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Magnetic Structures of Some Multiferroics

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Abstract

We studied crystal and magnetic structures of some composite and single-phase multiferroics: $(x)MFe_2O_4$ + $(1\text{-}x)BaTiO_3$, $Ni_{3-y}Co_yV_2O_8$, and $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$. Composite multiferroics $(x)MFe_2O_4$ + $(1\text{-}x)BaTiO_3$ with x = (0.2; 0.3; 0.4) and M = (Ni, Co) have ferrimagnetic structure, which is described by the propagation vector k = 0. Oxides $Ni_{3-y}Co_yV_2O_8$ with y = (0.1; 0.3; 0.5) possess a modulated magnetic structure, described by the vector $k = (\delta, 0, 0)$, where δ = 0.283 and 0.348 at 7.4 K for y = 0.1 and 0.5, respectively. In the $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ multiferroic a magnetic order is destroyed at 600 K and the Fe-ion magnetic moment decreases from $\mu = 3.46(5)\ \mu_B$ at 300 K to zero at 600 K.

Keywords: multiferroic, magnetic structure, propagation vector, incommensurate-commensurate state, magnetic moment

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1. Introduction

Multiferroics are the class of crystalline materials in which, at least, two of three order parameters exist simultaneously: ferromagnetic or antiferromagnetic, ferroelectric, and ferroelastic degrees of freedom [1]. Multiferroics are classified on heterogeneous (composite) and homogeneous (single-phase) compounds. A study of magnetic properties of heterogeneous and homogeneous multiferroics and their evolution with temperature, stresses, radiation, electrical, magnetic fields and so on are necessary to shed light on the origin of a magnetoelectric effect. This effect allows controlling the polarization of a material using an external magnetic field and vice versa – a change of the magnetization with an electrical field. According to a phenomenological theory, the magnetoelectric response in a single-phased material is limited by dielectric constant and magnetic permeability [2]. Search of materials with high ferromagnetic and ferroelectric properties is actual task now. A magnetoelectric effect in composite multiferroics is significantly higher in its value than that in homogeneous materials [3]. Due to large magnetoelectric effect, such multiferroics have good perspective for application as magnetic sensors, capacity electromagnets, elements of magnetic memory, logic elements of information processing systems etc. [4, 5]. In single-phase multiferroics a value of interaction between magnetic and ferroelectric degrees of freedom relates with a spin-orbital couple, and so, depends on crystal state and magnetic structure of a sample. Therefore, for understanding mechanism of magnetoelectric effect in composite and single-phase multiferroics it is important to determine structure and magnetic characteristics and their evolution with temperature and concentration of doping elements.

The aim of the paper is studying crystal and magnetic structures of some multiferroics by X-ray and neutron diffraction.

2. Methods

Composite multiferroics $(x)MFe_2O_4$ + $(1\text{-}x)BaTiO_3$, with x = (0.2; 0.3; 0.4) and M = (Ni or Co), have been synthesized from the spinel $NiFe_2O_4$ (or $CoFe_2O_4$) and barium titanate ($BaTiO_3$). Mixing components in the desired ratio, we made pellets of the $(x)MFe_2O_4$ + $(1\text{-}x)BaTiO_3$ samples, which were heat-treated at 1150 μC for 4 hours. High resolution X-ray powder diffractions (XRD) patterns were recorded at room temperature (RT) using Bruker D8 diffractometer with Cu K_α radiation (wavelength λ = 1.54056 μ). Patterns were obtained in the range scattering (10 – 120) degrees. Neutron powder diffraction (NPD) patterns have been recorded at 293 K using the D2 diffractometer installed on a horizontal channel of the RWW-2M reactor (Zarechny, Russia). We used neutron length was λ = 1.805 μ.

Powder samples of $Ni_{3-y}Co_yV_2O_8$ with y = (0.1; 0.3; 0.5) were synthesized using a solid-state reaction method with NiO, Co_3O_4, and V_2O_5 as starting materials. Reagents were mixed in the desired ratio and heated in Al_2O_3 crucibles. Samples were annealed in air at 800 °C. The XRD measurements were performed at RT with an X-ray diffractometer (Philips X'PERT MPD) using Cu K_α radiation. The NPD patterns were recorded in temperature range from 2.8 K up to 9.0 K with the HRPD diffractometer, installed at the HANARO reactor in the Korea Atomic Energy Research Institute. The wavelength of the incident beam was λ = 1.837 μ.

