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Theoretical study on defects associated with lead vacancies in $PbWO_4$ crystals*

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The defects associated with lead vacancies (V_{Pb}) in lead tungstate crystals ($PbWO_4$) are investigated by the relativistic self-consistent discrete variational embedded cluster method. We focus on the density of states and the effect of V_{Pb} on surroundings. The results show that the existence of V_{Pb} can diminish the bandwidth of WO_4^{2-} group, however, it can neither produce O^- and Pb^{3+} ions nor result in absorptions at 350 and 420 nm. The charge balance of V_{Pb} may be evenly compensated by the surrounding oxygen ions.

Keywords: $PbWO_4$ crystal, density functional theory, lead vacancy, density of state
PACC: 7115M, 7840, 2940

1. Introduction

Single crystals of lead tungstate ($PbWO_4$ or PWO) have become the subject of increasing interest in recent years, because of their potential usage in detectors for high-energy physics (HEP) experiments, i.e. as a scintillation material in an electromagnetic calorimeter detector. However, it is well known that a loss of PbO from the melt state occurs in the stoichiometric raw material during PWO crystal growth by the Czochralski method. The loss subsequently leads to the creation of casually distributed lead vacancies V_{Pb} and oxygen vacancies V_O. Such vacancies can form the absorption centres in the crystal, which will directly affect the scintillation properties of lead tungstate. So it is of great importance to study the effect of these vacancies on the electronic structures of surrounding atoms. In this paper, the defects associated with lead vacancy V_{Pb} in lead tungstate crystals are investigated by the relativistic self-consistent discrete variational embedded cluster method.

In the study of absorption properties, the colour centre bands at 350 and 420 nm have aroused special interest. The 350 nm absorption band locates just near the cut-off edge of PWO. It will decrease the transmission in this region.[1] Whereas the 420 nm absorption band, which overlaps with the scintillation component—blue luminescence of PWO, will degrade the light output. Furthermore, the light absorption in the range of 400–500 nm is the primary criterion in evaluation of the radiation hardness of PWO, so the 420 nm absorption band is the component that greatly affects the capacity for resisting radiation damage in the crystal.[1,2] In addition, many experiments have revealed that there is close relationship between 350 and 420 nm absorption bands. For example, Han *et al*[3] studied the sequentially annealing treatments of PWO from 640 to 1040°C, and in the optical absorption spectra of the crystal treated by pre- and post-UV irradiation, they found that the 420 nm absorption increases with the enhancement of 350 nm absorption, and is accompanied by the appearance of a long-wave absorption in the range of 500–700 nm, at the same time the radiation damage becomes serious. In the early period of research on PWO, Auffray *et al*[4] measured the light absorption spectra of one hundred crystals, the results also suggested the intimate relationship between 350 and 420 nm absorption bands.

Up to now, concerning the origination of the 350 and 420 nm absorption bands, there have been some different viewpoints as follows: Nikl and others[5–7] ascribed two hole centres Pb^{3+} (a hole trapped by a

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regular Pb^{2+} ion) and O^- (O^{2-} trapping a hole) to the 350 and 420 nm absorption bands, respectively. However, Annenkov *et al*[8–11] proposed that the 350 nm absorption band originated from O^- near the V_{Pb}, and the 420 nm absorption band originated from Pb^{3+} based on Frenkel defects. Furthermore, di-vacancy $(WO_3-WO_3)^{2-}$ and di-hole $O^-V_{Pb}O^-$ centres were responsible for the induced absorption within 500–700 nm, and $(WO_3)^{2-}$ ions distorted by Frenkel defects caused the absorption below 400 nm. Lin and others[12–14] recognized that the variation of the number of ($2V_{Pb}''$:V_O'') defect clusters after pre- and post-annealing treatments corresponded to the intensity of the 350 nm absorption. They proposed that the 350 nm intrinsic absorption band originated from the $V_F{}^-$ hole centres. They also suggested that the 420 nm radiation-induced absorption band originated from the $V_F{}^0$ (V_{Pb}+2h) di-hole centres. Therefore, the viewpoints concerning the mechanism of the absorption bands have not reached an agreement up to date. However, most of them suggested that the existence of V_{Pb} resulted in the absorptions at both 350 and 420 nm, which were regarded to be related to the defect of Pb^{3+} and O^- or $O_2{}^{3-}$. However, whether the existence of V_{Pb} can lead to the production of Pb^{3+} and O^- hole centres has no direct evidence by experiments, such as electron paramagnetic resonance (EPR) spectrometry. In order to explore the mechanism of the defects in PWO crystals, the defect states related to V_{Pb} are calculated and discussed in this study.

