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A theoretical study of $PbWO_4$ disordered models and their electronic levels into a band gap

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Abstract – Lead zirconate $PbWO_4$ is scheelite type compound and an important application of this material is due to their electro-optic properties. In many optoelectronic devices, noncrystalline semiconductors can replace crystalline ones, mainly when they present better optical properties. In this work, we related the optical properties and the structural order-disorder degree in lattice analyzing the band gap energy of the experimental and theoretical band gap energy of the ordered and disordered models.

$PbWO_4$ (PW) has been attracting much attention owing to their technological importance as inorganic scintillating crystal. Compared to other well-known scintillators as NaI:Tl[1], PW is most attractive because of their high density, short decay time, and high-irradiation damage resistance. At room temperature the lead tungstate (PW) presents a scheelite-type tetragonal structure with general formula $[AXO_4]$ and space group *I*41/*a*, where A= Ca, Sr, Ba, Pb and Eu and X=W.

Recently, Cavalcante, L.S. et al.[2], synthesized PW by complex polymerized method heat treated at different temperatures. They reveal the presence of localized energy levels into the band gap of PW powders heat treated at 500 and 550 ºC, possibly due to the certain structural order–disorder degree in the lattice.

Theoretical calculations were performed to study the order-disorder effect in this material. For theoretical modeling of the PW, periodic DFT calculations with functional B3LYP were carried out by CRYSTAL03 computational code, to simulate crystalline PW and PW with structural defects, as Cavalcante suggest. These defects were simulated displacing the atoms of their original position. It were simulate four PW structures models, i) Ordered model (PW), ii) Disordered model displacing Pb atom of 0.5 Å in a z-axis (PW-Pb) iii) Disordered model displacing, simultaneously, Pb and W atoms of 0.3 Å in a z-axis (PW-PbW) and iv) Disordered model displacing W atom of 0.5 Å in a z-axis (PW-W). The atomic centers of Pb, W and O atoms were described by ECP DURAND-31G*, W given by Cora et al.[3] and 6-31d1, respectively. The crystallographic data of the PW crystalline were obtained in Cavalcante´s work. These models were analyzed by band gap and can bee useful to represents different degree of order-disorder in the mater[4].

Table 1: Optical band gap energy of the PW powders.

Temperature (ºC)	500	550	600	650	700
Optical band gap (eV)	2.66	3.42	3.46	3.50	3.52

Table 2: Theoretical band gap energy.

Theoretical Models	PW	PW-Pb	PW-PbW	PW-W
Gap Energy (eV)	4.1	3.79	3.58	2.74

Table 1 show the optical band gap energy for PW and reveal that the increase of temperature promotes a reduction of defects in PW lattice. In other words, the increase of temperature promotes an increase in the degree of structural order in the lattice. In table 2, we can note that the PW-W is the most disordered model, and such disorder is characterized by the reduction of the band gap energy. That suggests a larger number of defects in the lattice than the other disordered models. The increase degree of structural ordering in theoretical models is given by: PW-W < PW-PbW < PW-Pb < PW.

We propose that these reductions in the band gap energy in disordered models reveal the presence of localized energy levels into the band gap induced by the lift of degeneracy of the orbital of the valence band and conduction band. To confirm this suggestion, density of states (DOS) and band structures will be realized to each model. Therefore, we can indicate what atoms and orbitals actuate in the band gap.

References

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