Journal of Electron Spectroscopy and Related Phenomena 184 (2011) 508–516

Contents lists available at SciVerse ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

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

Valence and magnetic state of transition-metal and rare-earth ions in single-crystal multiferroics RMn_2O_5 (R = Y, Bi, Eu, Gd) from X-ray photoelectron spectroscopy data

A.T. Kozakov[a], A.G. Kochur[b,*], A.V. Nikolsky[a], K.A. Googlev[a], V.G. Smotrakov[a], V.V. Eremkin[a]

[a] Scientific-Research Institute of Physics at Southern Federal University, 194 Stachki, Rostov-na-Donu 344194, Russia
[b] Rostov State University of Transport Communication, 2 Narodnogo Opolcheniya, Rostov-na-Donu 344038, Russia

ARTICLE INFO

Article history:
Received 1 February 2011
Received in revised form 17 August 2011
Accepted 20 August 2011
Available online 27 August 2011

Keywords:
Orthorhombic manganates
Hexagonal manganite
Multiferroics
XPS
Multiplet structure

ABSTRACT

Single crystals of orthorhombic multiferroics RMn_2O_5 (R = Y, Bi, Eu, Gd), and of hexagonal manganite $YMnO_3$ are grown. X-ray photoelectron spectra of the core levels of the Mn, Y, Bi, Eu, Gd, and O atoms in multiferroics are obtained at room temperature with the ESCALAB 250 microprobe system with monochromatization of the exciting X-ray radiation. X-ray photoelectron spectra of Mn2p, Mn3s, R4s, and R4d (R = Eu, Gd) levels are assigned based on one-configuration isolated-ion approximation calculations with taking the temperature effect into account. It is shown using the photoelectron spectroscopy methods that both Mn^{3+} and Mn^{4+} ions are present in orthorhombic multiferroics, while Eu and Gd are in trivalent state. Paramagnetic moments per structural unit are calculated and compared with those determined from our spectroscopic data and with the data from other authors.

1. Introduction

Multiferroics are the substances where both electric dipoles and magnetic moments can be ordered simultaneously. They demonstrate magnoelectric (ME) effect, i.e., electric dipoles ordering upon application of magnetic field, or magnetic ordering upon application of electric field. The possibility of the ME effect was discussed by Curie [1] based on symmetry considerations. Later on, many prominent physicists addressed general questions of magnetoelectricity, P. Debye, L. Landau, Van Vleck among them.

Smolenskii and Ioffe [2] were the first to predict simultaneous electric and magnetic ordering in concrete ABO_3 perovskite-type compounds. Later on, Smolenskii with co-workers synthesized the first multiferroics which combined ferroelectric and antiferromagnetic properties (see [3] and references therein).

Europium manganate was the first compound among the rare-earth orthorhombic manganates RMn_2O_5 (R = rare earth, Y, or Bi), in which simultaneous segnetoelectric and magnetic orderings were discovered in 1988 [4,5]. Up to now, other materials of the RMn_2O_5 family were synthesized, their crystal structures [6–9], phase transitions temperatures [10,11], the peculiarities of their electric and magnetic subsystems and interaction between them [12–15] were studied. Those studies allowed assigning the whole family to multiferroics. Generally, the rare-earth manganates have three magnetic sublattices, R^{3+}, Mn^{3+}, and Mn^{4+} [8]. Mn^{3+} and Mn^{4+} occupy two different crystallic positions in the RMn_2O_5 compounds.

The neutron diffraction data show that the magnetic structure in the RMn_2O_5 compounds is complex enough, the magnetic moments of the Mn^{3+} and Mn^{4+} ions form spiral ordering in space below the T_N temperature, which is about 40 K for all the RMn_2O_5 materials [5–8]. Except neutron diffraction, the studies of static magnetic sensitivity were performed [7,16–21] both at temperatures lower than T_N and in a paramagnetic region. In the latter case, the studies provide the information on the paramagnetic moment of a compound which can be expressed with local magnetic moments on the compound's magnetic ions. The scarce existing data on local ionic and paramagnetic moments of the RMn_2O_5 compounds need to be supported by other methods. Therefore, it is interesting to estimate the local moments on the transition and rare-earth ions from Mn2p, Mn3s, and R4s X-ray photoelectron spectra (XPS) [22–27].

