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Study on defects associated with interstitial oxygen in $PbWO_4$ crystal*

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The defects associated with interstitial oxygen in lead tungstate crystals ($PbWO_4$) are investigated by the relativistic self-consistent discrete variational embedded cluster method. The research work is focused on the density of states of interstitial oxygen defects and relational Frankel defects. The transition state method is used to calculate excitation energy of different electron orbits. Simulation results show that the existence of defects related to interstitial oxygen can diminish the bandwidth of the WO_4^{2-} group, and it might produce the green luminescence. Frankel defects associated with interstitial oxygen could result in the absorption at 420nm.

Keywords: $PbWO_4$ crystal, density functional theory, interstitial oxygen, density of states
PACC: 7115M, 7840, 2940

1. Introduction

Lead tungstate crystals (PWO) have been chosen as detector material for electromagnetic calorimeter in the compact muon solenoid (CMS) detectors of the large hadron collider (LHC) at the European Laboratory of Particle Physics (CERN) due to its high density, short radiation length, and fast decay time.[1] However, it is well known that inevitable defects will be produced in the process of $PbWO_4$ crystal growth, which will result in the degradation of optical transmission, light yield and radiation hardness of $PbWO_4$ crystal.[2] In recent years, various methods have been adopted to improve the performance of PWO to meet the strict requirements by decreasing the amount of different kinds of defects. Experiments showed that lead and oxygen defects are the main defect forms in lead tungstate crystal. For lead and oxygen vacancy defects, we have already reported our studies in a previous paper.[3] In this paper, we focus on the defects related to interstitial oxygen and the Frankel defects associated with oxygen.

Qi *et al*[4] studied the local structures around Pb and W atoms in PWO crystals by means of measuring the extended x-ray absorption fine structure (EXAFS) at the Pb and W L-edge and found that the interstitial oxygen can exist in the first Pb–O shell. Lin *et al*[5] conducted similar experiments on La-doped crystals. The results revealed the existence of interstitial oxygen ions in rare earth doped PWO crystals.

Related experiments showed that interstitial oxygen ions may have effects on the absorption in PWO crystals. Zhang *et al*[6] found that some doped PWO crystals showed a 420nm absorption band in optical transmission spectra after irradiation at a low dose rate. They suggested that it originated from interstitial oxygen atoms inside PWO crystals. Han *et al*[7] used an air annealing process to study the behaviour of interstitial oxygen inside PWO crystals. When the annealing temperature was below 640°, the absorption at 350nm increased, while if the annealing temperature was above 640°, the absorption at 350nm decreased, and even disappeared. Furthermore, studies showed that the interstitial oxygen defects may have influences on the green emission of PWO crystal.[8]

Based on the brief survey above, it could be concluded that the effect of interstitial oxygen on the absorption mechanism of lead tungstate crystals is still

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undetermined. Therefore, we conducted further study on the interstitial oxygen and its relative defects by a theoretical method, trying to explore the mechanism of the interstitial oxygen defects in PWO crystals.

2. Computational method and the cluster models

We use the relativistic self-consistent discrete variational embedded cluster method (DVM),[9] which has a high calculation precision with a relatively smaller workload, and fits the calculations for big molecules. This is a numerical self-consistent method based on the density functional theory. In order to improve the exchange interaction potential for calculations of ionic crystals, Ceperley and Alder's parametrization is used to produce the exchange interaction function in terms of the local density.

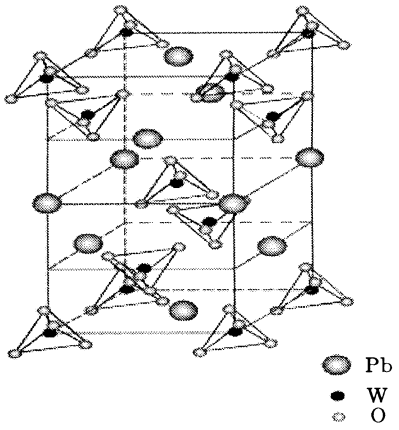


Fig.1. The structure of $PBWO_4$ crystal.

