Optical properties and electronic structure of $RAlO_3$ (R = La, Gd, Y, Yb, Lu) perovskites

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Motivation and Summary

Yttrium-aluminum perovskite ($YAlO_3$ or YAP) is well-known host material for solid-state lasers, scintillators and various kinds of converting and storage phosphors. YAP crystal possesses deformed perovskite-like structure with orthorhombic symmetry (space group D_{2h}^{16} – *Pbnm*). Other rare-earth-based aluminates and their solid solutions with the same type of structure (e.g. $LuAlO_3$, $GdAlO_3$, $YbAlO_3$ etc.) are also well known. A great amount of optical and luminescent properties of these crystals is determined not only by the specific doping creating energy levels inside the band gap of the material, but also by presence of native and uncontrolled impurity defects, their ionization energy and location generated by them trapping levels in band gap. Therefore the width of the forbidden band gap is very important.

The present work is devoted to systematic study of the electronic band gap widths of $RAlO_3$ perovskites with various RE cations (R = La, Gd, Y, Yb, Lu). Both experimental and theoretical methods are applied to determine dependence of the band gap width on type of the RE cation. The DFT-based theoretical calculations with use of the Plane-Wave Pseudopotential method [1] were carried out in order to establish the electronic band structures of $RAlO_3$ crystals. Results obtained from the calculations for the studied materials are compared with corresponding experimental results for optical absorption in the VUV-UV range.

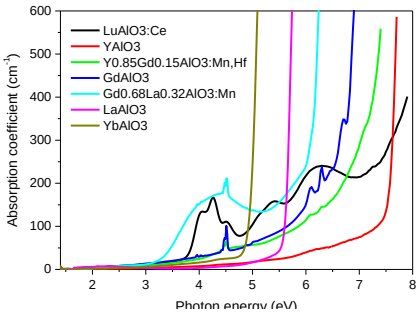

Fig. 1. Room-temperature optical absorption spectra of some $RAlO_3$ perovskites.

Compound	E_g, eV
$LuAlO_3$	≥8.0
$YAlO_3$	7.6
$GdAlO_3$	6.7
$LaAlO_3$	5.6
$YbAlO_3$	4.9

Table 1. Band gaps of $RAlO_3$ perovskites estimated from the absorption measurements.

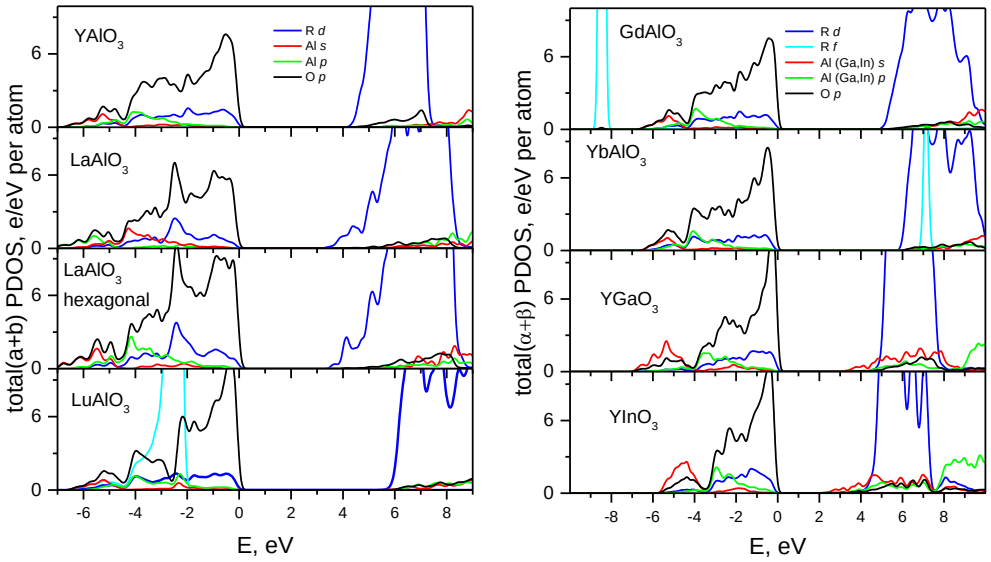

Fig. 2. Calculated partial densities of states of $RM^{III}O_3$ perovskites (R = Y, La, Lu, Gd, Yb; M^{III} = Al, Ga, In).

