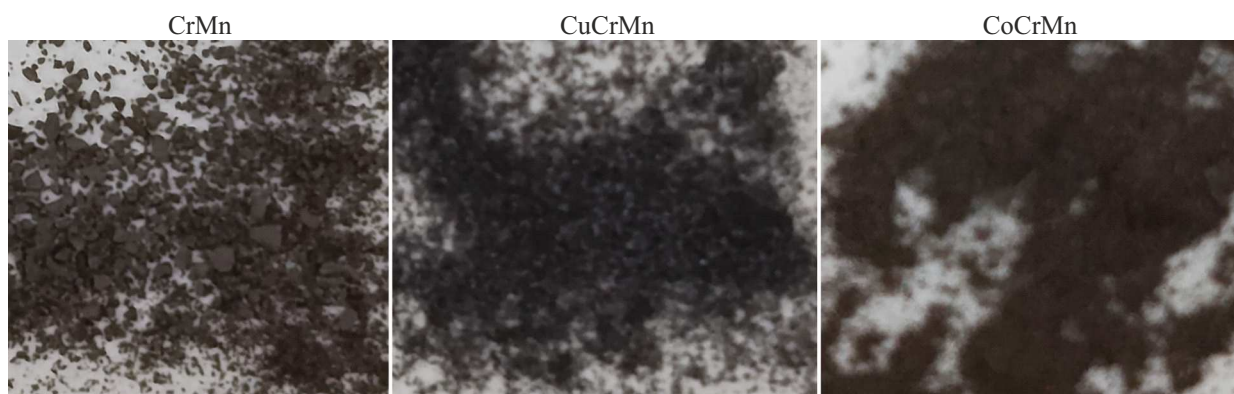


**Figure 3.** Photographs of the synthesized samples  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  (CrMn),  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  (CuCrMn) and  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  (CoCrMn).

constant of  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  is expectedly larger than the cell parameter for the monodoped chromium pyrochlore  $\text{Bi}_2\text{CrNb}_2\text{O}_{9+y}$  ( $10.459(2) \text{ \AA}$ ) [19] ( $R(\text{Cr(III)})_{\text{c.n.-6}} = 0.615 \text{ \AA}$ ,  $R(\text{Mn(II)})_{\text{c.n.-6}} = 0.83 \text{ \AA}$ ,  $R(\text{Co(II)})_{\text{c.n.-6}} = 0.745 \text{ \AA}$ ,  $R(\text{Cu(II)})_{\text{c.n.-6}} = 0.73 \text{ \AA}$  — Shannon ionic radii of cations together with coordination numbers are given hereinafter) [20]. Cell constant of the studied pyrochlore is nearest to the cell parameter of  $\text{Bi}_{1.6}\text{Mn}_{0.4}(\text{Mn}_{0.8}^{3+}\text{Nb}_{1.2})\text{O}_7$  ( $10.478 \text{ \AA}$ ) studied in [10], while the stoichiometric coefficient at bismuth atoms is different. Cell parameter of  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  almost coincides with that of  $\text{Bi}_{1.6}\text{Mn}_{0.4}(\text{Mn}_{0.8}^{3+}\text{Nb}_{1.2})\text{O}_7$  ( $10.478 \text{ \AA}$ ), despite a lower stoichiometric coefficient at bismuth atoms. Cell parameter of  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  is compared with that for monodoped chromium pyrochlores such as  $\text{Bi}_2\text{CrNb}_2\text{O}_{9+y}$  ( $10.459(2) \text{ \AA}$ ) [21] and  $\text{Bi}_{1.6}\text{Cr}_{0.8}\text{Ta}_{1.6}\text{O}_{7.6}$  (space group  $Fd-3m$ : 2,  $10.45523(3) \text{ \AA}$ ), taking into account that the stoichiometric coefficient at bismuth atoms is underestimated. Thus, the presence of cobalt(II) and copper(II) cations increases the pyrochlore lattice cell parameter. Proximity of the lattice cell parameter of  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  to  $\text{Bi}_2\text{CrNb}_2\text{O}_{9+y}$  can indicate the presence of oxidized manganese cations whose radius is smaller than the ionic radius of Mn(II) ( $R(\text{Mn(III)})_{\text{c.n.-6}} = 0.645 \text{ \AA}$ ,  $R(\text{Mn(IV)})_{\text{c.n.-6}} = 0.53 \text{ \AA}$ ) [20]. Direct comparison of cell parameters of samples that are similar in chemical composition is difficult due to a different amount of bismuth(III) cations in samples affecting the lattice cell parameter.

