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Electronic band structures of the scheelite materials – $CaMoO_4$, $CaWO_4$, $PbMoO_4$, and $PbWO_4$

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Abstract

Density functional calculations using the linearized-augmented-plane-wave (LAPW) method were carried out for the scheelite materials $CaMoO_4$, $CaWO_4$, $PbMoO_4$, and $PbWO_4$ in order to determine their ground state electronic properties. The results indicate that $CaMoO_4$ and $CaWO_4$ have direct band gaps at the center of the Brillouin zone, while $PbMoO_4$ and $PbWO_4$ have band extrema at wave vectors away from the zone center with possibly indirect band gaps. The magnitudes of the band gaps increase in the order: $PbMoO_4 < PbWO_4 < CaMoO_4 < CaWO_4$. The valence and conduction bands near the band gap are dominated by molecular orbitals associated with the $MoO_4^{-\alpha}$ and $WO_4^{-\alpha}$ ions, where $\alpha \approx 2$. The valence band widths are 5 eV and 5.5 eV, for the Ca and Pb materials respectively. In the Pb materials, the Pb 6*s* states form narrow bands 1 eV below the bottom of the valence bands and also hybridize with states throughout the valence bands, while the Pb 6*p* states hybridize with states throughout the conduction bands. In the Ca materials, the Ca 3*d* states contribute to a high density of states 3-4 eV above the bottom of the conduction bands.

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I. INTRODUCTION

The calcium and lead molybdates and tungstates are naturally occuring minerals which can also be made synthetically and which have very interesting luminescence and structural properties. The mineral names associated with these materials are powellite ($CaMoO_4$), scheelite ($CaWO_4$), wulfenite ($PbMoO_4$), and stolzite ($PbWO_4$). The name “scheelite” is also used to describe the common crystal structure of these materials. These materials have been very extensively studied during the past century. For example, a 1948 monograph by Kröger[1] presents a thorough summary of the luminescence properties of these and related materials and their solid solutions. Recently, $PbWO_4$ has attracted special interest because of plans to use it as a scintillator in detectors at the Large Hadron Collider in CERN.[2] There are still some very fundamental questions concerning the electronic properties of these materials, especially concerning the nature of the states of the ideal crystal in the vicinity of the band gap. In order to address some of these questions, we have calculated the self-consistent electronic structure of the four materials in the framework of density functional theory[3,4] using a relativistic linearized-augmented-plane-wave (LAPW)[5,6] technique.

The paper is organized as follows. In Section II the crystal structure is described. The calculational method is discussed in Section III. The results for the densities of states, the band structures, and the electron density distributions are presented in Section IV. In Section V the work is analyzed in terms of earlier theoretical and experimental work and the main results are summarized.

II. CRYSTAL STRUCTURE

The scheelite crystal structure is characterized by the tetragonal space group $I4_1/a$ or C_{4h}^6 (listed as No. 88 in the *International Tables*[7]). In this structure, the primitive unit cell has two ABO_4 units (where A = Ca or Pb and B = Mo or W). The A and B sites have S_4 point symmetry and the crystal has an inversion center. The O sites have only a trivial point symmetry, and are arranged in approximately tetrahedral coordination about each B site. The crystal has three crystal parameters $\{x, y, z\}$ which describe the location of the O sites. There are a number of equivalent ways to describe the structure which have appeared in the literature.[8] Table I lists some representative values of the crystal parameters that have been determined by X-ray and neutron diffraction with the $\{x, y, z\}$ defined relative to the origin of the crystal at the inversion center and confined to the sector $0 < \{x, y\} < \frac{1}{2}$ and $0 < z < \frac{1}{8}$. The starred references indicate the values used in the present electronic structure calculations.

The crystal structure has been described[8] as highly ionic with $A^{+\alpha}$ cations and tetrahedral $BO_4^{-\alpha}$ anions, where $\alpha \approx 2$. The $BO_4^{-\alpha}$ anions are themselves highly ionic with formal charges of $B^{+\beta}$ and $O^{-\gamma}$, where $4\gamma - \beta \equiv \alpha$. If there were no covalent bonding, β and γ would take the values 6 and 2, respectively. The tetrahedral $BO_4^{-\alpha}$ anions have short B–O bond lengths ranging from 1.77 Å for $CaMoO_4$ to 1.79 Å for $PbWO_4$ which are quite rigid even under pressure.[9] Figure 1 shows a perspective drawing of the crystal structure of $PbWO_4$ in the conventional unit cell, indicating the a– and c– axes and the nearly tetrahedral bonds between O and W. Also included in this figure is a plane which passes through two W–O bonds and one of the Pb sites. A contour map of the valence electron density which is indicated on this plane will be discussed further in Section IV.