Table 2. Calculated band gaps of $RM^{III}O_3$ (R = Y, La, Lu, Gd, Yb; M^{III} = Al, Ga, In) perovskites.

Compound	Structure type, symmetry group	V_{xc}	E_g, eV	Notes
$YAlO_3$	orthorhombic, PBNM	GGA-PBE	4.86	
		GGA-RPBE	4.89	
		GGA-PW91	4.87	
		GGA-WC	4.84	
		GGA-PBESOL	4.85	
		HF-LDA	15.07	
		sX-LDA	6.85	
		PBE0	7.22	
		B3LYP	7.08	
		HSE03	6.51	
		HSE06	6.43	
$LaAlO_3$	orthorhombic, PBNM	GGA-PBE	3.35	
$LaAlO_3$	trigonal, R-3C	GGA-PBE	3.42	
		PBE0	5.21	
		HSE03	4.82	
		B3LYP	5.38	
$LuAlO_3$	orthorhombic, PBNM	GGA-PBE	5.49	
		PBE0	7.85	
		HSE03	7.08	
		B3LYP	7.51	
$GdAlO_3$	orthorhombic, PBNM	GGA-PBE	5.08	Hubbard U = 6.0 eV for Gd *f*
$YbAlO_3$	orthorhombic, PBNM	GGA-PBE	5.66	Hubbard U = 20.0 eV for Yb *f*
$YGaO_3$	hexagonal, P 63 C M	GGA-PBE	2.77	
		PBE0	4.93	
		B3LYP	4.58	
$YInO_3$	orthorhombic, PBNM	GGA-PBE	2.09	

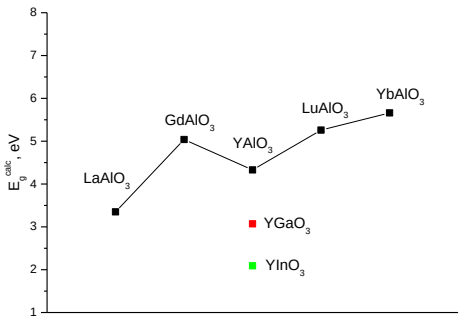

Fig. 3. Band gap values of $RM^{III}O_3$ perovskites (R = Y, La, Lu, Gd, Yb; M^{III} = Al, Ga, In) calculated with GGA-PBE [2] exchange-correlation functional.

References:

[1] M. C. Payne, M. P. Teter, D. C. Allan, et al. // Rev. Mod. Phys. 64 (1992) 1045-1097.
[2] J. P. Perdew, K. Burke, M. Ernzerhof // Phys. Rev. Lett. 77, 3865–3868 (1996).

Conclusions

- Experiments on the optical absorption spectroscopy allowed to estimate the band gap energies E_g^{exp} of $RAlO_3$ (R = Y, La, Lu, Gd, Yb) perovskites.
- Use of PBE0 exchange-correlation functional gives calculated band gaps E_g^{calc} of $RAlO_3$ close to their experimental estimations E_g^{exp} for R = Y, La and Lu.
- The difference in E_g^{exp} between $YAlO_3$ and $LaAlO_3$ (2 eV) is well reproduced in calculations with PBE0 (2.01 eV), however for GGA-PBE this difference is underestimated (1.44 eV).
- GGA-PBE gives the same difference in E_g^{calc} for ($YAlO_3$ vs $LuAlO_3$) and ($YAlO_3$ vs $YGaO_3$) cases as PBE0.
- Use of GGA-PBE in case of $RAlO_3$ (R = Y, La, Lu) perovskites is justified since it satisfactory reproduces the tendencies in E_g^{exp}.

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