Microstructure and local chemical analysis of samples were studied by the scanning electron microscopy (Figure 4). Samples have a porous dense microstructure formed by fused and interlinked elongated ceramic grains with mean size of  $2 \mu\text{m}$ . Elemental mapping has shown uniform metal cation distribution over the sample surface. EDS analysis has shown that quantitative ratios of elements contained in the synthesized samples corresponded to the specified theoretical composition.

Energy positions of XPS spectra positions (in eV): 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$

| Peak                | 1      | 2      | 3      |
|---------------------|--------|--------|--------|
| $\text{Bi}4f_{7/2}$ | 158.76 | 158.81 | 158.86 |
| $\text{Bi}4f_{5/2}$ | 164.07 | 164.14 | 164.16 |
| $\text{Nb}3d_{5/2}$ | 206.35 | 206.43 | 206.40 |
| $\text{Nb}3d_{3/2}$ | 209.09 | 209.19 | 209.14 |
| $\text{Cr}2p_{3/2}$ | 576.42 | 576.49 | 576.42 |
| $\text{Cr}2p_{1/2}$ | 586.20 | 586.02 | 586.10 |
| $\text{Mn}2p_{3/2}$ | 641.40 | 641.35 | 641.31 |
| $\text{Mn}2p_{1/2}$ | 653.28 | 653.28 | 652.99 |
| $\text{Co}2p_{3/2}$ | 780.36 |        |        |
| Co2p satellite      | 785.97 |        |        |
| $\text{Co}2p_{1/2}$ | 796.57 |        |        |
| $\text{Cu}2p_{3/2}$ |        | 934.02 |        |
| Cu2p satellite      |        | 941.86 |        |
| $\text{Cu}2p_{1/2}$ |        | 954.14 |        |
| Cu2p satellite      |        | 961.76 |        |

We proceed to XPS spectra of pyrochlores: 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  as shown in Figure 5 and in the table. Oxide precursor spectra are shown for comparison. Figure 5, *a* shows XPS spectra in a wide energy range, and Figure 5, *b–g* shows spectral dependences in the area of  $\text{Bi}4f$ ,  $\text{Nb}3d$ ,  $\text{Cr}2p$ ,  $\text{Mn}2p$ ,  $\text{Co}2p$  and  $\text{Cu}2p$  ionization thresholds of a sample. The figures show decomposition of spectral dependences into peaks simulated by the Gaussian-