It is very important to choose the cluster to calculate the crystal electronic structure by the cluster-embedding calculation method.[10] PWO crystals grown artificially have the Stolzite structure, with tetragonal symmetry and $I4_1/a$ space group, in which each Pb^{2+} ion is surrounded by eight O^{2-} ions which belong to eight WO_4^{2-}, and these eight O^{2-} ions can be divided into two groups forming a penetrated tetrahedron. The bond lengths are: W–O: 0.1795nm, Pb–O: 0.2580/0.2637nm. Figure 1 shows the structure of PWO crystals. For simulating the defects associated with oxygen, we take $(Pb_8W_5O_{20})^{6+}$ cluster as the basal cluster. This cluster takes W as its centre, WO_4^{2-} is regarded as a whole inside the cluster and is surrounded by eight Pb^{2+} and four WO_4^{2-}. According to experimental results,[11] interstitial oxygen atom occupies one free corner of the approximate cube formed by W–O tetrahedron. As shown in Fig.2, the interstitial oxygen atom has two possible positions, namely position *a* or *b* in the cluster. The cluster model for the study of electronic structure of interstitial oxygen defects is formed on the basis of $(Pb_8W_5O_{20})^{6+}$, termed as cluster 1 and cluster 2, in which the interstitial oxygen ion takes either *a* or *b* position of the cluster. Cluster 3 (Fig.3) is the model for a cluster related with Frankel defect. Inside this cluster, the interstitial oxygen ion takes position *a*, while the oxygen vacancy occupies one former oxygen position of WO_4^{2-}. Cluster 4 is almost the same as cluster 3, only the interstitial oxygen takes position *b*. All the cluster models are given in Table 1.

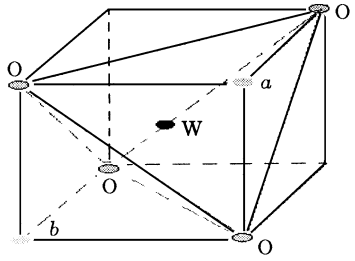


Fig.2. Possible interstitial oxygen positions in the cube.

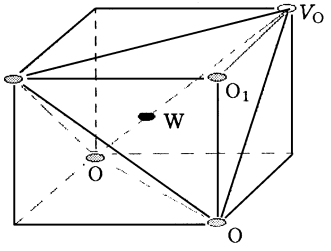


Fig.3. The structure diagram of cluster 3.

Table 1. Cluster models related to the interstitial oxygen defects.

Cluster	Description of the cluster models
1	WO_4^{2-} is at the centre position, surrounded by other 4 WO_4^{2-} and 8 Pb^{2+}, and position *a* is occupied by one interstitial oxygen ion.
2	WO_4^{2-} is at the centre position, surrounded by other 4 WO_4^{2-} and 8 Pb^{2+}, and position *b* is occupied by one interstitial oxygen ion.
3	one of the oxygen ion of WO_4^{2-} is taken out of cluster 1
4	one of the oxygen ion of WO_4^{2-} is taken out of cluster 2

In the simulation, boundary conditions for the crystal are described as 'Embedding cluster scheme': the potentials of the crystal ions outside the clusters are simulated by the Madelung potential; pseudopotentials are used to avoid false charge transfer from the clusters to the external 'host'. The original basis sets are composed of free ionic and atomic orbits and these basis sets are optimized in the iterative way to fit the occupation number of each molecule orbits. During the calculation, the crystal environment outside the clusters are constructed with 125 unit cells, the Diaphantus principle is applied in the numerical integration.[12] The integration sampling points are 24000 in total (at least 500 points for each atom). The simulation parameters are shown in Table 2.

