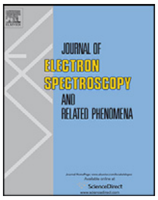
Journal of Electron Spectroscopy and Related Phenomena 184 (2011) 16–23

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec



X-ray photoelectron study of the valence state of iron in iron-containing single-crystal ($BiFeO_3$, $PbFe_{1/2}Nb_{1/2}O_3$), and ceramic ($BaFe_{1/2}Nb_{1/2}O_3$) multiferroics

A.T. Kozakov[a], A.G. Kochur[b,*], K.A. Googlev[a], A.V. Nikolsky[a], I.P. Raevski[a], V.G. Smotrakov[a], V.V. Yeremkin[a]

[a] *Scientific-Research Institute of Physics at Southern Federal University, 194 Stachki av., Rostov-na-Donu 344190, Russia*
[b] *Rostov State University of Transport Communication, Chair of Physics, 2 Narodnogo Opolcheniya, Rostov-na-Donu 344038, Russia*

ARTICLE INFO

Article history:
Received 26 July 2010
Received in revised form 19 October 2010
Accepted 23 October 2010
Available online 9 November 2010

Keywords:
X-ray photoelectron spectra
Multiplet structure
Lead ferroniobate
Barium ferroniobate bismuth ferrite
Hematite
Fe valence state

ABSTRACT

Fe2p, Fe3p, and Fe3s X-ray photoelectron spectra (XPS) are measured with high resolution in single-crystal multiferroics $BiFeO_3$ and $PbFe_{1/2}Nb_{1/2}O_3$, as well as in reference samples Fe_2O_3, $FeSO_4{\cdot}7H_2O$, $FeC_2O_4{\cdot}2H_2O$. The spectra are assigned based on an isolated-ion approximation calculation. Single-crystal multiferroics and Fe_2O_3 are shown to have the Fe ions only in the Fe^{3+} valence state. Ceramic samples of $BaFe_{1/2}Nb_{1/2}O_3$ with various relative Fe^{2+}/Fe^{3+} abundances are synthesized in various conditions. An approximate method to determine the Fe^{2+}/Fe^{3+} ratio in a sample is suggested. The method is based on the fitting of the sample's 2p XPS with a superposition of Fe^{2+} and Fe^{3+} 2p spectra. An effect of temperature regimes of sintering and annealing on the Fe^{2+}/Fe^{3+} ratio is demonstrated.

1. Introduction

Lead ferroniobate $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) and bismuth ferrite $BiFeO_3$ (BFO) are well-known multiferroics combining ferroelectric and ferro-/antiferromagnetic properties. They belong to the structural type of perovskites and, at room temperatures, they have rhombohedrically distorted prototypic cell with a space group of symmetry R3c. A rhombohedric elementary cell contains two formula units [1]. In $BiFeO_3$, the ferroelectric-to-paraelectric transient temperature is $T_c = 830\,^{\circ}C$ while antiferromagnetic-to-paramagnetic $T_N = 370\,^{\circ}C$ [2]. As for the PFN, it has two ferroelectric phase transitions [3]. One transition at 335 K is from the monoclinic ferroelectric phase to tetragonal phase, ferroelectric as well, another one at 376 K from ferroelectric to paraelectric phase. Moreover, PFN has two magnetic phase transitions. At Néel temperature $T_N = 150$ K antiferromagnetic-to-paramagnetic transition takes place [4] while at temperatures lower than 10 K PFN demonstrate ferromagnetic properties. [5].

The crystal structure of BFO is composed of the chains of octahedral FeO_6 complexes connected by vertexes while the Bi ions are in cavities between the octahedrons. The octahedrons are significantly distorted, and the Bi ions are shifted towards the Fe ions [6]. The Fe ions are also shifted from the octahedron's centres, so as each Fe ion has three oxygen neighbors at 1.96 Å and three at 2.11 Å.

In PFN, half of the Fe^{3+} ions are replaced with the Nb^{3+} ions [3]. The crystal structure of the PFN is also represented by the chains of the octahedrons FeO_6 and NbO_6, with the Pb ions in cavities. Both Fe and Nb ions are somewhat shifted from the octahedron's centres so as for two Fe(Nb) ions their distance from oxygen ions is 2.004–2.06 Å, whereas for four other Fe(Nb) ions this distance is 2.13–2.15 Å [7,8].