The sample $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ was synthesized by crystallization in a solution. The NPD patterns have been recorded with the high resolution powder diffractometer B1 mounted on a horizontal channel of the reactor in Institute of Laue-Lanjevine (Grenoble, France). The neutron wavelength was λ = 1.5395 μ; measurements have been carried out in the range (300 – 1000) K and the scattering interval (10 – 130) degrees.

The analysis of all XRD and NPD patterns was performed using the software package "Fullprof" [6].

3. Results

Fig. 1a shows observed and calculated XRD patterns of composite multiferroic $0.2(NiFe_2O_4)$ + $0.8(BaTiO_3)$ at RT. The XRD patterns of $x(MFe_2O_4)$ + $(1\text{-}x)BaTiO_3$ composites with x = (0.3 and 0.4), and M = (Ni and Co) are similar to patterns, presented in Fig. 1. The $NiFe_2O_4$ (or $CoFe_2O_4$) is a magnetic component of composites and it crystallizes in the cubic structure (space group $Fd\text{-}3m$), in which Fe-ions occupy the half of the 8a and 81 % of 16d sites, respectively. The Ni-ions occupy 50 % of the 8a and 19 % of 16d

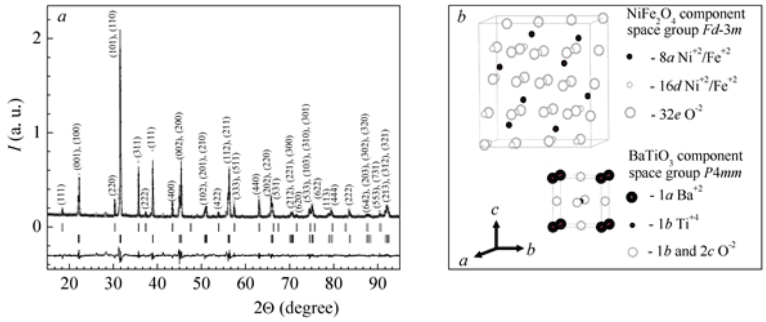

Figure 1: In (*a*) observed (points), calculated (line), and difference (bottom) XRD patterns of composite multiferroic 0.2($NiFe_2O_4$) + 0.8($BaTiO_3$). In (*b*) crystal structures of magnetic ($NiFe_2O_4$) and ferroelectric ($BaTiO_3$) components.

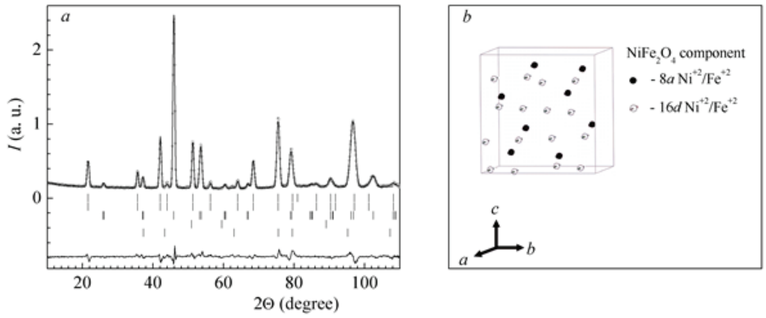

Figure 2: In (*a*) observed (points), calculated (line), and difference (bottom) NPD patterns of the composite multiferroic 0.2($NiFe_2O_4$) + 0.8($BaTiO_3$) at 293 K (RWW-2M reactor, λ = 1.805 μ). In (*b*) their magnetic structures with a propagation vector k = 0.

positions, respectively. The $BaTiO_3$ is a ferroelectric component; its crystal structure is tetragonal structure and belongs to *P4mm* space group. Crystal unit cells of magnetic and ferroelectric components of composite multiferroic are presented in Fig. 1b.

Fig. 2a represents observed and calculated NPD patterns of the composites 0.2($NiFe_2O_4$) + 0.8($BaTiO_3$) at RT; a spin ordering in magnetic component is presented in Fig. 2b. The magnetic structure is described by the propagation vector k = 0. Magnetic moments of Ni/Co- and Fe-ions are antiparallel and their values are given in Table 1. A difference between magnetic moment values at the 8*a* and 16*d* positions is caused by a distinction of the Fe- and Ni/Co-ion moment magnitudes. As one can see in Table 1, the Fe-ion magnetic moment is by the factor 1.8 more than Ni-ion moment. An average magnetic moment increases slowly in the 8*a* position and decreases in the 16*d* site with a rise of the concentration x, pointing to a displacement of the Ni-ions from the 16*d* position to the 8*a* site. Therefore, a presence of the $BaTiO_3$ in the composite multiferroics induces a driving force to move the Ni-ions and decrease a degree of inverse spinel structure.