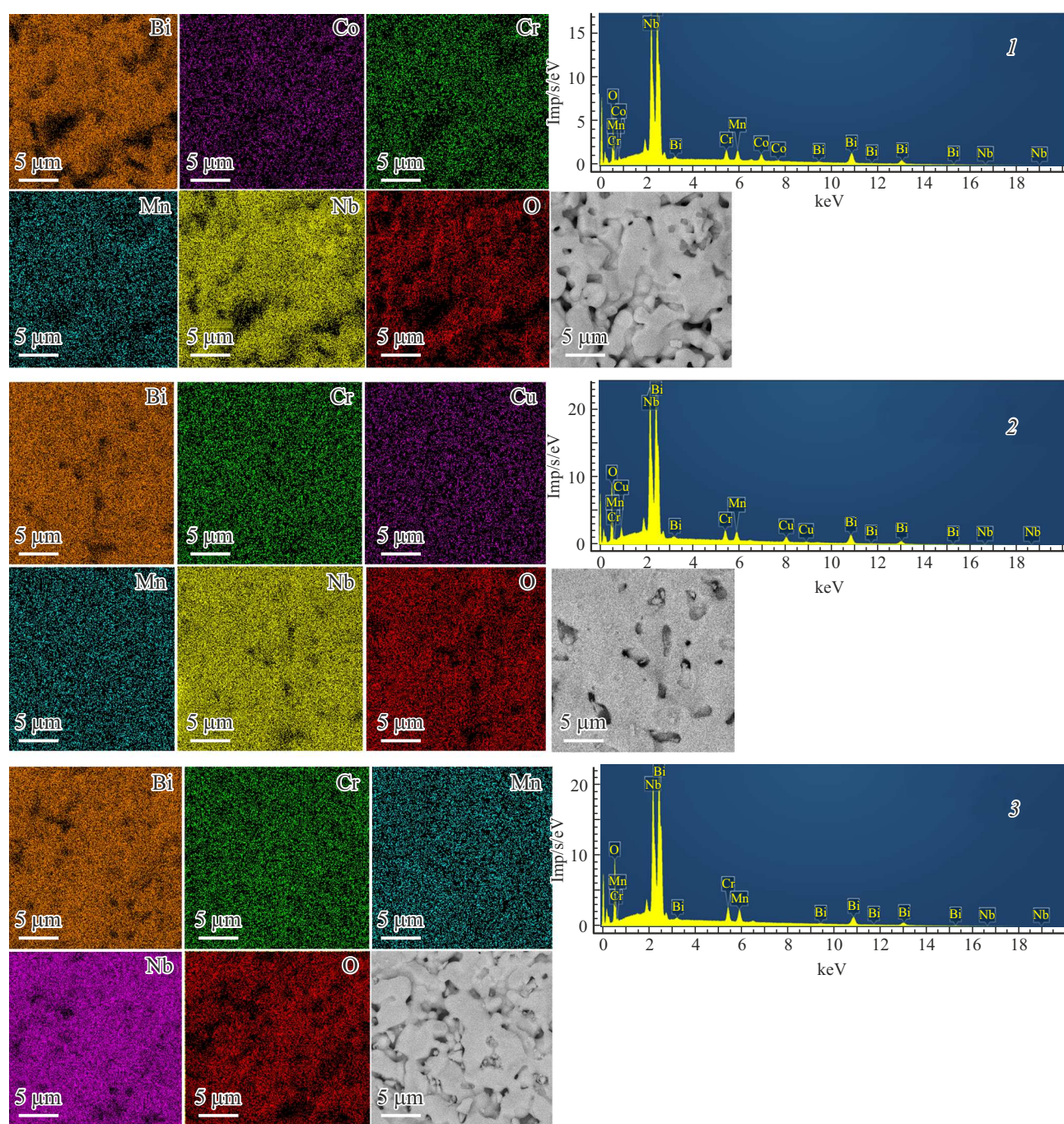


**Figure 4.** EDS spectra and element maps of the samples: 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ .

Lorentzian curves, and background lines are simulated by the Shirley or smart approximation. SurveyXPS spectrum analysis (Figure 5, *a*) detected a  $\text{C}1s$  peak associated with organic impurities of a sample. Impurities make an indefinite contribution to the  $\text{O}1s$  peak intensity, therefore only metal spectra were used for the chemical analysis of the sample surface.

Comparison of XPS spectra of test samples 1–3 and  $\text{Bi}_2\text{O}_3$  (Figure 5, *b*) has shown that the energy position

of the  $\text{Bi}4f$  bands had a typical shift to a low-energy region compared with the binding energy in  $\text{Bi}_2\text{O}_3$ . Maximum shift of the  $\text{Bi}4f$  spectrum towards lower energies (by 0.19 eV) occurs for  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , for  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_9$  - it is 0.14 eV, and for  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  - it is 0.09 eV. Binding energy in  $\text{Bi}_2\text{O}_3 E_{\text{BE}}(\text{Bi}4f_{7/2}) = 158.93$  eV. Signal shift to a low-energy region occurs when the effective positive charge of bismuth cations in pyrochlore decreases compared with