The aim of this work is to study the valence and magnetic state of the transition and rare-earth ions in single crystals of the orthorhombic manganates RMn_2O_5 (R = Eu, Gd, Y, Bi) via core level X-ray photoelectron spectroscopy.

The spectra are assigned based on calculations in the intermediate-coupling isolated-ion approximation. The isolated-ion approximation, in spite of its crudeness, often allows

---

* 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 © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2011.08.006

understanding the nature of the main features of the XPS spectra, and identification of valence and magnetic state of an atom. It has recently been successfully applied to the study of 3d-metals in polynuclear metalloorganic complexes [28–30] and iron-containing multiferroics [31].

2. Crystal structure of the RMn_2O_5 manganates

The RMn_2O_5 manganates crystallize into the *Pbam* space symmetry group at room temperatures [5,7,10,32,33]. The principal structural units are the $Mn^{4+}O_6$ octahedrons and $Mn^{3+}O_5$ pyramids. The quadrivalent Mn^{4+} ions lie in the centres of the O_6 octahedrons, while the trivalent Mn^{3+} ions in the centres of a distorted quadratic bases of the $Mn^{3+}O_5$ pyramids. The $Mn^{4+}O_6$ octahedrons form the chains parallel to the *c* axis of the orthorhombic cell of the *Pbam* symmetry. Two pyramids $Mn^{3+}O_5$ with a joint base edge form a $Mn_2{}^{3+}O_8$ group, which connects the neighbouring octahedron chains through the joint oxygen atoms. The R^{3+} ions are surrounded by the bound $Mn^{4+}O_6$ octahedrons and Mn^{3+} O_5 pyramids forming a distorted pentagon in the *ab* plane, therefore, the R^{3+} is surrounded by eight oxygen ions [5,7,10,32,33]. Generally, the 4f magnetic moments of the R^{3+} ions and the 3d magnetic moments of the Mn^{4+} and Mn^{3+} ions are responsible for the complex magnetism in the RMn_2O_5 family.

Hexagonal $YMnO_3$ manganite, as well as YMn_2O_5, is assigned to multiferroics [5,32,34,35]. The crystal structure of manganites is non-centrosymmetrical [5]. They are ferroelectrics and antiferromagnets with the temperatures of the ferroelectric transition T_c of 570–990 K, and the temperatures of magnetic ordering T_N of 70–130 K. $RMnO_3$ crystallize into two structural phases, hexagonal and orthorhombic. Ferroelectric ordering takes place only in the hexagonal phase, whereas magnetic ordering happens in both phases. In a hexagonal ferroelectric structure, each Mn ion is surrounded by three in-plain oxygen atoms, and two out-of-plain oxygen atoms, therefore, the Mn ion is affected by a trigonal field. Basically, the structure consists of the $Mn^{3+}O_5$ bipyramids, which, being connected by the vertexes, form the layers perpendicular to the six-fold axis. The Mn ions are in the centres of the bipyramids, and the rare-earth ions are between the bipyramid layers [5,32,34,35].

3. Experimental

3.1. Crystal growth

The YMn_2O_5, $EuMn_2O_5$ and $GdMn_2O_5$ crystals were obtained from the flux $PbO–PbF_2–B_2O_3$ in the temperature interval from 1200 °C to 900 °C at the cooling rate of 5–8 °C/h. The solvents molar ratio was $PbF_2:PbO = 1.5:1$. The addition of B_2O_3 used as a mineralizer was not greater than 1 wt% of the charge mass. The concentration of the crystallized material in a charge was 25–30 wt%.

We used a 75 cm^3 platinum crucible with a hermetic platinum lid. After pouring off the mother melt, the crystals were washed clean by boiling in nitric acid. All the crystals had the shape of the elongated prisms of the size of up to 4 mm along the edge.

The crystals of $BiMn_2O_5$ in the form of the black-colour prisms were obtained from the flux $Bi_2O_3–MnO_2–B_2O_3$ (48.7:48.7:2.6 wt%) in the temperature interval 920–810 °C at the cooling rate of 5 °C/h.