Fig. 3 shows observed and calculated NPD patterns of the $Ni_{2.9}Co_{0.1}V_2O_8$ multiferroic at 2.85 K (*a*), 4.85 K (*b*), and 7.40 K (*c*). Fig. 4 presents observed and calculated NPD patterns of the $Ni_{2.5}Co_{0.1}V_2O_8$ at 2.83 K (*a*), 4.20 K (*b*), and 7.30 K (*c*). Both samples crystallize in the orthorhombic structure, described by the space group *Cmca*. They

Composite multiferroic	μ_{8a} (μ_B)	μ_{16d} (μ_B)
0.2($CoFe_2O_4$) + 0.8($BaTiO_3$)	3.1(2)	-4.6(9)
0.3($CoFe_2O_4$) + 0.7($BaTiO_3$)	3.5(1)	-4.1(7)
0.4($CoFe_2O_4$) + 0.6($BaTiO_3$)	3.8(8)	-3.8(7)
0.2($NiFe_2O_4$) + 0.8($BaTiO_3$)	3.6(1)	-3.0(8)
0.3($NiFe_2O_4$) + 0.7($BaTiO_3$)	3.8(9)	-2.7(7)
0.4($NiFe_2O_4$) + 0.6($BaTiO_3$)	3.9(8)	-2.8(6)

Table 1: The Fe/Co-ion and Fe/Ni-ion magnetic moments at the 8*a* and 16*d* positions for *x*($CoFe_2O_4$) + (1-*x*)$BaTiO_3$ and *x*($NiFe_2O_4$) + (1-*x*)$BaTiO_3$ composite multiferroics, respectively; the concentration *x* = (0.2; 0.3; and 0.4).

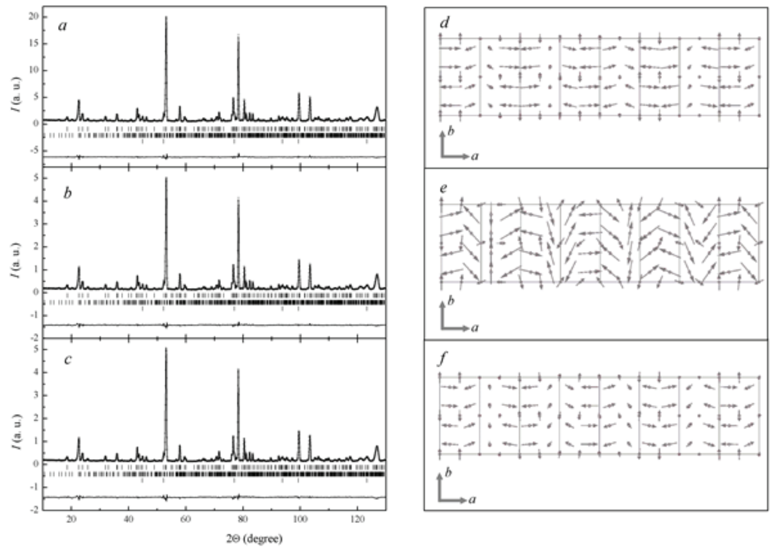

Figure 3: Observed (points), calculated (line), and difference (bottom) NPD patterns of the $Ni_{2.9}Co_{0.1}V_2O_8$ multiferroic at (*a*) 2.85 K, (*b*) 4.85 K and (*c*) 7.40 K (HRPD, HANARO reactor, λ = 1.837 μ). Magnetic structures with a propagation vector *k* = (δ, 0, 0) at (*d*) 2.85 K, (*e*) 4.85 K and (*f*) 7.40 K.

belong to frustrated Kagome-staircase structures [7]. The structure is characterized by edge-sharing MO_6 octahedra, which are isolated by nonmagnetic vanadium ions. The Ni/Co-ions form buckled planes, containing two inequivalent positions the 4*a* and 8*e*.

