ELECTRONIC STRUCTURES OF LUMINESCENCE CENTERS IN PURE AND DEFECTIVE SCINTILLATION CRYSTALS AWO_4 (A = Pb, Cd, Zn)

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Abstract

The electronic structures of the set of molecular clusters of dielectric oxide crystals AWO_4 (A = Pb, Cd, Zn), the sizes of which increase sequentially are *ab-initio* calculated by the Restricted Hartree-Fock (RHF) method. The results of calculations of molecular orbitals and energy dependences of partial densities of electronic states of different clusters are compared each to other and to experimental data. It is found that calculated electronic structures of the tungstate groups and cations which are surrounded in cluster by certain number of the nearest neighbor atoms of the crystals quite well represent the experimentally obtained value of the forbidden gap of corresponding AWO_4 crystal.

1. Introduction

Dielectric oxide crystals AWO_4 (A = Pb, Cd, Zn) are well known materials, which are widely used in various scintillation applications. $PbWO_4$ crystals are characterized by tetragonal crystal lattice of the scheelite type and possess space symmetry group I_4/a [1]. The cadmium and zinc tungstates are monoclinic wolframite-type crystals with the space group P2/c [2].

During the recent years the optical properties of these crystals were intensively studied experimentally [3, 4] and theoretically [5]. According to generally accepted view, the centers of luminescence in AWO_4 crystals are spatially and energetically localized objects, therefore, the intention to clarify the nature of luminescence in these crystals by means of calculations of the electronic structure of a separated crystal fragment – cluster looks quite grounded. Up to now we have published several works, where we developed our cluster approach in investigations of the electronic structure of luminescence centers in oxide crystals [6, 7]. In this work we intend to investigate in what way the size of a cluster determines representation of the optical properties of corresponding AWO_4 crystal.

2. Calculation Details

The following sequence of clusters was chosen for consideration. Firstly we consider only the anion component of a tungstate crystal – tungstate molecular group (WO_4^{2-} in the case of lead tungstate, and WO_6^{6-} in the case of cadmium and zinc tungstates). This was done, because the majority of researcher assume that luminescence of these crystals originates from the tungstate groups [3]. At the same time, almost all authors recognize that tungstate groups in AWO_4 undergo the influence of the corresponding cations of the crystals. In order to take into account this influence in calculations we constructed larger clusters, which contained two formula units – two cations and two tungstate groups. In the case of lead tungstate such cluster was denoted as PWO-2 (CWO-2 in the case of cadmium tungstate). And the third

types of clusters were the clusters in which the tungstate group and the cation were surrounded by the nearest neighbor atoms of the crystals. Such cluster of lead tungstate crystal is denoted as PWO-12. It was constructed of 12 FUs $PbWO_4$ (72 atoms). The cluster of $CdWO_4$ crystal is denoted as CWO-16. It was constructed of 104 atoms of the crystal, which represent 4 closely lying fragments of tungstate chains of WO_6 octahedrons (16 full FUs). Similar cluster of $ZnWO_4$ is denoted as ZWO-16. The central element (CE) was selected in each cluster. The CE comprises one tungstate group and the cation closest to it.

Calculations are carried out *ab-initio* by the Restricted Hartree-Fock (RHF) method using the PC GAMESS version [8] of the GAMESS (US) QC package [9]. Details of the calculations of partial densities of states (PDOS) $N_{a,r}(E)$ were described in our work [6]. The electronic structure of the CE was extracted from the results of the calculations of the whole cluster (energy levels of molecular orbitals ε_i and decomposition coefficients $C^i_{a,r}$ of molecular wave functions Ψ_i into atomic orbitals $\varphi_{a,r}$ where the index a denoted an atom, and r – an atomic orbital) in the following way. Only those $C^i_{a,r}$, which represent atoms of the CE were taken into account in calculation of $N_{a,r}(E)$.

3. Results and Discussion.

$PbWO_4$. As it is known, the edge of fundamental absorption of lead tungstate is located near 4 eV [4]. The photo-luminescence of $PbWO_4$, a blue band with maximum at 2.9 eV is excited in band with maximum at ~4 eV [10]. The calculated energies of molecular orbitals of tungstate group WO_4^{2-} with symmetry of free tungstate anion T_d are presented in Fig. 1a (the upper row of vertical strokes). The lowest energy of $3t_2$ - $3a_1$ transition in such group is 5.12 eV. It is obvious from the obtained values of transition energies that the excitation band of the luminescence at 4 eV or with fundamental absorption of the lead tungstate in this spectral region can be hardly associated with transitions in tungstate groups. Then the following question arises. Can calculations of such kind as we use give results, which will allow ascribing (at least qualitatively) of light absorption in this energy region (near 4 eV) to electronic transitions in certain object of the crystal (tungstate group, lead cation, point defect, etc.). Here are two possible ways to answer this question. The first is to take into account possible distortion of tungstate group induced by the crystal field. Due to this distortion the energies of MOs of tungstate group can be shifted with respect to the energies of free tungstate anion resulting in shifts of transition energies. In order to test this we

