Cryst. Res. Technol.	34	1999	5–6	715–718

M. KOZIELSKI, A. JEZIERSKI*, D. KASPROWICZ, M. SZYBOWICZ

Institute of Physics, Poznañ University of Technology, Poland;
*Institute of Molecular Physics, Polish Academy of Sciences, Poznañ, Poland

Band Structure of $SrLaGaO_{3+\delta}$ and $SrLaAlO_{3+\delta}$

The influence of oxygen on the electronic structure of strontium lanthanum gallate $SrLaGaO_{3+\delta}$ (SLG) and strontium lanthanum alluminate $SrLaAlO_{3+\delta}$ (SLA) crystals is presented. The band structures of SLA and SLG crystals were calculated by ab-initio tight-binding linear muffin tin orbital (TB LMTO) method within an atomic sphere approximation. The self-consistent band calculations indicate that $SrLaGaO_4$, $SrLaAlO_4$ and $SrLaAlO_3$ are semiconductors, while $SrLaGaO_3$, $SrLaGaO_{3+\delta}$ and $SrLaAlO_{3+\delta}$ for $\delta = 2$ and 3 have the metallic character.

Keywords: oxides, point defects, band structure

1. Introduction

Strontium lanthanum gallate $SrLaGaO_{3+\delta}$ for $\delta = 1$ (SLG) and strontium lanthanum alluminate $SrLaAlO_{3+\delta}$ for $\delta = 1$ (SLA) single crystals are interesting as substrates for high superconducting thin films from the standpoint of lattice matching and their dielectric properties. Good quality of epitaxial layers requires both crystallographic perfection and appropriate physical properties of substrate material.

The crystals $SrLaGaO_4$ and $SrLaAlO_4$ belong to a group of compounds with the general formula $ABCO_4$, where A = Sr or Ca , B = La or another rare earth and C = Ga, Al or some transition elements (FAVA et al.; PAJACZKOWSKA et al.; BLASSE). These compounds crystallize in the perovskite-like tetragonal structure (space group I4/mmm (D_{4h}^{17})). The C atoms possesses octahedral coordination in the unit cell and are surrounded by six oxygen atoms.

The presence of the oxygen point defect for as-grown SLA and SLG crystals was found (GLOUBOKOV et al.; RYBA-ROMANOWSKI et al.). This defect appears as oxygen vacancies as well as excess of the oxygen atoms in the unit cell, which is associated with the crystal growth conditions.

In this paper the results of a study of the influence of oxygen content in the unit cell on the electronic structure of $SrLaGaO_{3+\delta}$ and $SrLaAlO_{3+\delta}$ crystals for $\delta = 0$, 1, 2 and 3 are described and discussion.

2. Method of calculations

The electronic structures of $SrLaGaO_{3+\delta}$ and $SrLaAlO_{3+\delta}$ were calculated by the ab-initio tight binding linear muffin tin orbital (TB LMTO) method (ANDERSEN; ANDERSEN et al.) within the atomic sphere approximation (ASA). The exchange correlation potential was assumed in the form proposed by von Barth and Hedin (VON BARTH, HEDIN) and the non-local corrections of Langreth-Mehl-Hu (HU, LANGRETH; MINFOBRIEF, TANG) were included. The self-consistent band calculations were performed for 294 k-points in the irreducible wedge of the tetragonal body centred Brillouin zone. The electronic structure was computed for the experimental values of lattice parameters (Table 1).

Compound	*a* [nm]	*b* [nm]	*c* [nm]
$SrLaGaO_4$	0.3842	0.3842	1.2679
$SrLaAlO_4$	0.3756	0.3756	1.2637

Table 1. The lattice parameters of SLG and SLA.

We start the band calculation for the tetragonal $La_2Ga(Al)O_4$ compounds (space group I4/mmm). In the case of $SrLaGaO_4$ and $SrLaAlO_4$ we substitute one La by Sr atom. The substitution Sr by La leads to the change of local environment of oxygen atoms. We found two additional positions in the unit cell that can be occupied by oxygen atoms. The positions of atoms in the unit cell in Table 2 are listed. The symbol □ denotes vacancies in the unit cell. The chemical formula can be rewritten as $SrLaGa(Al)O_{3+\delta}$□1□2. In order to estimate the influence of extra oxygen atom on the band structure we performed self-consistent band calculations for the base systems $SrLa(Ga/Al)O_4$ and also for the cases when one or two free positions (□1 and □2 Table 2) were occupied by oxygen atoms ($SrLa(Ga/Al)O_5$ and $SrLa(Ga/Al)O_6$). We have also calculated the electronic structure for the case when one oxygen atom located at the position (0, 0, 0.1680) was removed.