2.Computational method and the cluster models

We use the relativistic self-consistent discrete variational embedded cluster method,[15] which has a high calculational precision with a relatively less 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 are used to produce the exchange interaction function under the construction of the local density.

It is very important to choose the cluster to calculate the crystal electronic structure using the cluster-embedding calculation method. $PbWO_4$ crystals grown in laboratory have the stolzite structure with a tetragonal symmetry and $I4_1/a$ space group, in which each Pb^{2+} is surrounded by eight O^{2-} which belong to eight $WO_4{}^{2-}$, and these eight O^{2-} can be divided into two groups forming a penetrated tetrahedron. The bond lengths are: W—O: 0.1795 nm, Pb—O: 0.2580/0.2637 nm. Figure 1 shows the structure of $PbWO_4$ crystals. Considering the structural characteristics of $PbWO_4$ crystals, $WO_4{}^{2-}$ is regarded as a whole to be put inside the cluster. The forms of the clusters selected in the calculation are $(Pb_8W_5O_{20})^{6+}$ and $(Pb_5W_8O_{32})^{6-}$. The former takes W as its centre, surrounded by eight Pb^{2+} and four $WO_4{}^{2-}$, while the latter takes Pb^{2+} as its centre, surrounded by eight $WO_4{}^{2-}$ and four Pb^{2+}.

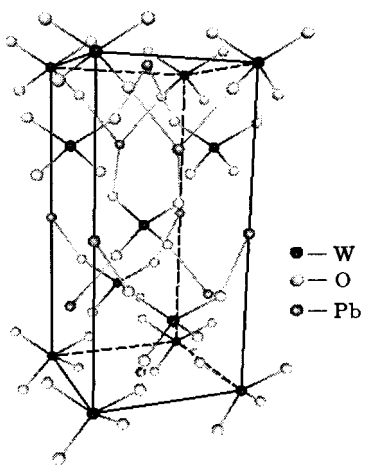


Fig.1. The structure of PWO crystal.

The electronic density of state of V_{Pb} has been calculated in our previous paper.[16] In the present, the effect of V_{Pb} on the surroundings as well as the charge compensation mechanism of V_{Pb} is further explored. The cluster model for the study is formed with $(Pb_8W_5O_{20})^{6+}$, termed as cluster 1, in which the nearest Pb to the centre is taken out. This new cluster model is used to analyse the electronic density of states of $WO_4{}^{2-}$ around V_{Pb}, and the effect of V_{Pb} on the surroundings. In order to verify the applicability of cluster 1, we choose another cluster $(Pb_5W_8O_{32})^{6-}$ for comparison, termed as cluster 2, in which the nearest Pb to the centre is taken out.

In order to further evaluate the viewpoint that the existence of V_{Pb} can lead to the production of Pb^{3+} and O^- hole centres, we again explore the V_{Pb} with the basic cluster $(Pb_5W_8O_{32})^{6-}$ by taking out Pb^{2+} in the centre, i.e. V_{Pb} is surrounded by eight $WO_4{}^{2-}$ and four Pb^{2+}. During the calculation, the total charge of the cluster is kept to be –6. This means that two electrons are missed in the cluster so that we can observe whether the holes will be localized in some specific

ions or ionic radicals. But in such a cluster, V_{Pb} lies in the centre of the cluster, so the whole cluster exhibits the perfect symmetry, which might make such a simulation different from the actual case. In order to simulate the actual case precisely, we consider that the relaxation of crystal lattice exists, and the crystal is in the steadiest state only when the total energy of the crystal is the lowest. We have investigated whether O^- and Pb^{3+} could exist in the crystal in detail. All the cluster models are shown in Table 1.

Table 1. Cluster models related to the V_{Pb}.

Cluster No	Description of the cluster models
1	WO_4^{2-} is at the centre, surrounded by 4 WO_4^{2-} and 7 Pb^{2+}, and one of the nearest Pb^{2+} ions is taken out.
2	Pb is at the centre, surrounded by 8 WO_4^{2-} and 4 Pb^{2+}, and one of the nearest Pb^{2+} is taken out.
3	V_{Pb} is at the centre, surrounded by 8 WO_4^{2-} and 4 Pb^{2+}, and the relaxation of oxygen is considered.

