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## Valence States of Metal Ions in $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ Thin Films

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We report valence states of ions in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  thin films grown by a reactive dc magnetron sputtering. The measurements were performed by means of high-energy X-ray photoelectron spectroscopy using synchrotron radiation. It was found that Ce ion in the compound is either in tetravalent or trivalent chemical state, manganese is in divalent, trivalent and tetravalent states, while La ion existing in oxide and hydroxide chemical species is in trivalent state.

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### 1. Introduction

Hole-doped manganese perovskites,  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  (here A is a divalent alkaline earth metal), exhibiting mixed valence of Mn ions ( $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ ) demonstrate a rich variety of electric transport and magnetic properties (metal-insulator transition, colossal magnetoresistance (CMR) phenomena). Similar electron-doped systems with mixed Mn valence ( $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ ) could be obtained by doping of the compounds with tetravalent cations such as Ce, Sn, and others. Nevertheless, valence state of ions in electron-doped manganites had not yet been sufficiently studied compared with the hole-doped systems.

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Since physical properties of the manganese perovskites depend strongly on microstructure and oxygen content, the aim of this work was to examine the chemical states of the ions and chemical composition of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  thin films after different sample treatment procedures.

## 2. Experimental

Thin  $\text{La}_{2/3}\text{Ce}_{1/3}\text{MnO}_3$  films were deposited on lattice-matched single crystal  $\text{NdGaO}_3(100)$  substrates by means of dc magnetron sputtering. The X-ray photoelectron spectroscopy (XPS) data were obtained with the tunable high-energy X-ray photoelectron spectrometer at the X-ray wiggler beam line BW2 of HASY-LAB (Hamburg). At the excitation energy of 3000 eV, the kinetic energy of the La and Ce core levels does not superimpose any of the Auger electron emission peaks originating from the atoms of the layer. The angle dependent data were obtained by rotating the sample relative to the electron analyzer counting electrons in the synchrotron radiation orbit plane at  $45^\circ$  relative to the incoming beam.

## 3. Results and discussion

X-ray diffraction (XRD)  $\theta-2\theta$  scans demonstrated high crystalline quality of the grown  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  thin films although weak reflexes seen at about  $28^\circ$  and  $33^\circ$  indicated presence of a negligible amount of  $\text{CeO}_2$  [1].

The Ce  $3d$  core level spectra measured at normal and grazing emission angles are shown in Fig. 1 (left part). It can be seen that the Ce  $3d$  state components  $3d_{5/2}$  and  $3d_{3/2}$  have complex multiplet structures consisting of four peaks ( $v, v', v'', v'''$ ) and ( $u, u', u'', u'''$ ), respectively. The peaks ( $v'''$  and  $u'''$ ) correspond to  $\text{Ce}^{4+} 3d^9 4f^0 L^0$  final states (here  $L$  is a ligand hole). The multiplet states arise from different cerium  $4f$  level occupancies in the final state: the lowest binding energy (BE) peaks ( $v, u$ ) and ( $v'', u''$ ) correspond to the mixed  $3d^9 4f^1 L^{-1}$  and  $3d^9 4f^2 L^{-2}$  final-state configurations of  $\text{Ce}^{4+}$  ions, respectively. The peaks  $v'$  and  $u'$  corresponding to a spin-orbit doublet of  $\text{Ce}^{3+}$  are observed at 864 and 902.6 eV for the  $3d_{5/2}$  and the  $3d_{3/2}$  levels of trivalent  $3d^9 4f^2 L^{-1}$  ion states. The relative concentration of  $\text{Ce}^{3+}$  calculated from XPS spectra showed 12% of the bulk (normal emission geometry) and about 20% of the topmost layer (grazing emission geometry), respectively. This difference in  $\text{Ce}^{3+}$  concentration is, probably, related to different stoichiometry of oxygen in the bulk and surface of the films. Increase in intensity of the peaks  $v'$  and  $u'$  after  $\text{Ar}^+$  ions sputtering (compare  $v'$  peak intensities in Fig. 1) and increase in trivalent cerium up to 18% in the bulk and 22% in the surface layer was observed. Therefore, sputtering by  $\text{Ar}^+$  ions partially reduces the  $\text{Ce}^{4+}$  ion concentration and increases the trivalent ion concentration in the  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  films.

