



## Research articles

Magnetic susceptibility of solid solutions  $\text{Bi}_2\text{SrNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ N.A. Zhuk<sup>a,\*</sup>, N.V. Chezhina<sup>b</sup>, V.A. Belyy<sup>c</sup>, B.A. Makeev<sup>d</sup>, M.V. Yermolina<sup>e</sup>, A.S. Miroshnichenko<sup>a</sup><sup>a</sup> Syktyvkar State University, Oktjabrskij prospect, 55, Syktyvkar, Republic of Komi 167001, Russia<sup>b</sup> St. Petersburg State University, Universitetsky pr. 26, St. Petersburg 198504, Russia<sup>c</sup> Institute of Chemistry of the Komi Science Center UB RAS, Pervomaiskaya st. 48, Syktyvkar, Republic of Komi 167982, Russia<sup>d</sup> Institute of Geology of the Komi Science Center UB RAS, Pervomaiskaya st. 54, Syktyvkar, Republic of Komi 167982, Russia<sup>e</sup> University of Illinois at Chicago, 845 W. Taylor St., MC 111, Chicago, IL 60607, USA

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## ABSTRACT

The state of iron atoms and their interatomic interactions were investigated by the method of magnetic dilution in  $\text{Bi}_2\text{SrNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$  with a layered perovskite-like structure. It was found that the solid solutions are characterized by increased values of the magnetic moment of iron atoms, compared with purely spin values of Fe(III). This was explained by the presence of exchange-bound aggregates of Fe(III) atoms with antiferro- and ferromagnetic types of exchange. The dependencies of the exchange parameters and cluster distribution on the iron content of  $\text{Bi}_2\text{SrNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$  solid solutions were calculated.

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## 1. Introduction

Bismuth-containing layered perovskite-like ferroelectrics were first described by Aurivillius [1]. Aurivillius phases are characterized by high Curie temperatures, low rates of degradation of residual polarization and piezoelectric properties under unipolar electric fields. High dielectric permittivity of the phases determines their use as components of composite film systems for devices of data processing and long-term storage (FRAM), as well as producing piezoelectric and pyroelectric converters based on them [2–8].

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 the crystal structure of the Aurivillius phases described by the general formula  $\text{A}_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}$ , in which the cationic positions A with cuboctahedral surroundings are occupied by ions of large radius ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Ln}^{3+}$ ), when the high-charge cations with a small radius ( $\text{Cr}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ ) are located in the octahedral positions B [9–15]. The parameter  $m$  corresponds to the number of the  $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$  layers in the perovskite-like blocks.

Previous studies of magnetic dilution in the iron-containing solid solutions of bismuth niobates  $\text{Bi}_2\text{BaNb}_2\text{O}_9$  ( $m = 2$ ) and  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  ( $m = 1.5$ ) have shown that iron (III) atoms are prone to aggregation forming multinuclear clusters predominantly with an antiferromagnetic type of indirect exchange, the intensity of which

depends on the efficiency of overlapping of the atomic orbitals of oxygen and the  $d$ -element [16,17]. This paper explores the influence of structural distortion and the nature of the second coordination sphere atoms on the pattern and intensity of the interactions between iron atoms in  $\text{Bi}_2\text{SrNb}_2\text{O}_9$  solid solutions. The structure of  $\text{Bi}_2\text{SrNb}_2\text{O}_9$  (Fig. 1) is described by the space group  $A2_1am$  ( $a = 0.55189(3)$ ,  $b = 0.55154(3)$  and  $c = 2.51124(9)$  nm [18–20]) and contains two perovskite-like layers of niobium-oxygen octahedra. The strontium bismuth niobate  $\text{Bi}_2\text{SrNb}_2\text{O}_9$  refers to relaxor ferroelectrics ( $T_c = 420\text{--}440$  °C) [21]. The partial replacement of Bi(III) ions in the fluorite-like layers by Sr(II) ions leads to blurring of the phase transition and to the relaxation character of the dielectric polarization. The mismatch between the sizes of the cuboctahedral voids of perovskite-like blocks and strontium atoms causes geometric distortions of the structure, manifested in the asymmetry and angular slope of the niobium-oxygen octahedra [18–20].