Hematite (α-Fe_2O_3), which we use here as a reference compound, has a rhombohedral crystal structure of corundum with Fe^{3+} cations inside distorted octahedrons of the rhombohedral lattice [3,4]. Distances between the iron located approximately in the centre of the octahedron and the oxygen atoms displaced from the position of a regular octahedron as reported by various sources are 1.95–1.945 Å and 2.08–2.11 Å [9,10]. α-Fe_2O_3 is also antiferromagnetic (above 260 K, it is a weak ferromagnet) [9,10].These data show that one of the major structural units of the hematite (an octahedron FeO_6), without changing significantly its size, forms the structural units of bismuth ferrite and lead ferroniobat, although in the lattice of the PFN the octahedrons are somewhat bigger. In all those three compounds, the magnetic properties are due to the Fe ions octahedrically surrounded with the oxygen ions.One

---

[*] Corresponding author. Tel.: +7 863 235 75 92; fax: +7 863 245 06 13.
E-mail address: agk@rgups.ru (A.G. Kochur).

0368-2048/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2010.10.004

of the problems which has not yet been resolved, is the question of whether BFO and PFN contain not only Fe^{3+} but also Fe^{2+} ions. This issue becomes especially important for the thin films made exclusively of $BiFeO_3$, where both A and B sites of the perovskite structure are substituted [11–15]. Specifically it is supposed that the presence of the Fe^{2+} ions due to the oxygen vacancies determines the semi-conducting properties of this compound, and its high electric conduction [11].

In a number of works, attempts have been made to see whether both Fe^{3+} and Fe^{2+} are present in a multiferroic, based on the shape of the Fe2p X-ray photoelectron spectrum (XPS) [11–15]. The approach applied suggested a priori that the Fe2p XPS of single-crystal multiferroics can be treated the usual way, when the structureless maximum of the $Fe2p_{3/2}$ X-ray spectra is decomposed into a superposition of symmetric components. The $Fe2p_{3/2}$ component with the binding energy of 710.8–711 eV was assigned to the Fe^{3+} state while that with 709.5–710 eV, to the Fe^{2+} state.

This approach seems to be questionable. Indeed, it is known since the sixties [16] that due to the multiplet splitting effect in the configurations $2p^5 3d^n$ the spectra having to do with the 2p-vacancies in 3d-metals with unfilled 3d-subshells have complex asymmetric profiles. The effect of the multiplet splitting on 2p XPS of Mn^{2+} in MnF_2 is studied in [17]. Both $2p_{3/2}$ and $2p_{1/2}$ components of the Mn2p XPS are found to be complex asymmetric groups of multiplet components. Since both in Mn^{2+} and in Fe^{3+} the ionic configuration of the 3d-metal ion is the same, one should expect similarity in the profiles of the 2p XPS of those two ions.

The aim of this work is to study the valence state of the Fe ions in single-crystal $BiFeO_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ using 2p, 3s and 3p XPS. The trivalent iron α-Fe_2O_3, and bivalent iron $FeSO_4{\cdot}7H_2O$ and $FeC_2O_4{\cdot}2H_2O$ compounds are used as reference ones.

We also study Fe2p-spectra of the $BaFe_{1/2}Nb_{1/2}O_3$ ceramic samples obtained at various sintering temperatures and annealed in presence of CO. We propose an approximate method of Fe^{2+}/Fe^{3+} determination based on decompositions of the Fe2p spectral profiles into superpositions of the Fe^{2+} and Fe^{3+} spectra, which are distinctly different from each other.

The spectra are assigned based on an intermediate-coupling isolated-ion calculations.

2. Experimental

Cubic shape single crystals of $BiFeO_3$ with the cubic edge of 1 mm were grown from the solution-melt of 0.756 Bi_2O_3 + 0.179 Fe_2O_3 + 0.065 NaCl at the crystallization temperature range of 930–820 °C by the method described in [18]. The dendrite forms of $BiFeO_3$ were obtained from the solution-melt $Bi_2O_3 + Fe_2O_3 + B_2O_3$ (89.6:7.7:2.7% wt.) as proposed in [19], in the temperature range of 850–620 °C at the cooling rate of 5 °C/h. In addition, black isometric Fe_2O_3 crystals of pseudocubic habit with the structure of hematite were obtained in the temperature range of 1000–850 °C from the system $Bi_2O_3 + Fe_2O_3 + B_2O_3$ (82.4:13.1:4.5% wt.). Single crystals of $PbFe_{0.5}Nb_{0.5}O_3$ (PFN) in the form of black crystalline aggregate up to 3–5 mm on edge, were obtained by mass crystallization from the solution-melt in the temperature range of 1010–850 °C. The mixture of PbO and B_2O_3 (0.35:0.65 wt.) was used as a solvent.