III. CALCULATIONAL METHODS

The calculations reported in this paper were performed with the LAPW technique using the **WIEN97**[6] code. The exchange-correlation functional was taken within the local density approximation using the form developed by Perdew and Wang[10]. The calculational and convergence parameters used for all four materials are listed in Table II. The muffin tin radii for O, Mo, and W were chosen to be slightly less than half the O–Mo and O–W bond lengths. For Pb, the muffin tin radius of 1.9 Bohr was chosen in order to avoid the numerical instabilities of "ghost" states. The plane wave expansion cut-offs were chosen to be 6 Bohr^{-1} for expanding the wavefunctions and 14 Bohr^{-1} for expanding the densities and potentials. The **k**-point sampling was chosen to be 6 irreducible points within the Brillouin zone. For this choice of parameters, the bottleneck of the calculation is diagonalization of the plane wave Hamiltonian matrices which have a dimension of roughly 5000. We estimate that the convergence error of the calculation is dominated by the plane wave cut-off and the total energy error is at most 0.2 eV. The **k**-point sampling error for the total energy is estimated to be at most 0.01 eV. Although, for structural optimization studies, the convergence parameters would have to be increased, the present choice of parameters ensures very good convergence of the one-electron energies, with estimated errors of at most 0.002 eV. In fact, for this choice of plane- wave cut-off parameters, non-relativistic LAPW density of states results for $CaMoO_4$ were compared with the density of states determined from a completely independent calculational method — namely the PAW technique.[11,12] The two density of states plots were *virtually indistinguishable* over a 66 eV range of upper core, valence, and conduction band states, providing further evidence of the convergence of the one-electron energies.

Both scalar-relativistic and spin-orbit contributions were calculated self- consistently using the **WIEN97**[6] code. In each self-consistency iteration, the scalar relativistic Hamiltonian was diagonalized in the usual LAPW representation. The full relativistic Hamiltonian was then evaluated and diagonalized in the basis of the scalar relativistic eigenstates, with the spin- orbit interaction approximated as a spherically symmetric contribution confined within each muffin-tin sphere. This approximation has been well studied and has been shown to work well for elements in the 5th row of the periodic table.[5] It may, however cause greater errors for W and Pb which are in the 6th row of the periodic table.

IV. RESULTS

Density functional theory[3,4] is designed to accurately determine the ground state total energy and electron density of many- electron materials. The one-electron energies $E_{n\mathbf{k}}$

and their corresponding wavefunctions $\Psi_{n\mathbf{k}}(\mathbf{r})$ are variational parameters which are only qualitatively related to the measurable spectrum of the material. For example, although it is tempting to interpret the energy gap as the energy difference between the bottom of the first unoccupied band and the top of the last occupied band, density functional theory is notorious for underestimating the measurable band gap of most materials. Nevertheless, by focusing on the comparison of the results for the four materials of this study we can obtain useful qualitative information about their ground state properties.

A. Densities of states

The densities of states were calculated by approximating the delta function in energy with a Gaussian smearing function[13] of the form:

$$N^x(E) \equiv \sum_{n\mathbf{k}} f^x_{n\mathbf{k}} w_{\mathbf{k}} \frac{e^{-(E-E_{n\mathbf{k}})^2/\sigma^2}}{\sqrt{\pi}\sigma}. \tag{1}$$

The Gaussian smearing parameter was chosen to be $\sigma = 0.1$ eV. In Eq. (1), $w_{\mathbf{k}}$ is the Brillouin zone sampling weight factor and $f^x_{n\mathbf{k}}$ is a weight factor associated with the state $n\mathbf{k}$. The 6 $\mathbf{k}$-point sampling of the Brillouin zone did a good job of approximating the occupied densities of states. However, for states having larger dispersion such as in the upper portion of the conduction band, the approximation deteriorated somewhat. For the total density of states N^T, $f^T_{n\mathbf{k}}$ is equal to the degeneracy (including spin degeneracy) of the state. For the partial density of states N^a, $f^a_{n\mathbf{k}}$ is equal to the degeneracy multiplied by the fractional charge within the muffin tin sphere a for the state. In addition to the total density of states, there are 4 interesting choices for partial densities of states that will be presented below.