## 2. Experimental

The solid solutions of cubic modification were synthesized by the standard ceramic method from “special pure” grade bismuth (III), niobium (V) and iron (III) oxides at the temperatures of 750 °C and 1100 °C. Phase composition of the samples was monitored by means of scanning electron microscopy (an electron scanning microscope Tescan VEGA 3LMN, an energy dispersion spectrometer INCA Energy 450) and X-ray phase analysis (a DRON-4-13 diffractometer,  $\text{CuK}\alpha$  emission). The unit cell parameters of the

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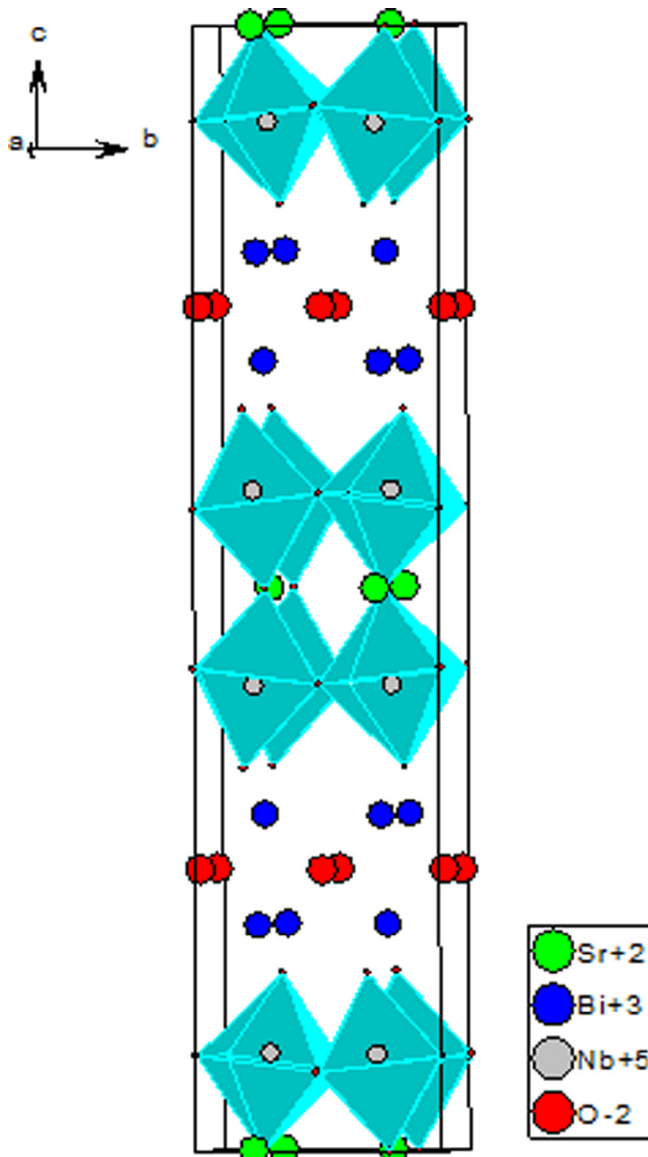


Fig. 1. The unit cell of  $\text{Bi}_2\text{SrNb}_2\text{O}_9$ .

solid solutions were calculated using the CSD program package [22].

The quantitative measurement of iron in the solid solution samples was performed by atom-emission spectrometry (a SPECTRO CIROS ISP spectrometer with inductively coupled plasma) with the accuracy of 5% of the index  $x$  in the solid solution formula.

The magnetic susceptibility of the solid solution samples was measured by the Faraday method in the temperature range of 77–400 K at 16 fixed temperatures and at the magnetic field strengths of 7240, 6330, 5230, and 3640 Oe. A semicommercial installation created in the laboratory of magnetochemistry of St. Petersburg State University and consisting of an electromagnet, an electronic balance, and cryostat was used for magnetic susceptibility measurements. The accuracy of relative measurements was 2%.

### 3. Results and discussion

The solid solutions  $\text{Bi}_2\text{SrNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$  were synthesized in the concentration range  $x \leq 0.05$  (Figs. 2, 3). Atoms of iron (III), which are close in size to atoms of niobium (V), isomorphically substitute the octahedral cationic positions in the perovskite-like layers (R

$(\text{Nb(V)})_{c.n.=6} = 0.064 \text{ nm}$ ;  $\text{R(Fe(III))}_{c.n.=6} = 0.0645 \text{ nm}$ ) [23]. X-ray diffraction of the solid solutions showed that their crystal structure corresponds to the structure of  $\text{Bi}_2\text{SrNb}_2\text{O}_9$ . With increasing iron content in the solid solutions, the parameters  $a$  and  $b$  decrease, and  $c$  increases: from  $a = 0.55045(4) \text{ nm}$ ,  $c = 2.5054(9) \text{ nm}$ ,  $b = 0.55066(2) \text{ nm}$  ( $x = 0.003$ ) to  $a = 0.55017(4) \text{ nm}$ ,  $c = 2.5072(9) \text{ nm}$ ,  $b = 0.55037(3) \text{ nm}$  ( $x = 0.050$ ).

