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Electronic structure of La 3d in gallate and aluminate single crystals

E. Talik[a], A. Novosselov[b], M. Kulpa[a], A. Pajaczkowska[b],*

[a]*Institute of Physics, University of Silesia, 40-007 Katowice, Poland*
[b]*Institute of Electronic Materials Technology, 01-919 Warsaw, Poland*

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Abstract

An investigation of the 3d X-ray photoelectron spectra of lanthanum in $LaGaO_3$, $SrLaAlO_4$, $SrLaGaO_4$ and $SrLaGa_3O_7$ is reported. The splitting of La 3d spectra is found to be more complicated that has been previously reported. The energy separation of the doublet structure $\underline{3d}^9 4f^0 L$ and $\underline{3d}^9 4f^1 \underline{L}$ decreases with the decrease of coordination number of the La ion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Single crystal; Electronic states; Photoelectron spectroscopies

1. Introduction

The investigation of electron structure of lanthanum in gallates and aluminates were performed in the group of compounds interesting as substrates for high-temperature superconducting (HTSc) thin films of $YBa_2Cu_3O_4$ (1:2:3), and $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2), and laser single crystals.

The following crystals of various chemical composition and structures were chosen: $SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) which crystallize in the tetragonal structure, space group *I*4/*mmm* (K_2NiF_4-type structure consisting of perovskite-type and rock-salt layers) [1]. $LaGaO_3$ (LG) crystallizes in orthorhombic perovskite, space group *Pbnm* [1,2]. $SrLaGa_3O_7$ (SLG3) crystallizes in the tetragonal structure of melilite belonging to the space group $P42_1m$, and doped crystals exhibit optically nonlinear properties [3].

The lanthanum 3d electron structure was mainly investigated by X-ray photoelectron spectroscopy (XPS) in metal alloys and shows one double peak [4]. Two double peaks of La 3d were found in some oxides, sulfur and boride compounds. This was explained by the fact that La $3d_{3/2}$ and La $3d_{5/2}$ spin–orbit components are each split into a doublet structure corresponding to states with the configuration $\underline{3d}^9 4f^0 L$ and $\underline{3d}^9 4f^1 \underline{L}$ where L indicates the oxygen(sulfur) ligand and the underlining denotes a hole [5]. The satellite peaks ascribed to charge transfer states appear in the photoelectron spectra of lanthanide (Ln) ions and the peak intensity and positions of those satellite peaks vary with the electronic state of the Ln ion. The lanthanides provide an example where the most probable final state involves less screening of the core hole than the lowest energy final state. This is opposite to other metals where the well-screened final state is also more probable and hence gives the more intense peak [6].

Our investigations of SLG crystal revealed that the electron structure of La 3d is more complicated that has been previously reported [4,5].

2. Experimental

The investigated single crystals were grown by the Czochralski method [1] using high purity of starting components. The high quality of the obtained crystals was checked by several methods [1,3].

The XPS spectra of SLA, SLG, LG and SLG3 were measured with monochromitized Al Kα radiation (1486.6 eV) at room temperature using PHI 5700/660 Physical Electronics Spectrometer. The spectra of the photoelectrons as a function of their kinetic energy were analyzed by a hemispherical mirror analyzer with an energy resolution about 0.3 eV. To eliminate the surface contamination all samples were broken under vacuum conditions of $<1.0\times 10^{-9}$ Torr before the analysis. Thus, it was possible to

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*Corresponding author.
E-mail address: itme3@atos.warman.com.pl (A. Pajaczkowska).

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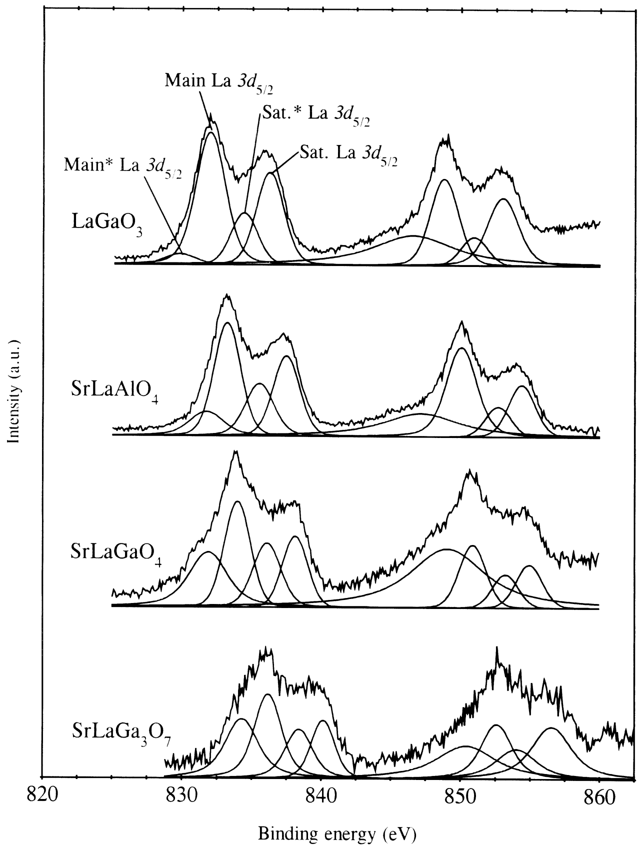

Fig. 1. Experimental results and theoretical fitting of the spectrum of La 3d electrons in $LaGaO_3$, $SrLaGaO_4$, $SrLaAlO_4$ and $SrLaGa_3O_7$.

measure XPS spectra of fresh surface without exposing the surface to air.