	SLG				SLA		
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sr	0	0	0.3639	Sr	0	0	0.3643
La	0	0	-0.3639	La	0	0	-0.3643
Ga	0	0	0	Al	0	0	0
O1	0.5	0	0	O1	0.5	0	0
O2	0	0	0.1680	O2	0	0	0.1680
□1	0.5	0	-0.2361	□1	0.5	0	-0.2503
□2	0	0.5	-0.2361	□2	0	0.5	-0.2503

Table 2: Positions of atoms in SLG and SLA unit cells

3. Results and discussion

Figures 1 and 2 illustrate the total electronic density of states (DOS) for $SrLa(Ga)O_{3+\delta}$ and $SrLa(Ga)O_{3+\delta}$, for $\delta = 1$, 2 and 3, respectively. The Fermi level E_F is located at energy $E = 0$ eV. The oxygen *s* and *p* states are located below $E = -15$ eV. The Ga and Al *p* states are situated between $0 < E < -8$ eV.

We observe the minimal energy gap 1.32 eV between (0, 0, 0) and (0.5, 0.5, 0.152) directions in $SrLaGaO_4$ and the minimal energy gap 3.35 eV between (0, 0, 0) and (1, 1, 0.297) in $SrLaAlO_4$. The energy gap in $SrLaAlO_3$ is 0.44 eV between (1, 1, 0.297) and (0, 1, 0.297) directions.

For $\delta = 2$ and 3 the $SrLa(Ga/Al)O_{3+\delta}$ compounds have the metallic character. However, the small distortion due to some kind of natural defects or internal stresses can lead to their semiconducting character.

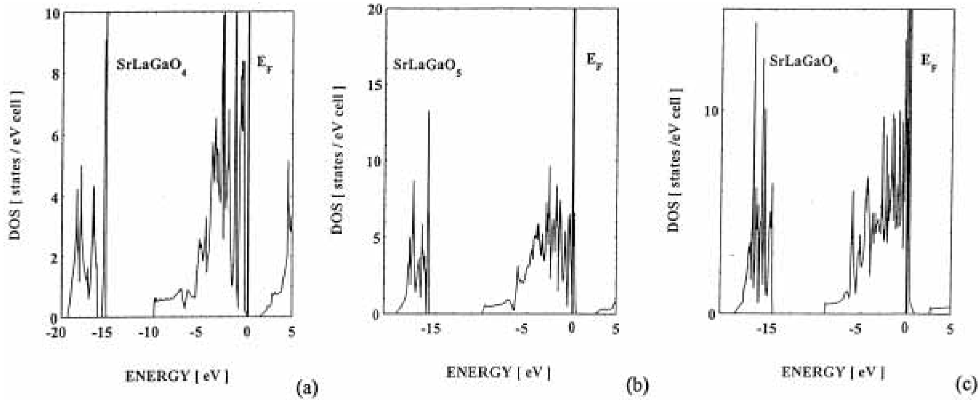

Fig.1: The electronic densities of states for (a) SrLa(Ga)O_4□1□2, (b) SrLa(Ga)O_5□1 and (c) SrLa(Ga)O_6 compounds. □ - denotes the oxygen vacancy.

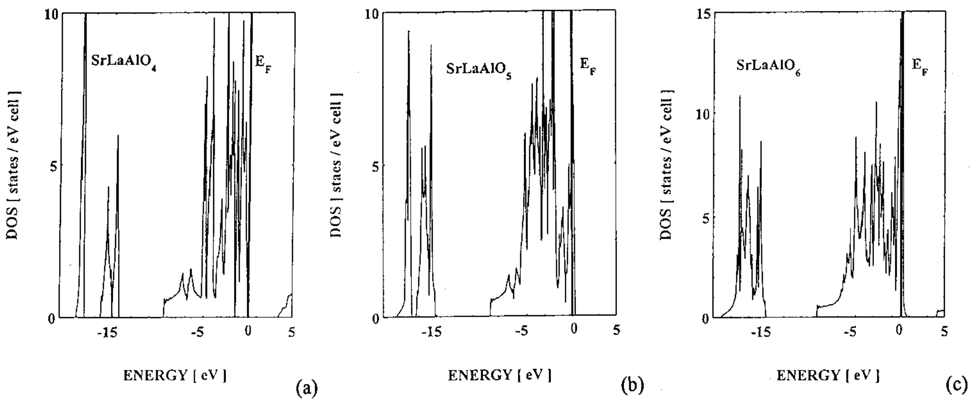

Fig.2: The electronic densities of states for (a) SrLa(Al)O_4□1□2, (b) SrLa(Al)O_5□1 and (c) SrLa(Al)O_6 compounds. □ - denotes the oxygen vacancy.