Ceramic samples of $BaFe_{0.5}Nb_{0.5}O_3$ were obtained from initial fine-dispersed powder by sintering at the temperature of 1340 °C. To increase the Fe^{2+} abundance, some of the samples were additionally annealed in presence of CO at various temperatures.

X-ray photoelectron spectra were obtained using X-ray photoelectron microprobe ESCALAB 250. XPS were excited with a monochromatized AlKα-line radiation. Absolute resolved energy interval was of 0.5 eV, which was determined by the $Ag3d_{5/2}$ line. The diameter of the X-ray spot on a sample was 500 μm; it was small enough to study the samples obtained. Combined exposure to slow electrons and ions was employed to remove the positive charge on the sample. Contamination-free surfaces of single crystals were obtained by the diamond file scribing in vacuum within a sample-preparation chamber at a pressure of about 1×10^{-8} torr. The state of the surface was monitored using Bi4f, Nb3d, and O1s XPS lines for bismuth ferrite, lead ferroniobate, and hematite. The carbon content on the surface of all three crystals was vanishingly small: the C1s line was hardly visible on the background. However, the intensity of the C1s line was still enough to calibrate the core levels binding energies. The C1s level binding energy was taken to be 285 eV.

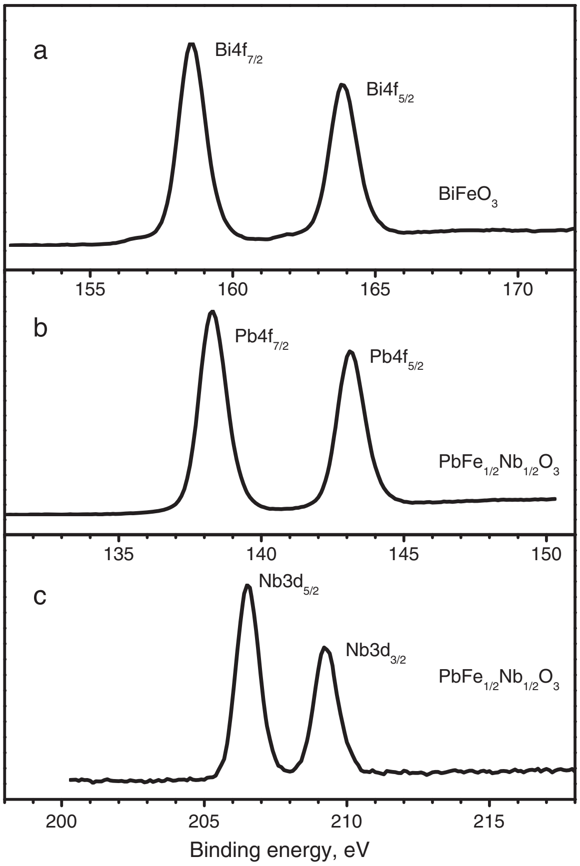


Fig. 1. X-ray photoelectron spectra: Bi4f in $BiFeO_3$ (a), Pb4f in $PbFe_{1/2}Nb_{1/2}O_3$ (b), and Nb3d in $PbFe_{1/2}Nb_{1/2}O_3$ (c).

All the X-ray photoelectron spectra presented in Figs. 1–5 and 7,8 are the raw spectra which underwent no smoothing. Relative mean standard deviation $\sigma/N \approx 1/N^{1/2}$ (N being the number of counts at the maximum of an electron line) was about 0.3% for all the spectra with the exception of the $PbFe_{1/2}Nb_{1/2}O_3$ Fe3s line, for which σ/N was about 1%.

Bi4f, Pb4f, and Nb3d XPS lines from the surfaces of $BiFeO_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ are shown in Fig. 1a–c. O1s XPS lines from Fe_2O_3, $BiFeO_3$, and $PbFe_{1/2}Nb_{1/2}O_3$ are presented in Fig. 2a–c.

It is evident from the doublet Bi4f $_{7/2,5/2}$, $Pb4f_{7/2,5/2}$, and $Nb3d_{3/2,1/2}$ lines (see Fig. 1) that bismuth, lead and niobium are each in a single chemical state. Decomposition of the O1s lines (Fig. 2) shows that together with the component A corresponding to oxygen–metal bonds, there is also a smaller-intensity component B, which may be assigned either to an adsorbed oxygen, or to the surface effects [20,21]. Its percentage for Fe_2O_3, $BiFeO_3$ and $PbFe_{1/2}Nb_{1/2}O_3$ is 14%, 10%, and 6%. It is believed [20,21] that such intensities of those components do not distort the results of the XPS studies.