The boundary conditions for the clusters are described by "Embedding cluster scheme".[17] The potentials of the crystal ions outside the clusters are simulated by Madelung potentials; pseudo-potentials are used for the cluster ions to avoid false charge transfer from the clusters to the external "host".[18] The original basis sets are composed of free ionic and atomic orbits, and these basis sets are optimized in the iterative process according to the occupation of molecule orbits. During the calculation, the crystal environments outside the clusters are constructed by 125 unit cells, the Diaphantus' principle is applied in the numerical integration,[19] and the integration sampling points are totally 24000 (i.e. 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 well 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[20] to calculate the excitation energy. Ionization energy E_{ion} is the negative value of the orbit energy which is achieved by taking out half an electron from the primary neutral molecule

$$E_{ion} = E(n_i - 1) - E(n_i) \cong -\left.\frac{\partial E}{\partial n_i}\right|_{n_i - \frac{1}{2}} = -\varepsilon_{iT}. \quad (1)$$

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

$$E_{i\to j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_{jT} - \varepsilon_{iT}. \quad (2)$$

3. Results and discussion

Figures 2 and 3 show the electronic densities of states of the ions associated with lead vacancies in clusters 1 and 2, respectively. The electronic structures of them are quite similar. This means that the calculation is stable and reliable. From the results, we find that the bandwidth of WO_4^{2-} is apparently decreased because of the existence of V_{Pb}. The bandwidth of the central WO_4^{2-} in cluster 1 calculated with the transition state method is 4.1 eV, which could cause the absorption around 300 nm but cannot result in the absorptions at 350 and 420 nm. As far as the ionic valences are concerned, we can see that each oxygen ion possesses almost the same valence, and the case for lead ions is similar. This indicates that there is no extremely low-valence oxygen or high-valence lead ions existing around V_{Pb}.

In order to elucidate precisely the effect of V_{Pb} on the valences of the surrounding ions, we take cluster 3 as the basic cluster and consider the crystal lattice relaxation of the oxygen nearest to the V_{Pb}. Through a great deal of calculations, we find that the total energy of the cluster will reach to the lowest, when the relaxation distance of the oxygen is 0.02 a in the direction from the V_{Pb} to the oxygen lattice site (a is the distance from the oxygen to the cluster centre). The valences of W, O, Pb ions are around +4.0, −1.4 and +1.8, respectively. The main difference of the ionic

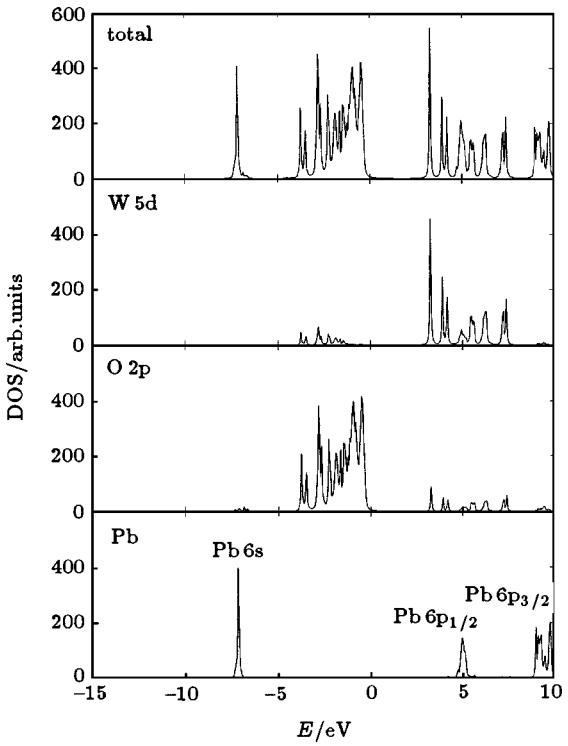


Fig.2. The density of states of the ions associated with lead vacancy in cluster 1.