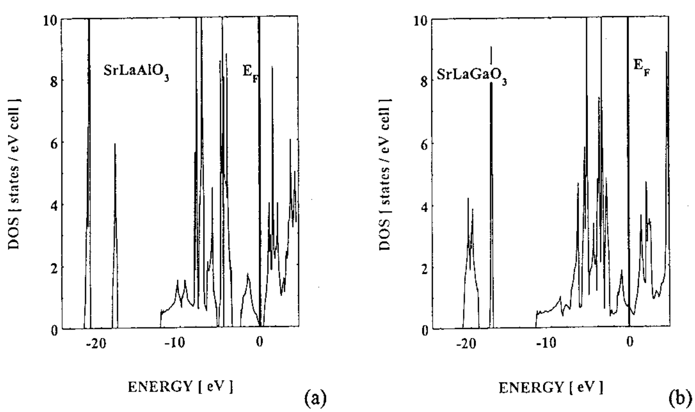

Fig. 3: The electronic densities of states for (a) SrLaGaO_3□1□2 and (b) SrLaAlO_3□1□2 compounds in case, when one oxygen atom is removed.

Fig. 3 presents the total density of states (DOS) in $SrLaGaO_3$ and $SrLaAlO_3$ compounds in case, when additional oxygen is removed. In $SrLaAlO_3$ we observe the small energy gap. However, $SrLaGaO_3$ has a metallic character, although in Γ point of Brillouin zone an internal gap is observed.

In conclusion, the band structures of SLA and SLG by ab-initio tight-binding linear muffin tin orbital (TB LMTO) method within an atomic sphere approximation (ASA) can be calculated. This method shows that $SrLaGaO_4$ and $SrLaAlO_4$ are dielectrics with the energy gap 1.32 and 3.35 eV, respectively. In $SrLaAlO_3$ a small energy gap is also observed. The additional oxygen atoms remove the energy gap and lead to the metallic states.

Acknowledgements

This work was partly supported by the State Committee for Scientific Research Project No 7 TO 8A 032 11 (M.K., D.K. and M.S.).

References

ANDERSEN, O.K., JEPSEN, O., SOB, M.: in: Electronic Structure and Its Applications, M.Yussouff ed., Lecture Notes in Physics vol. 283 (Springer-Berlin,1987)

ANDERSEN, O.K.: Tight-Binding LMTO programs, Version 4.7, Max-Planck Institut für Festkörperforschung (1994)

BLASSE, G.: J. Inorg. Nucl. Chem. **27** (1965) 2683

FAVA, J., OUDALOV, YU., REAU, J.M., LE FLEM, G., HAGENMÜLLER, P.: Compt. Rend. (Paris) **C274** (1972) 1837

PAJACZKOWSKA, A., BYSZEWSKI, P.: J. Crystal Growth **128** (1993) 694

GLOUBOKOV, A., JABLOÑSKI, R., RYBA-ROMANOWSKI, W., SASS, J., PAJACZKOWSKA, A., UECKER, R., REICHE, P.: J. Cryst. Growth **147** (1995) 123

HU, D., LANGRETH, D.C.: Phys. Scr. **32** (1985) 391

MIN, B.I., JANG, Y.R.: J. Phys. Condens. Matter **3** (1991) 5131

RYBA-ROMANOWSKI, W., GOLAB, S., SOKÓLSKA, I., PISARSKI, W.A., DOMINIAK-DZIK, G., PAJACZKOWSKA, A., BERKOWSKI, M., J. Alloys Comp. **217** (1995) 263

VON BARTH, U., HEDIN, L.: J. Phys. **C5** (1972) 1629

(received June 26, 1998; accepted July 21, 1998)

Authors' addresses:

Dr hab. M. KOZIELSKI*, mgr D. KASPROWICZ, mgr M. SZYBOWICZ
Institute of Physics, Poznan University of Technology,
Piotrowo 3, 60-965 Poznañ, Poland
*Corresponding author.
E-mail: markoz@phys.put.poznan.pl.; Fax: (061) 8-782-324.

Dr hab. A. JEZIERSKI
Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17, 60-179 Poznañ , Poland