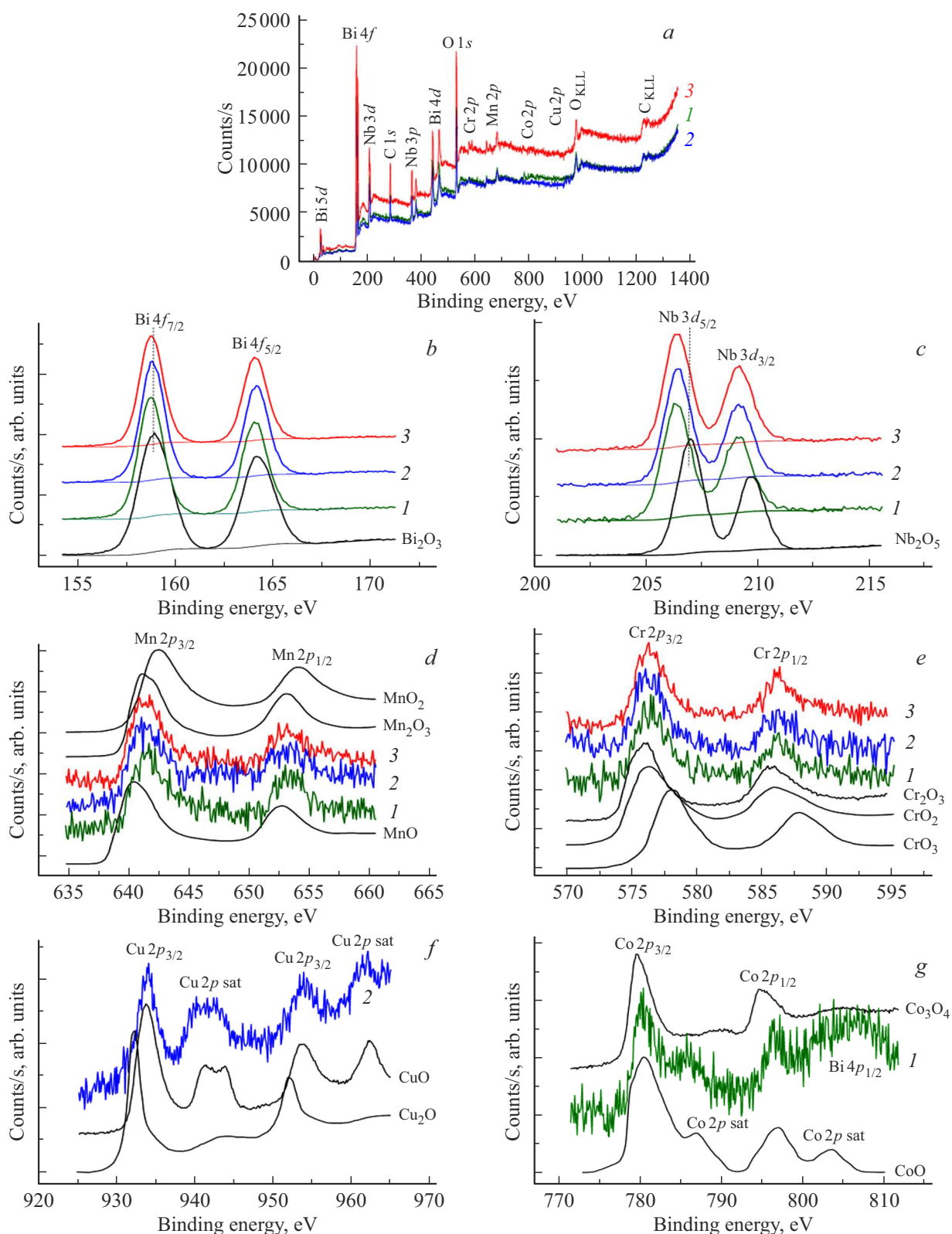


**Figure 5.** XPS spectra: 1 —  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ . Survey spectra (a); XPS Bi 4f spectra of samples and  $\text{Bi}_2\text{O}_3$  (b); Nb 3d spectra of samples and  $\text{Nb}_2\text{O}_5$  (c); Mn 2p spectra of manganese oxides and cations in samples (d); XPS spectra of chromium oxides and Cr 2p spectra of samples (e); XPS Cu 2p spectra for  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  and copper oxides (f); Co 2p spectra of cobalt oxides and  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  (g).