Mn  $2p_{3/2}$  spectra of the  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  films consisting of a number of superimposed peaks are displayed in the right part of Fig. 1. Complex character of the spectra is evident in the plots of the second derivative (see bottom in Fig. 1

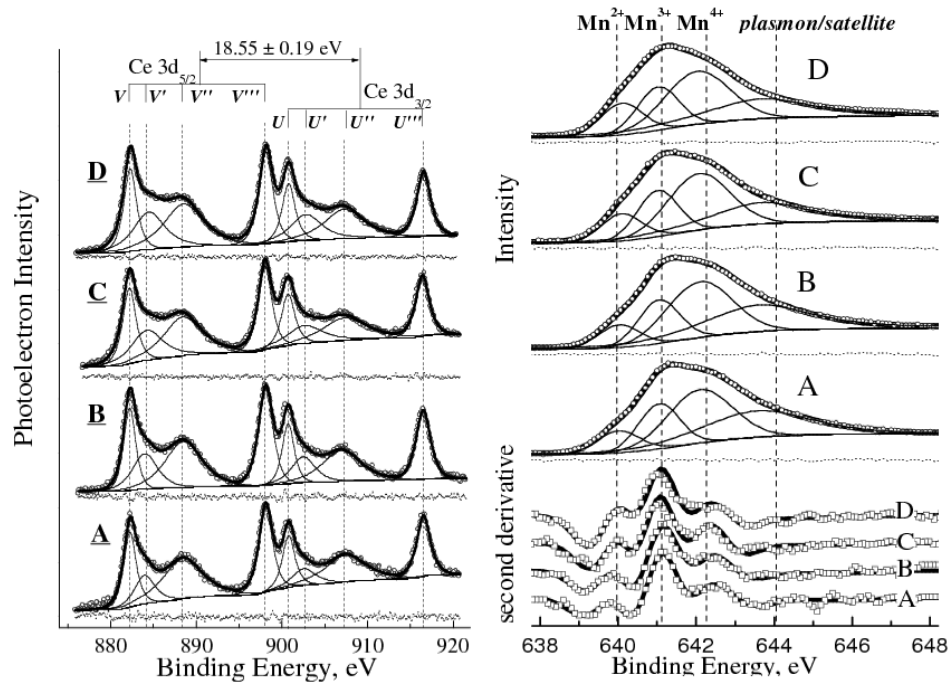


Fig. 1. Ce 3d (left part) and Mn 2p (right part) spectra of epitaxial  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  films just after deposition (curves A and B) and after  $\text{Ar}^+$  sputtering (curves C and D), measured at normal (A and C) and grazing (B and D) photoemission angles. Open circles represent the experimental spectra, thin solid lines are the spectral components, thick solid line is the spectra envelope and subtraction, and the dotted lines are for the residuals of peak fitting.

(right part)). The Mn  $2p_{3/2}$  spectra can be deconvoluted into three Mn peaks with different valence states. The formal valence of Mn in a bulk of the as-grown films is larger than 3 and thus it determines electron hopping between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions similar to that in hole-doped  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3+\delta}$  [2]. This is confirmed by coincidence of the Mn  $2p$  spectrum of the as-grown  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\gamma}$  film with that of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3+\gamma}$  [3]. These results can be used to predict transport and magnetic properties of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\gamma}$  films [1, 3]. In the topmost layer (grazing emission), the formal manganese valence is lower compared to that in a bulk. This is in consistence with lower oxygen content in the surface of  $\text{La}_{2/3}\text{Ce}_{1/3}\text{MnO}_3$  films. Preferential sputtering of oxygen by  $\text{Ar}^+$  ions results in reduced number of  $\text{Mn}^{4+}$  ions. The spectra are in good agreement with those obtained for  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}^{3+}$  films with reduced oxygen content obtained after annealing in vacuum at  $550^\circ\text{C}$  [3].

The La  $3d_{5/2}$  core level spectra measured before and after surface sputtering were deconvoluted into two doublets, corresponding to oxide and hydroxide

species. Sputtering of the films by  $\text{Ar}^+$  ions resulted in a more efficient removal of lanthanum hydroxide from film surface compared to similar process observed earlier for  $\text{LaNiO}_{3-x}$  films [4].

#### 4. Summary

Composition and valence states of ions in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\delta}$  thin films were investigated by means of high-energy XPS using synchrotron radiation. Investigations of Ce  $3d$  core level spectra showed that Ce ions are in tetravalent and trivalent chemical states. Partial conversion of tetra-cerium to trivalent ions has been indicated after  $\text{Ar}^+$  ion sputtering. Manganese in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}^{3+}$  thin films was found to be in divalent, trivalent and tetravalent states while La present in oxide and hydroxide species was trivalent.

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#### References

- [1] R. Butkutė, J. Devenson, M.A. Rosa, M. Godinho, A.K. Oginskis, F. Anisimovas, A. Vailionis, B. Vengalis, *Thin Solid Films* **515**, 599 (2006).
- [2] J.R. Sun, C.F. Yeung, K. Zhao, L.Z. Zhou, C.H. Leung, H.K. Wong, B.G. Shen, *Appl. Phys. Lett.* **76**, 1164 (2000).
- [3] D.J. Wang, C.M. Xiong, G.J. Liu, Y.W. Xie, B.G. Shen, J.R. Sun, *Physica B* **371**, 187 (2006).
- [4] S. Mickevičius, S. Grebinskij, V. Bondarenka, B. Vengalis, K. Sliuzienė, B.A. Orlovski, V. Osinniy, W. Drube, *J. All. Comp.* **107-111**, 107 (2006).