Figure 2 compares the total densities of states (N^T) for the 4 compounds within a 110 eV range, with the zero of energy taken at the top of the last occupied band. The upper core states are labeled according to their dominant atomic character. The similarities in the electronic structure of the four materials is quite apparent from this figure. The one-electron energies of the upper core states including the Pb $5p_{1/2,3/2}$, Pb $5d_{3/2,5/2}$, W $5s$, W $5p_{1/2,3/2}$, W $4f_{5/2,7/2}$, Mo $4s$, Mo $4p_{1/2,3/2}$, Ca $3s$, Ca $3p$, and O $2s$ states have very small relative chemical shifts in these materials. The O $2s$ states are among the upper core states forming a narrow band having a width of about 2 eV. In the Pb materials, this O $2s$ band peaks at -17 eV and is degenerate with the Pb $5d_{3/2}$ states but separated from the very narrow Pb $5d_{5/2}$ band at -14 eV. In the Ca materials, the O $2s$ band peaks at -16 eV and is well separated from other core states of the system.

Partial densities are presented on expanded scales in Figs. 3, 4, 5, and 6. The muffin-tin sphere radii used to calculate the weight factors for the partial densities of states are listed in Table II. In general, these radii are much smaller than typical atomic radii for these atoms and the total muffin-tin volume accounts for only 10–12% of the volume of the crystal. Nevertheless, one can obtain qualitative information about the atomic origins of the valence and conduction band states of these materials.

The partial densities of states based on charge within each muffin tin sphere (N^a for a = Ca, Pb, Mo, W, or O) are presented for the valence and conduction bands in Fig. 3. In $PbMoO_4$ and $PbWO_4$ there is a narrow Pb contribution to the density of states, having a width of 0.5 eV and centered at -7.1 eV and -7.2 eV respectively, separated by more that 1 eV from the bottom of the main part of the valence bands. These bands, due to the Pb $6s$ states, accommodate 4 electrons per unit cell. Since the Pb $6s$ wavefunctions are so diffuse, there is significant mixing with O and Mo or W states as will be discussed below. For all four materials, the main part of the valence bands accommodates 48 electrons per unit cell with a band width of 5 eV for the calcium materials and 5.5 eV for the tungsten materials. The shape of the density of states for these valence bands has two main features. The lower portion of the bands has roughly equal contributions from O and Mo or W states per atom, while the upper portion contains states of primarily O character. If we had plotted the partial density of states per unit cell, the O contributions would be 4 times larger than the contributions from Ca, Pb, Mo, and W presented in Fig. 3. From this point of view, it is clear that O states dominate the character of these valence bands. In fact, these valence bands accommodate the same number of electrons per unit cell (48) as if they were filled with pure O $2p$ states. The bottom of the conduction bands of these materials is dominated by Mo and W states. The calcium materials have additional conduction band contributions from the Ca states at approximately 3-4 eV above the bottom of the conduction band.

In order to investigate the nature of the valence and conduction bands further, we analyzed the partial densities in three additional ways — in terms of the $2p\sigma$ and $2p\pi$ contributions on the O sites (Fig. 4), the crystal field split $4d$ or $5d$ contributions on the Mo or W sites (Fig. 5), and in terms of the partial wave composition of the Ca and Pb contributions (Fig. 6).

On the oxygen sites, the valence band states are almost entirely described by atomic-like $2p$ wavefunctions. The strong crystal field due to the nearby Mo or W ions splits the atomic $2p$ states into σ and π contributions as shown in the partial density of states plot of Fig. 4. From this figure, it is apparent that the σ-like contributions are weighted toward the bottom of the valence band and the top of the conduction band, while the π-like contributions are stronger at the top of the valence band and bottom of the conduction band.

The geometry in the vicinity of the Mo or W sites is approximately tetrahedral and the $4d$ or $5d$ states split into e-like and t_2-like states. The corresponding partial densities of states are plotted in Fig. 5. From this result it is apparent that the bottom of the valence band has roughly equal contributions from both the e-like and t_2-like states, while the top of the valence band has very little contribution from either symmetry. The bottom of the conduction band, however, is dominated by e-like contributions while the upper conduction band is dominated by t_2-like contributions. Not included in this plot are the Mo $5s$ and $5p$ and W $6s$ and $6p$ contributions, since these were found to be negligible.