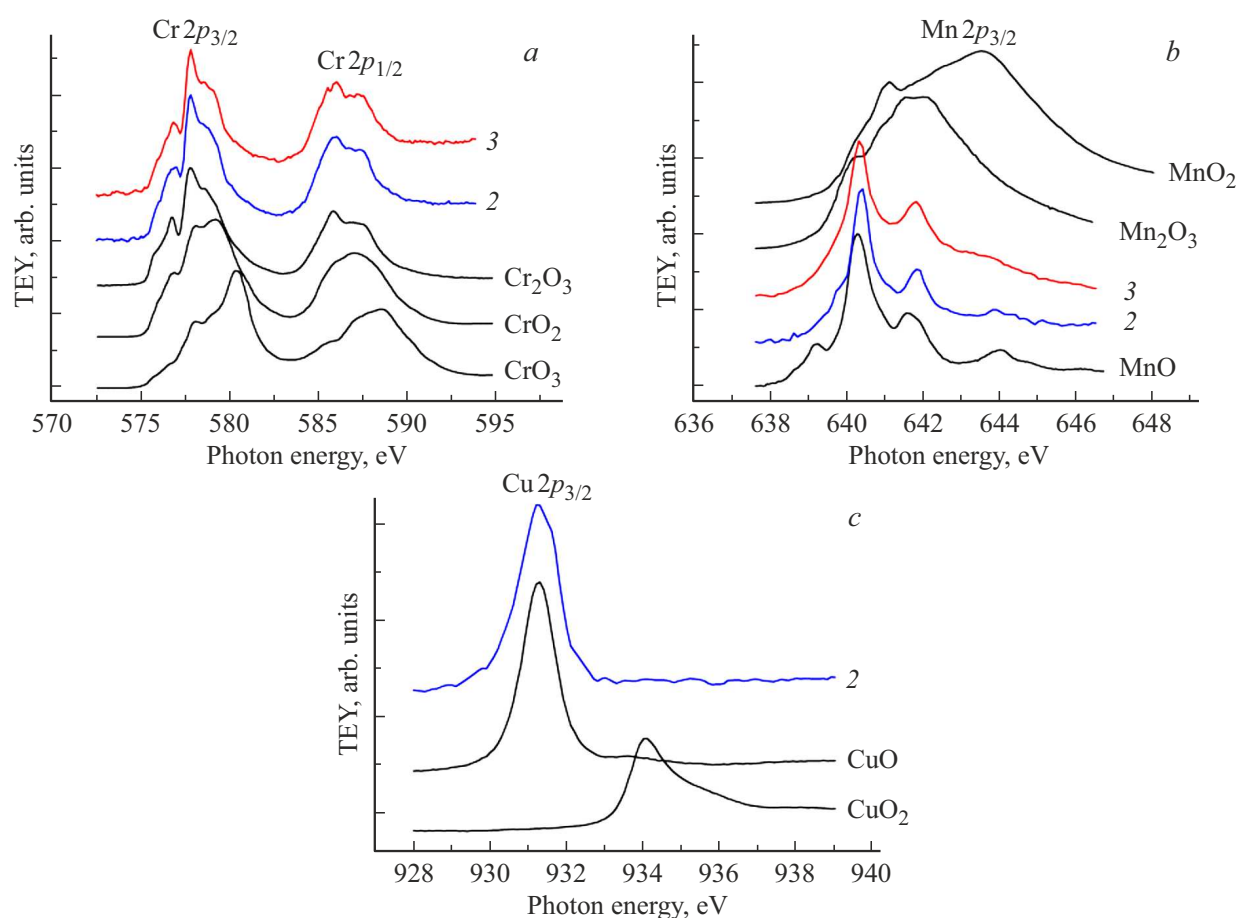


**Figure 6.** (a) NEXAFS Cr $2p$ , (b) Mn $2p$  and (c) Cu $2p$  spectra: 2 —  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Cu}_{1/3}\text{Mn}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , 3 —  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$ . TEY — total electron yield.