Table 2. Initial basis sets and Funnel potential well parameters.

ions	Frozen core	Orbits for basis functions	Funnel potential parameters /arb. units		
			V_0	R_1	R_2
W^{6+}	1s-5s	5p,5d,6s	–2.5	1.5	2.0
Pb^{2+}	1s-5p	5d,6s,6p	–2.5	2.5	3.0
O^{2-}	1s	2s,2p,3s	–3.1	2.2	2.7

Considering the relaxation effect produced by the electronic transition in the crystal, we use the transition state method to calculate the excitation energy.[13] Since ionization energy $E_{\rm ion}$ is the negative differential value of the orbit energy E when taking out half an electron from the original neutral molecule,

$$E_{\rm ion} = E(n_i - 1) - E(n_i) \cong -\frac{\partial E}{\partial n_i}\bigg|_{n_i - \frac{1}{2}} = -\varepsilon_{i\rm T}. \quad (1)$$

Similarly, the excitation energy can be also achieved by taking out half an electron from the ith orbit while putting half an electron into the jth orbit, thus the excitation energy can be expressed as the energy difference between ith and jth orbit:

$$E_{i->j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_{j\rm T} - \varepsilon_{i\rm T}. \quad (2)$$

3. Results and discussion

Figures 4 and 5 show the electronic densities of states of cluster 1 and cluster 2, respectively (0 in the X axis denotes the Fermi energy level in all density of state diagrams of this paper). The electronic structures of these two clusters are quite similar. This result shows that the interstitial oxygen ions are not very sensitive to the two possible positions. Comparing with the density of states of pure PWO crystal,[14] we can find that the bandwidth of WO_4^{2-} is apparently decreased due to the existence of interstitial oxygen defects; W5d orbits are closer to the Fermi surface, and these orbits are hybridized with interstitial oxygen's 2p orbits in the band gap, forming the electron-trapping centre in PWO crystals. At the top of the valence band, O2p energy orbits are closer to the Fermi level while Pb^{2+} orbits do not change. The results suggest that the existence of interstitial oxygen ions may have two effects on the electronic structure of lead tungstate crystals: it could introduce O2p orbits of the interstitial oxygen into the forbidden gap, and it could also make W5d orbits closer to the Fermi surface.

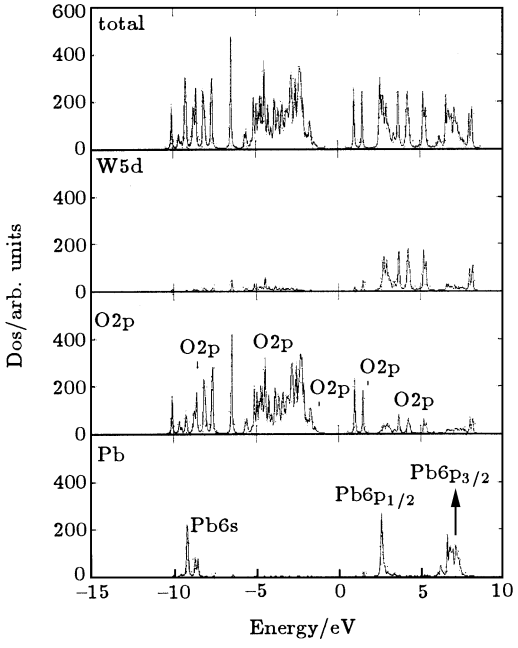


Fig.4. The density of states of cluster 1.

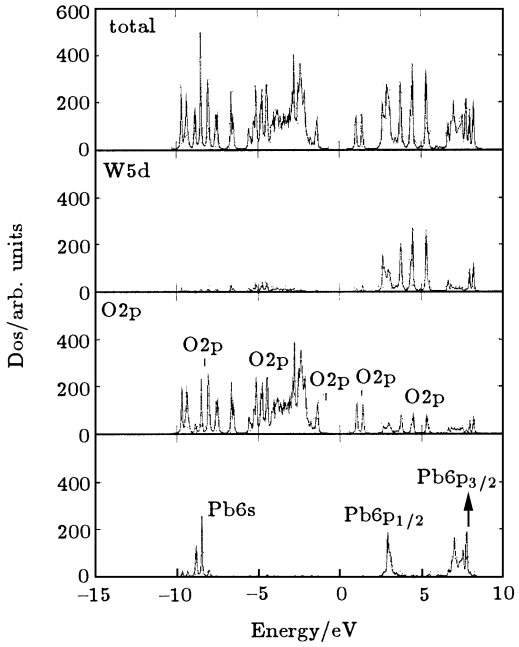


Fig.5. The density of states of cluster 2.