Thin (10–40 μm) hexagonal black-colour plates of $YMnO_3$ were grown from the flux 0.9 Bi_2O_3–0.1 $YMnO_3$ (molar) in the temperature interval of 1200–940 °C at the cooling rate of about 10 °C/h by the method of [36].

X-ray diffraction analysis of the samples (grinded into powder) was performed at room temperature on a DRON-2.0 diffractometer using CoKα-radiation. RMn_2O_5 crystals were found to have orthorhombic symmetry with the following cell parameters: $a = 7.284$ Å, $b = 8.239$ Å, $c = 5.682$ Å (YMn_2O_5); $a = 7.304$ Å, $b = 8.567$ Å, $c = 5.694$ Å ($EuMn_2O_5$); $a = 7.365$ Å, $b = 8.559$ Å, $c = 5.687$ Å ($GdMn_2O_5$); $a = 7.560$ Å, $b = 8.544$ Å, $c = 5.763$ Å ($BiMn_2O_5$). The symmetry group is Pbam, elementary cell contains $Z = 4$ formula units. $YMnO_3$ crystals were found to have hexagonal symmetry with a symmetry group Pb$_3$cm and the cell parameters $a = 6.142$ Å, $c = 11.413$ Å, $Z = 6$. In all the five cases, no secondary phases were detected by the X-ray diffraction method.

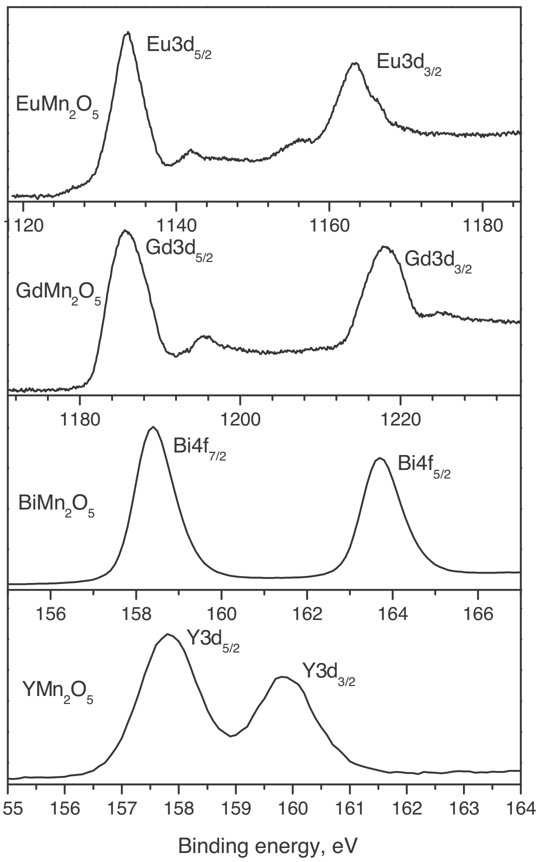

Fig. 1. XPS of the Eu3d-, Gd3d-, Bi4f-, and Y3d-levels in the $EuMn_2O_5$, $GdMn_2O_5$, $BiMn_2O_5$, and YMn_2O_5 single crystals.

3.2. X-ray photoelectron experiment

XPS from the surfaces of YMn_2O_5, $YMnO_3$, $BiMn_2O_5$, $EuMn_2O_5$, and $GdMn_2O_5$ were taken with an X-ray photoelectron microprobe ESCALAB 250 at the temperature of 23 °C. The spectra were excited with a monochromatized AlKα radiation. Absolute resolved energy interval was 0.5 eV, which was determined from 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 off 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^{-6} Pa.

The state of the surface was monitored using Bi4f, Y3d, Eu3d, Gd3d, and O1s lines. The carbon content on the surface of all three crystals was vanishingly small: the C1s line was hardly visible on the background. In Fig. 1, the Bi4f, Y3d, Eu3d, and Gd3d spectra from the surfaces of the single crystals RMn_2O_5 (R = Y, Bi, Eu, Gd) are presented. Fig. 2 shows the O1s lines from those samples. It