the bismuth charge in bismuth(III) oxide, suggesting that bismuth ions in the samples have an equal effective charge of  $+(3-\delta)$ . It is interesting that the  $\text{Bi}4f$  spectrum shift is greater in  $\text{Bi}_{1.73}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$  than in  $\text{Bi}_{1.57}\text{Cr}_{1/3}\text{Mn}_{1/3}\text{Cu}_{1/3}\text{Nb}_2\text{O}_{9-\Delta}$ , despite that the amount of bismuth cations in compound 1 is greater than in compound 2 and, therefore, the contribution of copper(II) cation charge will be greater than that in the cobalt-containing compound. This can suggest that there are few or no copper(I) cations in a sample. Moreover, ion content of manganese cations in the samples can be different. Shift of the  $\text{Bi}4f$  spectrum for  $\text{Bi}_{1.65}\text{Cr}_{1/2}\text{Mn}_{1/2}\text{Nb}_2\text{O}_{9-\Delta}$  can mean that there are Mn(II) cations in the sample and probably it is they that move into the bismuth positions. Low-energy shift is also detected for the Nb $3d$  spectrum (Figure 3, c). Low energy shift for three samples is comparable and varies within 0.60 (for samples 2 and 3), 0.64, 0.58 and 0.61 eV for samples 1–3, respectively, compared with the binding energy in  $\text{Nb}_2\text{O}_5$  ( $E_{\text{BE}}(\text{Nb}3d_{5/2}) = 207.01$  eV), which suggests that the effective charge of niobium cations decreases to  $+(5-\delta)$ . Decrease in the effective charge of bismuth and niobium cations can be associated with the distribution of some low-charge transition element cations to

the niobium and bismuth positions. The largest shift of the Nb $3d$  spectrum compared with the  $\text{Bi}4f$  spectrum suggests that transition element cations are predominantly distributed to the Nb(V) positions, rather than to the Bi(III) positions.

Comparison of the Mn $2p$  spectra of pyrochlore with the spectra of MnO,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  reported in the literature [22–24] shows (Figure 5, d) that the Mn $2p$  spectra for the samples correlate in the energy spectrum to a greater extent with the  $\text{Mn}_2\text{O}_3$  and MnO spectra. Positions of the Mn $2p$  spectra peaks of pyrochlore and  $\text{Mn}_2\text{O}_3$  almost coincide (Mn $2p_{3/2}$  and Mn $2p_{1/2}$  — 641 and 653 eV, respectively), which corresponds to Mn(III) ions. Mn(II) cations are acceptable in pyrochlore because the spread diffuse Mn $2p$  spectra of pyrochlore can represent a superposition of energetically closely spaced spectra from Mn(II) (640.5 eV) and Mn(III) (641 eV) ions. Cr $2p$  spectra of pyrochlores and chromium oxides are shown in Figure 3, e. Spectra of the studied pyrochlores are similar to each other. Shift of the pyrochlore spectrum relative to the Cr $2p$  spectrum of  $\text{Cr}_2\text{O}_3$  [25] to a high-energy region and insufficient selectivity of the pyrochlore broadband spectrum suggests that chromium cations in pyrochlores have an averaged charge state other than +3. It is suggested that

the Cr2*p* spectrum of pyrochlore represents a superposition of spectra from chromium cations in a charge state of +3, +4, +6 [25–27]. Meanwhile, when comparing the Cu2*p* spectrum of Bi<sub>1.57</sub>Cr<sub>1/3</sub>Mn<sub>1/3</sub>Cu<sub>1/3</sub>Nb<sub>2</sub>O<sub>9–Δ</sub> with the CuO spectra obtained in this work and the reported Cu<sub>2</sub>O spectra [28], it can be observed that the energy position of the base peaks in the pyrochlore spectrum (934 and 954 eV) almost coincides with the CuO spectrum (Figure 5, *f*). Cu2*p*-spectrum of pyrochlore clearly shows satellite peaks in the range of 938–945 and 960–965 eV that are typical for two-charge Cu (II) cations. While a low-energy influx in the spectrum at 932 and 952 eV coinciding with bands in the Cu<sub>2</sub>O spectrum can indicate that there is a small fraction of copper cations in the Cu (I) charge state. In this case it can be suggested that copper cations in pyrochlore are in a mixed valent state Cu (I, II).