In order to make further study on the effect of interstitial oxygen defects on PWO's emission and absorption, we calculate the transition energy of O2p→W5d near Fermi level by transition state method. The results are shown in Table 3. The transition energy is 3.3eV and 3.8eV for cluster 1 and cluster 2, respectively. As we have known, the excitation energy of green luminescence is 3.7eV for the lead tungstate crystal.[14] Shi *et al*[8] studied the PWO crystals under different annealing conditions and found that the green emission increased. Chen *et al*[15] also found that the green luminescence of PWO crystal could be restrained under vacuum annealing condition. So it is possible that the interstitial oxygen ions produce the green emission of PWO crystals. In our calculation, the valence of interstitial oxygen ion keeps about −1.

The electronic structure of the models with Frankel defects is also investigated by DVM method. Since the oxygen vacancy V_O has four different sites to occupy in W–O tetrahedron, the Frankel defects associated with the interstitial oxygen have also four probabilities for clusters 3 and 4. As the results show, with increasing distance between the interstitial oxygen ion and V_O in Frankel defects, the total energies of the four kinds of Frankel defects in cluster 3 are 2037, 2041, 2141 and 2148eV, respectively, while those in cluster 4 are 2040, 2051, 2148 and 2152eV, respectively. Using the lowest energy principle, we choose the first one in cluster 3 as the main Frankel defect, in which the distance between V_O and interstitial oxygen is the shortest.

Table 3. The transition energy related to interstitial oxygen defects.

Cluster	Defect forms	Transition level	The ground state results in eV	The transition state results in eV
1	$WO_4^{2-}+O_i$	O2p→W5d	2.8	3.3
2			3.3	3.8
3	WO_3+O_i	O2p→W5d	2.6	2.9

The electronic density of states for Frankel defects associated with the interstitial oxygen in cluster 3 is shown in Fig.6. Comparing Fig.4 with Fig.5, we can see that the W5d orbits in cluster 3 are much closer to the Fermi surface and easier to capture electrons. So the band gap becomes even narrower. The O2p→W5d transition energy is 2.9eV obtained by using transition state method (Table 3), which could cause the absorption around 420nm. As our work shows here, the absorption near 420nm in the PWO crystal is caused by Frankel defects associated with the interstitial oxygen.

Recently, many experiments[15−17] have shown that trivalent ions could decrease the 420nm absorption. Nikl *et al*[18] found that the absorption at 420nm decreased after vacuum annealing in the Nb-doped PWO sample. It is concluded that trivalent doped samples could restrain the oxygen vacancy and vacuum annealing process might diminish the interstitial oxygen. All these two processes could reduce the

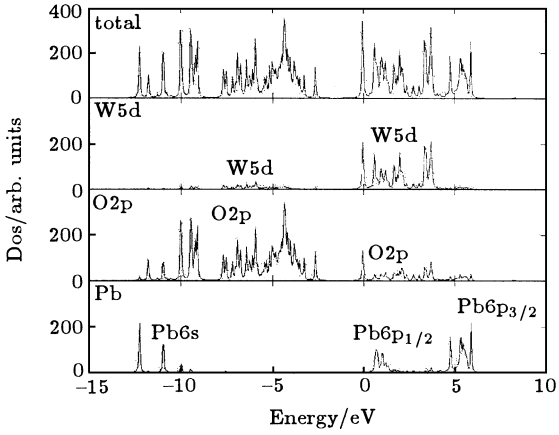


Fig.6. The density of states of WO_3+O_i defects in cluster 3.

Frankel defects associated with the interstitial oxygen, thus decreases the 420nm absorptions in PWO crystals.

4. Conclusion

In this paper, the electronic densities of states of defects associated with interstitial oxygen in lead tungstate crystals have been investigated by the relativistic self-consistent discrete variational embedded cluster method. Excitation energy is calculated by the transition state method. Based on the computation results, the changes of emission and absorption of PWO crystals caused by interstitial oxygen defects are discussed. We find that the existence of interstitial oxygen ions can decrease the bandwidth of WO_4^{2-}, and result in the green emission. The transition of O2p→W5d of oxygen Frankel defects can produce the absorption around 420nm in PWO crystals.

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