Based on the magnetic susceptibility measurements of the solid solutions, the paramagnetic components of the magnetic susceptibility  $[\chi^{\text{para}}(\text{Fe})]$  and the values of the effective magnetic moments  $[\mu_{\text{ef}}(\text{Fe})]$  of iron atoms were calculated for the temperature range of 77–400 K and for various concentrations of iron in  $\text{Bi}_2\text{SrNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$  ( $x \leq 0.05$ ). The diamagnetic correction factors were introduced taking into account the susceptibility of the matrix of bismuth niobate  $\text{Bi}_2\text{SrNb}_2\text{O}_9$  measured in the same temperature range.

The temperature dependences of the reciprocal paramagnetic component of the magnetic susceptibility of the solid solutions ( $x \leq 0.05$ ), calculated for one mole of iron atoms, obey the Curie-Weiss law in the temperature range of 77–400 K. The Weiss constant becomes negative at  $x \geq 0.007$ , which reveals the antiferromagnetic exchange interactions between iron atoms in the moderately concentrated solutions. In the highly diluted solutions, at  $x \leq 0.003$ , the magnetic exchange is predominantly of the ferromagnetic type.

The form of the isotherms of the paramagnetic component of the magnetic susceptibility of iron  $[\chi^{\text{para}}(\text{Fe})]$  in the solid solutions (Fig. 4) is typical for antiferromagnets. The value of the effective magnetic moment of single iron atoms calculated via extrapolation of the concentration dependences of the  $[\chi^{\text{para}}(\text{Fe})]$  values to infinite dilution of the solid solutions decreases with increasing temperature from 6.95  $\mu\text{B}$  (90 K) to 6.72  $\mu\text{B}$  (320 K) (Table 1). This indicates the ferromagnetic type exchange interactions between the paramagnetic atoms. The value of the magnetic moment exceeds the purely spin value for Fe(III) ( $\mu_{\text{ef}} = 5.92 \mu\text{B}$ , term  ${}^6\text{A}_{1g}$ ) and Fe(II) ( $\mu_{\text{ef}} = 4.9 \mu\text{B}$ ,  ${}^5\text{T}_{2g}$ ) atoms. It can be explained by the formation of exchange-bound aggregates of Fe(III) atoms with ferromagnetic exchange. The temperature dependences of the effective magnetic moment of the iron atoms (Fig. 5) allow us to conclude that the ferromagnetic type exchange, which is not typical for Fe(III), is dominant only in the highly diluted solutions ( $x \leq 0.003$ ), where the bond angle between the paramagnetic atoms and the geometric distortions of the coordination polyhedron of paramagnetic atoms significantly influence the nature of exchange. With the increase in concentration of the solid solutions, the ferromagnetic type of exchange in clusters is replaced by the antiferromagnetic one.

The composition of the solid solutions depending on the content of paramagnetic atoms was modeled using the theoretical calculation of the magnetic susceptibility and comparison of the obtained values with the experimental ones.

The experimental dependences of  $\chi^{\text{para}}(\text{Fe})$  on the solid solution concentration were calculated within the framework of the diluted solid solution model. According to this model, the magnetic susceptibility is defined as the sum of the contributions from single paramagnetic atoms and their exchange-bound aggregates of Fe(III) atoms. The equation for calculating the paramagnetic component of the magnetic susceptibility of iron atoms is a sum of contributions of the magnetic susceptibility of monomers, dimers, trimers and tetramers with the antiferro- and ferromagnetic types of interaction:

$$\begin{aligned} \chi_{\text{calc}}^{\text{para}}(\text{Fe}) = & a_{\text{Fe(III)}}^{\text{mon}} \chi_{\text{Fe(III)}}^{\text{mon}} + a_{\text{Fe(III)}}^{\text{dim}(f)} \chi_{\text{Fe(III)}}^{\text{dim}(f)} + a_{\text{Fe(III)}}^{\text{dim}(a)} \chi_{\text{Fe(III)}}^{\text{dim}(a)} \\ & + a_{\text{Fe(III)}}^{\text{trim}(f)} \chi_{\text{Fe(III)}}^{\text{trim}(f)} + a_{\text{Fe(III)}}^{\text{trim}(a)} \chi_{\text{Fe(III)}}^{\text{trim}(a)} + a_{\text{Fe(III)}}^{\text{tet}(a)} \chi_{\text{Fe(III)}}^{\text{tet}(a)} \\ & + a_{\text{Fe(III)}}^{\text{tet}(f)} \chi_{\text{Fe(III)}}^{\text{tet}(f)} \end{aligned} \quad (1)$$

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