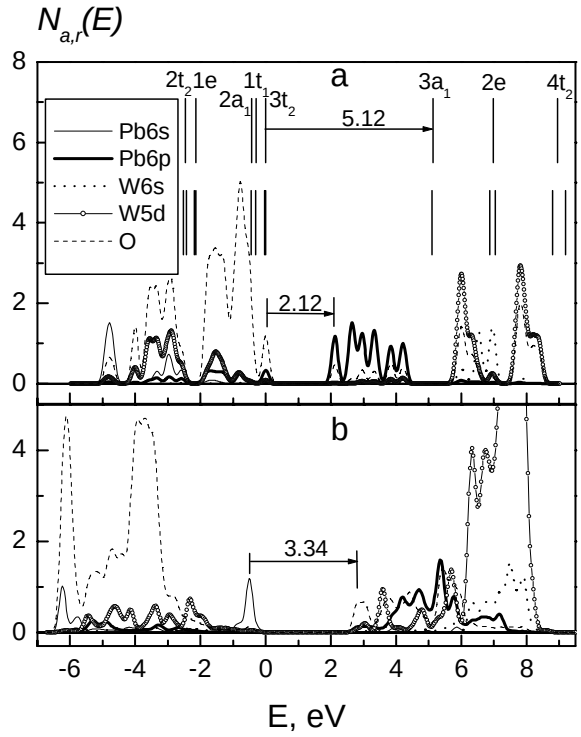

Fig. 1. Calculated MO energies of WO_4^{2-} groups (with T_d symmetry – upper strokes and with geometry as in $PbWO_4$ crystal – lower strokes), PDOS distributions $N_{a,r}(E)$ of PWO-2 cluster (a), and of the central element of PWO-12 cluster (b).

have modeled the distortion in calculation by taking the coordinates of O and W atoms being equal to coordinates of these atoms in $PbWO_4$ crystal. The results of this calculation are presented in the lower row of vertical strokes in Fig. 1a. As it is seen from the Figure, there are no substantial changes in positions of MOs, moreover the lowest energy of transition decreases only to 5.09 eV that is still far from 4 eV.

Another explanation of the question put above is that the transitions in Pb^{2+} cations have lower energies than tungstate groups and can provide the crystals absorption near 4 eV. It is obvious that in order to examine this in calculations the atomic orbitals of lead atoms must be involved into basis of the calculation. In order to realize this we constructed the cluster PWO-2, which contains Pb^{2+} cations (Fig. 1a). We have to note that unoccupied MOs of such system being of predominantly lead character are located below (from 2 to 4.5 eV) the MOs formed entirely by the states of tungstate group (from 6 to 9 eV). This means that the electronic states of Pb^{2+} cations should play an important role in formation of optical properties of $PbWO_4$ crystals. However, the energy distance between the highest occupied and the lowest unoccupied MOs of PWO-2 cluster is equal to 2.12 eV (Fig. 1a). This is much lower value than the energy of the fundamental absorption edge of the crystal (4 eV). Therefore we can conclude that the optical properties of lead tungstate crystal in the region of fundamental absorption can not be correctly described in calculation of a model system like PWO-2 cluster. In order to improve the situation we considered larger cluster PWO-12, in which the influence of the nearest atoms of the lead tungstate crystal on one Pb^{2+} cation and one WO_4^{2-} group is taken into account (Fig. 1b). As it is seen, the energy gap in this case (3.35 eV) is closer to 4 eV, than in the case of PWO-2 cluster. And moreover, if we consider the electronic transitions in Pb^{2+} cation and WO_4^{2-} group of the CE separately more accordance between calculations and experiment can be found. It was proved by good agreement between experimental reflection spectrum of $PbWO_4$ and calculated PDOS distribution of the CE [6]. So, we can conclude that the calculated electronic structure of the CE of PWO-12 cluster satisfactorily represents obtained experimentally optical properties of the lead tungstate crystal.

It should be also noted that such an object as Pb^{2+} cation of WO_4^{2-} tungstate group which is only partially surrounded in PWO-2 cluster by the nearest atoms of the crystal can be regarded as a defect center. Such centers can be lead cations and tungstate groups located on the crystal surface or on imaginary surface of micro-fragments in bulk of the crystal. As it is seen from the results of calculations (Fig. 1a), such defect centers are characterized by lower transition energies than the corresponding objects in the bulk of the crystal (associated with CE of PWO-12 cluster, Fig. 1b) and should have the electronic states in the forbidden gap of $PbWO_4$ crystal and, therefore, cause an additional absorption.