3. Results

XPS spectra of La 3d are shown in Fig. 1. A common feature in the spectra are satellites on the $3d_{3/2}$ and $3d_{5/2}$ peaks. The practical problem of fitting XPS spectra was thoroughly discussed and it was shown that XPS peaks are generally Lorentzian in shape with some Gaussian character. A product of Lorentzian and Gaussian function with a variable mixing parameter is quite effective in fitting XPS peaks [7]. In our case $3d_{3/2}$ and $3d_{5/2}$ spectra require a minimum of four components for fitting. The theoretical fitting of the spectra by the Gaussian functions and the background calculation according to a Tougaard algorithm were obtained using the SIMPEAK program. The results of the fitting are collected in Table 1 and describe the proposed multiplet structure.

The energy separation (ΔE) of the doublet structure measured on La $3d_{5/2}$ component of LG, SLA, SLG1 and SLGO3 was found to be 4.27, 4.25, 4.15 and 3.96 eV, respectively. These results are in accordance with $\Delta E \approx 4$–4.5 eV which have been reported for $LaMnO_3$ [5], several La perovskites [9] and La_2O_3 [10]. The difference between the La 3d spectra of LG, SLA, SLG and SLGO3 seems to be due to the difference of the coordination number of La ions located in the 8-fold coordinated site in SLG3, in the 9-fold coordinated site in SLA and SLG and in the 12-fold coordinated sites in LG. Thus, the comparison between XPS spectra of LG, SLA, SLG and SLG3 indicates that ΔE increases with increasing of coordination number of the La ion.

The proposed multiplet structure of the La 3d spectra might be caused by two opposing processes that contribute to the shift that is sometimes called a 'negative chemical shift' [8]. On the one hand, decreasing the coordination number of the La ion in an oxide lattice decreases the negative Madelung potential at the cationic site (an initial-state effect) as well as the polarization screening of the final state (a final state effect) producing a higher binding energy shift (BEs) for the La ion. On the other hand, as the coordination number of the La ion in an oxide lattice decreases, the electrochemical potential at the cationic site decreases (an initial-state effect) and the intra- and inter-atomic screening of the core hole (a final-state effect) are increased producing lower BEs for the La ion. The observed shift of the La 3d peak with decreasing the coordination number of the La ion in an oxide lattice to lower BEs indicates that the second effect above dominates.

Table 1

XPS binding energies (eV) of La $3d_{3/2}$ and $3d_{5/2}$ spectra of $LaGaO_3$, $SrLaAlO_4$, $SrLaGaO_4$ and $SrLaGa_3O_7$ referred to the Fermi level. For comparison, the literature data of La $3d_{5/2}$ spectra of $LaAlO_3$, $LaMnO_3$ and La are also presented

Material	XPS binding energies (eV)							
	Main La $3d_{5/2}$	Main La $3d_{3/2}$	Sat. La $3d_{5/2}$	Sat. La $3d_{3/2}$	Main* La $3d_{5/2}$	Main* La $3d_{3/2}$	Sat.* La $3d_{5/2}$	Sat.* La $3d_{3/2}$
$LaGaO_3$	831.97	848.77	836.24	852.97	829.79	846.53	834.39	850.91
$LaAlO_3$ [8]	834.95							
$LaMnO_3$ [5]	834.2							
$SrLaAlO_4$	833.20	850.03	837.45	854.35	831.72	847.11	835.52	852.67
$SrLaGaO_4$	833.96	850.86	838.11	854.92	831.87	849.05	836.09	853.20
$SrLaGa_3O_7$	836.18	852.59	840.14	856.54	834.30	850.40	838.41	854.01
La [4]	835.8	853						

4. Conclusions

The observed electron structure of La 3d spectra is very similar for all investigated single crystals in spite of their different structures. One can assume that this electron structure might not be associated with a defect structure of crystals. The theoretical fitting of the spectra by Gaussian functions and the background calculation according to a Tougaard algorithm leads to a complicated multiplet structure requiring a minimum of four fitting components. The difference between the energy separation of the doublet structure measured on the La $3d_{5/2}$ component of LG, SLA, SLG and SLGO3 seems to be due to the difference in coordination number of the La ions, which influences the electrochemical potential at the cationic site and produces lower BEs with decreasing coordination number of the La ions.

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