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XPS on $Nd_{0.6-x}Bi_xSr_{0.4}MnO_3$ nano powders

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ABSTRACT

The structural and electronic properties on $Nd_{0.6-x}Bi_xSr_{0.4}MnO_3$ nano powders with $x = 0$, 0.05 and 0.1 are reported. The compounds were prepared using sol-gel combustion method. X-ray diffraction studies confirm that all samples crystallize in orthorhombic structure having *Pnma* space group. The powders consist of spherical particles that tend to agglomerate, with average grain sizes of about 40–50 nm. XPS measurements reveal a shift toward lower binding energies of Mn 3*s*, Mn 2*p*, Nd 3*d*, and O 1*s* core levels with increasing Bi content, which can be explained by the larger 'c' lattice parameter and therefore larger atomic distances. The analysis of the core level XPS spectra proves the existence of both Mn^{4+} and Mn^{3+} ions in all samples, as well as the localization of Bi^{3+} ions in the perovskite lattice. The XPS valence-band is dominated by extensively hybridized Nd 4*f*-O 2*p* states, with contributions from Mn 3*d*-O 2*p* bonding and Mn 3*d* states.

1. Introduction

Rare-earth manganites with the chemical formula $R_{1-x}A_xMnO_3$ (where R = rare earth metal, A = alkaline-earth metal) are one of the most important class of materials which have been studied in the last years confirmed by the large number on results (> 16,900) searching "manganites" on WES. A mixed Mn^{3+} respectively Mn^{4+} valence could be easily induced by substituting the trivalent rare-earth metal with a divalent (monovalent) element. By substitutions, on R site, the crystal structure, the electronic, magnetic and transport properties are strongly affected. The strong interest in these materials is due to the both – basic and possible applications properties. Colossal magnetoresistance (CMR), metal-insulator transition, large magnetocaloric effect, multiferroic effect, charge ordering (CO), and phase separation are some of the most fascinating properties of these materials [1–10]. Many parameters, like A ion average radius, Mn^{3+}/Mn^{4+} ratio, the size mismatch of the cations, the vacancies, oxygen stoichiometry, the polaron effect, etc. play a crucial role. The physical properties of these materials are strongly affected by the grains size due to increasing the number of the surface atoms comparing with the number of volume atoms [11]. Manganite oxides have many technical applications like sensors, storage media, magnetic refrigeration, spintronics.

$Nd_{1-x}Sr_xMnO_3$ was reported to be an intermediate bandwidth manganites with two types of orbital order [12]. The first was reported in the region $0.52 \leq x < 0.63$, being of x^2-y^2 planar type OO state together with A-type antiferromagnetic order, the x^2-y^2 electrons conducting in ferromagnetic (FM) plane [13]. The second type is the heavily doped region, $0.63 \leq x \leq 0.80$, being of $3z^2$-r^2 rod-type OO state, associated with the *C*-type antiferromagnetic order in which charge dynamics shows one dimensional-like behavior along the F chain [14,15]. The transport and magnetic properties show high anisotropy [12]. The compound with $x = 0.6$ is ferromagnetic ordered, the Curie temperature T_C being higher than for the other doping concentrations at Sr site [16]. It was shown that a FM-metal to a PM - insulator transition is present around 280 K for the bulk sample. The reduction of the grain size to nanometric scale affects strongly the metal-insulator transition, the Curie temperature, and the resistivity. On the other hand, the magneto-resistance is almost not influenced by the dimensions of the grain sizes [17].

No data, according to our best knowledge, were reported on the influence of Bi substitution on the physical properties of $Nd_{1-x}Sr_xMnO_3$ compounds. It was shown that the increase of Bi concentration in $Pr_{0.6}Sr_{0.4}Mn_{1-x}Bi_xO_3$ powder samples with $x \leq 0.2$ has as result a weakening of the ferromagnetic order at low temperatures, T_C decreasing from 310 K ($x = 0.0$) to 225 K ($x = 0.2$) [18]. In $Pr_{0.6-x}Bi_xSr_{0.4}MnO_3$ compounds the metal-insulator transition and Curie temperatures decrease with the increasing of Bi concentration due to strong the hybridization between Bi($6s^2$) and O(2p) orbital [19]. An

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