We have refined a magnetic structure of these multiferroics and have determined that it is like a longitudinal spin wave with the vector *k* = (δ, 0, 0), where δ = 0.283 and 0.348 at 7.4 K for *y* = 0.1 and 0.5, respectively. Magnetic moments are predominantly oriented along the *a*-axis. Magnetic structures of the $Ni_{2.9}Co_{0.1}V_2O_8$ at 2.85 K, 4.85 K, and 7.40 K as well as of the $Ni_{2.5}Co_{0.5}V_2O_8$ at 2.83 K, 4.20 K, and 7.30 K are given in Fig. 3 and Fig. 4.

Fig. 5 presents temperature dependences of the propagation vector and the magnetic moment value at the 8*e* position for the $Ni_{3-y}Co_yV_2O_8$ samples with *y* = 0.1 and 0.5. As it is seen, the temperature evolution of the vector *k* for *y* = 0.1 is very weak, that confirms literature data, showing a substitution of 3.5 % Ni-ions by cobalt suppresses the explicit temperature dependence of the vector *k*, which is observed in the parent compound. However, we found that the vector *k* for *y* = 0.5 exhibited the definite temperature dependence, that differed from a dependence of the *k* in the undoped

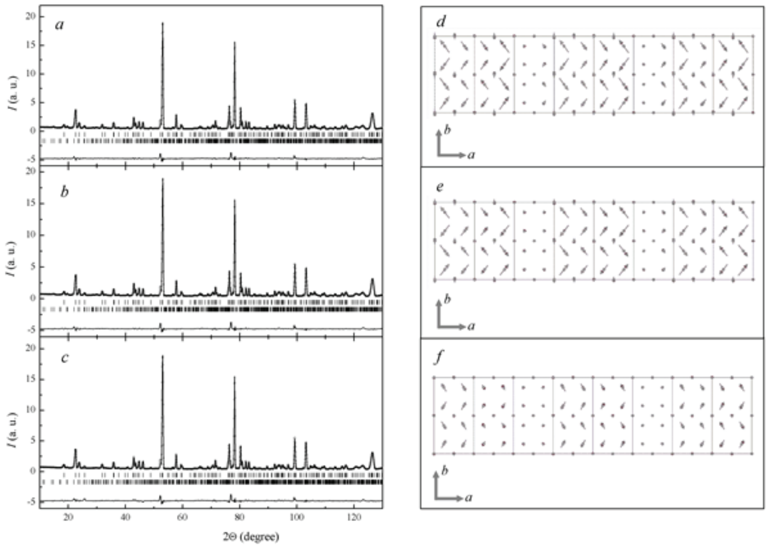

Figure 4: Observed (points), calculated (line), and difference (bottom) NPD patterns of the $Ni_{2.5}Co_{0.1}V_2O_8$ multiferroic at (*a*) 2.83 K, (*b*) 4.20 K and (*c*) 7.30 K (HRPD, HANARO reactor, λ = 1.837 μ). Magnetic structures with a propagation vector *k* = (δ, 0, 0) at temperature (*d*) 2.83 K, (*e*) 4.20 K, and (*f*) 7.30 K.

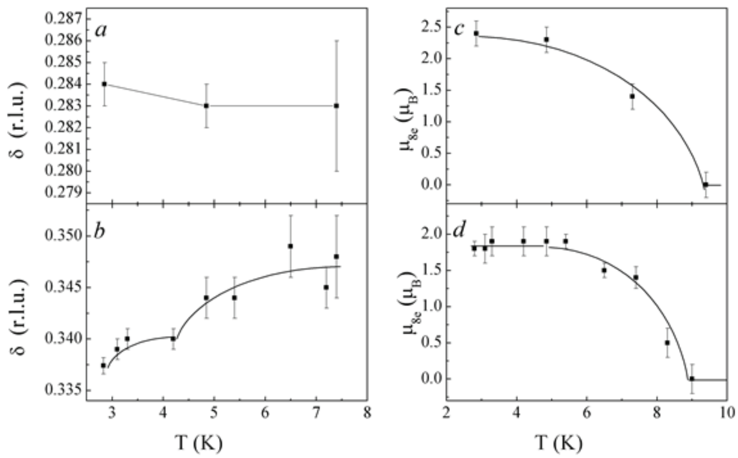

Figure 5: Temperature dependence of the propagation vector of $Ni_{3-y}Co_yV_2O_8$ for (*a*) *y* = 0.1 and (*b*) *y* = 0.5. Temperature dependence of the Ni/Co-ion magnetic moment at the 8*e* position for (*c*) *y* = 0.1 and (*d*) *y* = 0.5.

sample. For *y* = 0.5 the Ni/Co-ion magnetic moment decreases from 1.8 μ_B at 2 K down to zero at 9 K.