To check the charge state of 3*d* atoms, X-ray absorption analysis of samples 2 and 3 was carried out and results are shown in Figure 6. Let's look at the manganese spectra (Figure 6, *b*). Comparison of the composite material spectra with the spectra of oxides examined in this work shows that the composite material spectra coincide with the MnO spectrum in shape and energy position, but the peak intensity with an energy of about 641.8 eV is greater than in MnO, and its energy position correlates with the Mn<sub>2</sub>O<sub>3</sub> spectrum. This suggests that, as specified above from the XPS-spectra analysis, manganese atoms can be actually present in various valence states: Mn(II) and Mn(III). Let's look at the NEXAFSCr2*p* spectra of composite materials shown in Figure 6, *a*. The spectra have a rich structure and unlike the XPS spectra, it is difficult to decompose the NEXAFS spectra into components, however, when comparing the Cr2*p* spectra of a composite material and chromium oxides, it can be noted that composite material spectra almost coincide with the Cr<sub>2</sub>O<sub>3</sub> spectrum in position and relative intensity of the main lines. This indicates that chromium atoms in the compounds studied in this work have a charge state of +3. The same comparison of the Cu2*p* spectra of a composite material with the oxide spectra (Figure 6, *c*) expressly indicates a charge state of copper atoms of +2.

Energy range of the Co2*p* spectrum of Bi<sub>1.73</sub>Cr<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>Nb<sub>2</sub>O<sub>9–Δ</sub> near 805 eV includes a peak that is responsible for the Bi4*p*<sub>1/2</sub>-level binding energy (Figure 5, *g*), which hinders the perception of cobalt spectra. Meanwhile, when comparing the pyrochlore spectrum with the Co<sub>3</sub>O<sub>4</sub> spectra obtained in this work and the reported CoO spectra [29], it can be observed that the energy position of base peaks in the pyrochlore spectrum almost coincides with that of the CoO spectrum. Satellite peaks at 786 and 803 eV typical for two-charge Co (II) cations are clearly identified in both spectra. While the energy position of satellite peaks in oxides is different, they are shifted in the CoO spectra towards lower energies and are more intense. In this case it can be suggested that cobalt cations in pyrochlore are in the Co (II) state.

## Conclusion

The study shows that solid-phase synthesis of phase-pure multielement cubic Bi<sub>1.73</sub>Cr<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>Nb<sub>2</sub>O<sub>9–Δ</sub>, Bi<sub>1.57</sub>Cr<sub>1/3</sub>Mn<sub>1/3</sub>Cu<sub>1/3</sub>Nb<sub>2</sub>O<sub>9–Δ</sub>, Bi<sub>1.65</sub>Cr<sub>1/2</sub>Mn<sub>1/2</sub>Nb<sub>2</sub>O<sub>9–Δ</sub> with a deficient bismuth sublattice is possible. Different low-energy shift of the XPSBi4*f* and Nb3*d* spectra is detected for all samples, which is associated with nonuniform distribution of 3*d* transition elements in bismuth(III) and niobium(V) cation positions. Maximum low-energy shift of the Bi4*f* and Nb3*d* spectra is exhibited for the Bi<sub>1.73</sub>Cr<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>Nb<sub>2</sub>O<sub>9–Δ</sub> sample. According to the XPS and NEXAFS spectra data, chromium, cobalt and copper atoms are in the Cr<sup>3+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> charge state, and manganese atoms are in the mixed Mn<sup>2+</sup>/Mn<sup>3</sup> charge state.

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## Conflict of interest

The authors declare no conflict of interest.

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