

## The Influence of Partial Isomorphic Substitution on Band Structure and Optical Parameters of ABSO<sub>4</sub> Group Crystals

P.A. Shchepanskyi<sup>1,2</sup>, V.M. Gaba<sup>3</sup>, V.Yo. Stadnyk<sup>1</sup>, M.Ya. Rudysh<sup>1,2</sup>

<sup>1</sup> Ivan Franko National University of Lviv, Str. Kyrylo and Mefodiy 8, 79005 Lviv, Ukraine

<sup>2</sup> Jan Dlugosz University in Czestochowa, Al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

<sup>3</sup> Lviv Polytechnic National University, Str. S. Bandera 12, 79013 Lviv, Ukraine

Crystals represented by ABSO<sub>4</sub> formula belong to A<sub>2</sub>BX<sub>4</sub> group and are interesting due to their ferroelectric, ferroelastic, superionic, optical and other properties.

In this work partial isomorphic substitution K → NH<sub>4</sub> study on electronic and optical properties is provided by running first principle calculations of representative of K<sub>2</sub>SO<sub>4</sub> – (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> system, K<sub>1.75</sub>[NH<sub>4</sub>]<sub>0.25</sub>SO<sub>4</sub> crystal.

K<sub>1.75</sub>[NH<sub>4</sub>]<sub>0.25</sub>SO<sub>4</sub> crystal belongs to *Pnma* (№ 62) space group. Its lattice parameters are equal:  $a = 7.5562(3) \text{ \AA}$ ,  $b = 5.7917(2) \text{ \AA}$ ,  $c = 10.1016(4) \text{ \AA}$ , Cell volume = 442.08(5) Å<sup>3</sup>.

Since band structures for K<sub>2</sub>SO<sub>4</sub> (PS) [1] and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (AS) [2] crystals are known as well as for some other isomorphic crystals of that family, correlation between structure and properties can be revealed.

Calculations of the band structure in this work were carried out self-consistently using the Kohn-Sham formalism within density functional theory (DFT). As input parameters the X-ray analysis data was used. Basis was chosen in a form of plane waves. To describe the exchange-correlation interaction the exchange-correlation functional with the generalized gradient approximation (GGA) was used.

Band energy structure of K<sub>1.75</sub>[NH<sub>4</sub>]<sub>0.25</sub>SO<sub>4</sub> crystal reveals low dispersion of energy levels. Band gap is of a direct type and corresponds to the optical transitions in the  $\Gamma$  point of the Brillouin zone. Obtained  $E_g = 4.8 \text{ eV}$  value is for about 0.4 eV lower than calculated for K<sub>2</sub>SO<sub>4</sub> crystal [1].

Two top valence bands (VB) are almost entirely formed by *p*-electrons of oxygen from SO<sub>4</sub><sup>2-</sup> anion complexes. Contribution of potassium atoms electronic states is major for VB at -28 eV.

The bottom of the conduction band (CB) is formed mainly by hydrogen atoms (*s*-states); higher areas of this band – by mixed set of chemical elements and orbital moments.

Obtained band structure and density of states of the K<sub>1.75</sub>[NH<sub>4</sub>]<sub>0.25</sub>SO<sub>4</sub> crystal are quite similar to calculated for PS [1]. An exception is the fact that bottom of CB in K<sub>1.75</sub>[NH<sub>4</sub>]<sub>0.25</sub>SO<sub>4</sub> is formed by states of hydrogen, while similar role in K<sub>2</sub>SO<sub>4</sub> play potassium states. That leads to decreasing of band gap in the mixed crystal for about 0.4 eV in comparison with PS.

From the calculated dielectric function the refractive indices dispersion for three crystal optics directions is deduced. Order of obtained curves coincides with experimental. The difference is that dispersion of theoretically obtained curves is of the same magnitude for three directions of crystal, while magnitudes for experimental dependences differ, leading to the crossing  $n_x = n_y$  in the IR spectrum region. Such discrepancy is assumed to occur due to neglect of IR absorption of crystal in the simulations and presence of impurities in real crystal.

[1] B. Andriyevsky, M. Jaskolski, V.Y. Stadnyk, M.O. Romanyuk, Z.O. Kashuba, M.M. Romanyuk, *Computational Materials Science* **79** (2013) 442–447.

[2] B. Andriyevsky, K. Doll, M. Jansen, *Journal of Physics and Chemistry of Solids* **71** (2010) 357–363.