Fig. 6a shows NDP patterns of the $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ multiferroic at 300 K. A crystal structure of this multiferroic is rhombohedral up to about 1100 K and belongs to the *R*3*c* space group. The Ba-ions are placed in the Bi-sublattice and the Ti-ions partly occupy the Fe-sublattice of the $BiFeO_3$ structure (see Fig. 6b).

To refine a magnetic structure of the $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ we used the magnitude of the vector *k* = (0.0045, 0.0045, 0) from Ref. [8]. The magnetic structure is described as the cycloidal spiral. The Fe-ion moments are oriented ferromagnetically in planes

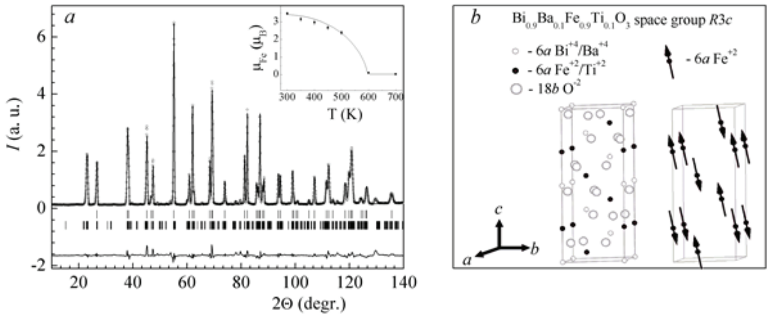

Figure 6: In (*a*) observed (points), calculated (line), and difference (bottom) NPD patterns of the $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ at 300 K (B1, Institute of Laue-Lanjevine reactor, λ = 1.5395 μ). In the insert the temperature dependence of Fe-ion magnetic moment. In (*b*) the crystal and magnetic structures at 300 K. The large symbols present the Bi/Ba-ions; the black symbols are Fe/Ti-ions; small symbols show the O-ions.

perpendicular to the [111] direction and antiferromagnetically in adjacent planes. Fig. 6 presents also the temperature dependence of Fe-ion magnetic moments. As one can see, moments decrease almost linear with temperature from (3.46 ± 0.05) μ_B down to (2.38 ± 0.08) μ_B over region (300 – 500) K. The temperature dependence of the moments becomes abrupt over region (500 – 600) K and they vanish then at 600 K by a magnetic phase transition of second order.

4. Conclusion

The X-ray and neutron diffraction experiments have been carried out on the multiferroics (x)MFe_2O_4 + (1-x)$BaTiO_3$ (with x = 0.2, 0.3, and 0.4; M = Ni and Co), $Ni_{3-y}Co_yV_2O_8$ (with y = 0.1, 0.3, and 0.5) as well as $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$.

In the composite multiferroic (x)MFe_2O_4 + (1-x)$BaTiO_3$ the magnetic component has the ferrimagnetic structure that is described by the propagation vector k = 0. The value of the Ni/Fe-ion magnetic moment increases at 8*a* position and decreases at the 16*d* sites, when the concentration x arises. Incommensurate magnetic structure of the $Ni_{3-y}Co_yV_2O_8$ oxides with y = (0.1, 0.3, and 0.5) is described by vector k = (δ, 0, 0), where δ = 0.283 and 0.348 at 7.4 K for y = 0.1 and 0.5, respectively. The Fe-spins are predominantly oriented along the *a*-axis. The Ni/Co-ion magnetic moment decreases from 2.4 μ_B at 2 K down to zero at 9 K for y = 0.1 and from 1.8 μ_B down to zero for y = 0.5. The $Bi_{0.9}Ba_{0.1}Fe_{0.9}Ti_{0.1}O_3$ multiferroic has a modulated magnetic structure with the propagation vector k = (0.0045, 0.0045, 0). The Fe-ion moments are oriented ferromagnetically in planes perpendicular to the [111] direction and antiferromagnetically in adjacent planes. The value of the Fe-ion moment decreases with temperature from 3.46(5) μ_B at 300 K and vanishes at 600 K.

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