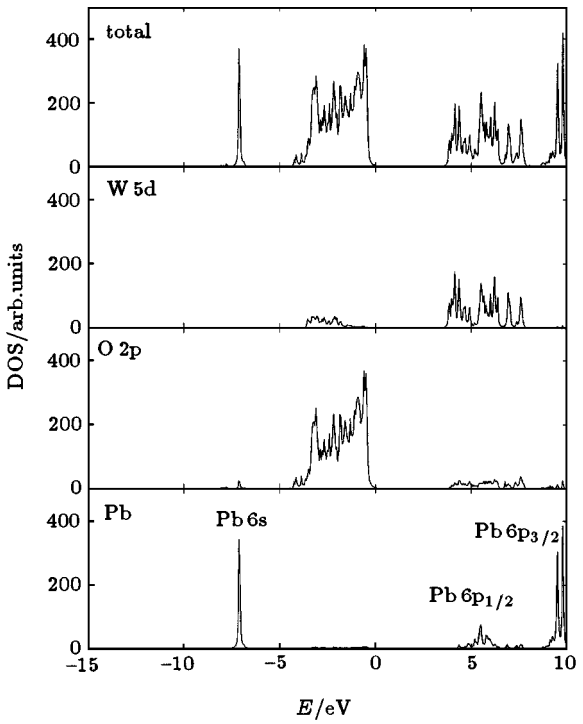


Fig.3. The density of states of the ions associated with lead vacancy in cluster 2.

Table 3. The valences of ions around V_{Pb}.

Cluster No	1	2	3
O^{2-}	–1.39,–1.39,–1.38,–1.42	–1.42,–1.42,–1.45,–1.41	–1.42,–1.42,–1.47,–1.44
WO_4^{2-}	–1.76	–1.81	–1.83
O^{2-}	–1.38,–1.37,–1.40,–1,41	–1.43,–1.43,–1.44,–1.43	–1.46,–1.45,–1.44,–1.47
WO_4^{2-}	–1.77	–1.82	–1.85
O^{2-}	–1.37,–1.41,–1.40,–1.40	–1.44,–1.41,–1.45,–1.43	–1.46,–1.45,–1.46,–1.45
WO_4^{2-}	–1.81	–1.82	–1.86
O^{2-}	–1.41,–1.44,–1.44,–1.41	–1.44,–1.45,–1.46,–1.44	–1.44,–1.44,–1.44,–1.42
WO_4^{2-}	–1.82	–1.84	–1.83
O^{2-}	–1.38,–1.39,–1.41,–1.40	–1.44,–1.43,–1.44,–1.45	–1.42,–1.42,–1.45,–1.42
WO_4^{2-}	–1.79	–1.83	–1.81
O^{2-}	—	–1.45,–1.45,–1.42,–1.43	–1.45,–1.42,–1.45,–1.46
WO_4^{2-}	—	–1.82	–1.83
O^{2-}	—	–1.45,–1.47,–1.45,–1.46	–1.44,–1.47,–1.47,–1.44
WO_4^{2-}	—	–1.84	–1.84
O^{2-}	—	–1.45,–1.46,–1.42,–1.46	–1.44,–1.46,–1.48,–1.45
WO_4^{2-}	—	–1.85	–1.85
	1.87	1.92	1.76
Pb^{2+}	1.86	1.91	1.76
	1.89	1.91	1.85
	1.87	1.90	1.87

valences between the calculation results and the perfect ions' (i.e. +6, –2 and +2 for W, O and Pb ions, respectively) is due to the covalence effect among the lattice ions. The negative charges of the oxygen ions around V_{Pb} are a bit less than the others because of the existence of V_{Pb}. The charge balance of V_{Pb} is evenly compensated by the neighbouring ions. No specific Pb or O ion can capture a hole solely. Similar results, as shown in Table 3, are deduced in the calculations on clusters 1 and 2. The results indicate that V_{Pb} cannot lead to the production of Pb^{3+}, O^- or $[O^-V_{Pb}O^-]$. But it can affect the bandwidth of WO_4^{2-} around it. The existence of O_2^{3-} is not excluded; however, we are more inclined to the point that the charge of V_{Pb} is evenly compensated by the neighbouring ions. In addition, oxygen vacancy V_O might also play an important role in view of V_{Pb} charge compensation. The study on V_O will be presented later.

4. Conclusion

In this paper, the defects associated with lead vacancies V_{Pb} in lead tungstate crystals ($PbWO_4$) have been investigated by the relativistic self-consistent discrete variational embedded cluster method. We find that the existence of V_{Pb} can decrease the bandwidth of WO_4^{2-}, but does not result in the absorptions at 350 and 420 nm. And also we find that the existence of V_{Pb} cannot lead to the production of O^- and Pb^{3+}. The charge of V_{Pb} may be evenly compensated by the surrounding oxygen ions.

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