$CdWO_4$. Analogous sequence of clusters was considered for cadmium and zinc tungstate crystals. Since the results of calculations for these two crystals are in great measure similar we consider here only the case of $CdWO_4$ (Fig. 2). As it is known from experimental data, the edge of fundamental absorption of cadmium tungstate is located near 5 eV [11]. The calculated energy levels of molecular orbitals of WO_6^{6-} tungstate group with atomic coordinates of the group in $CdWO_4$ crystal are presented in Fig. 2a. As it is seen, the energy distance between the highest occupied and the lowest unoccupied MOs equals to 2.70 eV. The energy gap of CWO-2 cluster (the latter is similar to PWO-2) is 4.18 eV, which is closer to experimental data. And, at last, the energy distance between two valuable peaks of occupied and unoccupied electronic density of the central element of CWO-16 cluster (5.11 eV, Fig. 2b) is much closer to experimentally detected edge of fundamental absorption. This means that the calculated energy gap of the central element of CWO-16 cluster better represents the

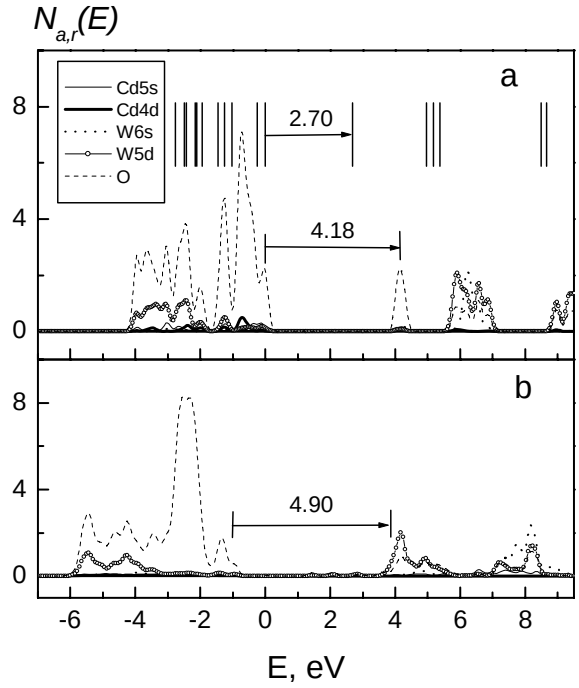

Fig. 2. Calculated MO energies of WO_6^{6-} group and PDOS distributions $N_{a,r}$ *(E)* of CWO-2 cluster (a); $N_{a,r}$ *(E)* distributions of the central element of CWO-16 cluster.

value of the forbidden gap (E_g) of the crystal than it was in the case of CWO-2 cluster or the WO_6^{6-} group. The situation is similar to the central element of PWO-12 cluster and $PbWO_4$ crystal (see above). Therefore the following general conclusion concerning the sizes of clusters in cluster modeling of the electronic structure of oxide crystals AWO_4 (A = Pb, Cd, Zn) should be made. The electronic structure of the tungstate group (WO_4^{2-} or WO_6^{6-}) and the A^{2+} cation which are surrounded in cluster by certain number of the nearest neighbor atoms of the crystals quite well represent the experimentally obtained value of E_g of corresponding AWO_4 crystal. Moreover, we found that addition of few formula units to PWO-12 cluster does not change (within the accuracy of 3 %) the PDOS distributions of the CE atoms of the cluster. But in order to prove that these distributions converge to some values when the size of the cluster increases, further investigations of larger clusters should be done. This is the aim of our future work.

Conclusion

From the calculations of the electronic structures of sequences of clusters with increasing sizes of AWO_4 (A = Pb, Cd, Zn) crystals it was found the following. The calculated energies of electronic transitions in the tungstate group (WO_4^{2-} or WO_6^{6-}) and the A^{2+} cation which are surrounded in cluster by the nearest neighbor atoms of the crystals quite well represent the experimentally obtained value of the forbidden gap of corresponding crystal.

Acknowledgement

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References

[1] J.M. Moreau, Ph. Galez, J.P. Peigneux, M.V. Korzhik, J. Alloys Compd. 46, 238 (1996).
[2] M. Daturi, M.M. Borel, A. Leclaire, et al., J. Chem. Phys. 93, 2043 (1996).
[3] V. Nagirnyi, M. Kirm, A. Kotlov, et al., J. Lumin. 102-103, 597 (2003).
[4] I.A. Kamenskikh, V.N. Kolobanov, V.V. Mikhailin, et al., Nucl. Instrum. Methods A 470, 270 (2001).
[5] Y. Abraham, N.A.W. Holzwarth, R.T. Williams, Phys. Rev. B62, 1733 (2000).

[6] Yu.A. Hizhnyi, S.G. Nedilko, M.U. Bilyi, Rad. Effects and Defects in Solids 157, 839 (2002).
[7] Yu.A. Hizhnyi, S.G. Nedilko, J. Lumin. 102-103, 688 (2003).
[8] A.A. Granovsky, http://classic.chem.msu.su/gran/gamess/index.html
[9] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, et al., J. Comput. Chem. 14, 1347-1363 (1993)
[10] M.U. Bilyi, S.G. Nedilko, Yu.A. Hizhnyi, et al., Ukrainian Phys. J. 47, 846-851 (2002).
[11] V. Nagirnyi, E. Feldbach, L. Jonsson, et al., Radiation Measurements 33, 601-604 (2001).