Finally, it is interesting to investigate the partial wave distribution of the Ca and Pb contributions to the valence and conduction bands. Since these sites are 2.5 Å or 2.6 Å away from the nearest neighbor O sites, the crystal field splittings for these states are very small. The Ca $4s$, $4p$, and $3d$ and Pb $6s$, $6p$, and $d-$like contributions are shown in Fig.6. The vertical scale has been expanded relative to that used in the previous figures in order to compensate for the small muffin tin used in the calculations. In fact, since the atomic or ionic wavefunctions corresponding to Ca 4s and 4p states and Pb 6s and 6p states are very diffuse, even a larger muffin tin radius could not contain the majority of the charge associated with these states. This figure shows that there is very little Ca 4s and 4p contributions to the valence and conduction band states between -6 eV and +8 eV. However, there is a significant contribution of the Ca 3d states above the Mo 4d and W 5d conduction band states. In the Pb materials, the corresponding Pb 5d states are filled as discussed above so that there is no appreciable d-like density in the valence and conduction band region. Although the Pb 6s states form a well-defined narrow band below the bottom of the valence band, there is some additional Pb 6s character throughout the valence bands of $PbMoO_4$ and $PbWO_4$. Figure 6 also shows significant contribution of Pb 6p states throughout the conduction bands of these materials.

B. Electronic band structure diagrams

Band dispersions for the four materials are plotted along 3 symmetry directions within the body-centered tetragonal Brillouin zone (Fig. 7) and presented in Figs. 8 and 9. The shapes of the bands for $CaMoO_4$ and $CaWO_4$ are very similar to each other. The valence band maxima and the conduction band minima are located at the Γ point so that these are direct gap materials. Although the values of the band gaps calculated within density functional theory are known to be underestimated[14], it is interesting to compare the gaps calculated for the two materials as listed in Table III. The dispersion of the valence bands is relatively small, with comparable dispersions along both the a- and c- directions. The lower part of the conduction band, which is composed primarily of e states associated with the Mo 4d or W 5d states, is separated by approximately 0.5 eV from the upper part of the conduction band formed from the t_2 states of Mo or W and the 3d states of Ca.

The shapes of the bands for $PbMoO_4$ and $PbWO_4$ are very similar to each other, but are somewhat different from those of the Ca materials. For the Pb materials, the band extrema are located away from the Γ point. Within the limited region of the Brillouin zone studied for the dispersion plot shown in Fig. 9, we can make the following statements about the band extrema. The valence band has maxima in the Δ directions and slightly lower maximum in the Σ directions. The conduction band minima are located in the Σ directions. The values of these indirect gaps are listed in Table III. The direct gaps for both materials appear to lie in the Σ direction and are approximately 0.1 eV larger than the minimum (indirect) band gaps listed in Table III.

The calculated ordering of the band gaps is given by $PbMoO_4 < PbWO_4 < CaMoO_4 < CaWO_4$. Experimental data for exciton reflectance peak, luminescence excitation threshold, and free-carrier threshold summarized in Table IV are consistent with this ordering.

C. Electron density distributions

In order to further understand the electronic states of these materials, we have constructed contour plots for their occupied and unoccupied states. Fig. 1 shows a perspective diagram of a $PbWO_4$ crystal together with a plane which contains two W–O bonds and also contains a Pb site. A contour plot of the valence electron density (including states within 5.5 eV of the valence band maximum, but not the narrow Pb 6s band) is also indicated on this plane. Most of the contours shown in this diagram are associated with the 4 atoms in the plane, although there are significant contributions from two O's at the top of the diagram which lie in front or in back of the plane.

We have used the plane indicated in Fig. 1 to construct a series of contour diagrams for various partitions of the electronic charge densities of the four materials. Since the plots for $CaMoO_4$ and $CaWO_4$ and for $PbMoO_4$ and $PbWO_4$ look so similar to each other, we present only the plots for $CaMoO_4$ and $PbWO_4$. These contour plots all have the same uniform contour level spacing for all of the plots, namely the contour levels are spaced at intervals of 0.2 e/Å^3, with the first contour level chosen to be 0.1 e/Å^3.

Fig. 10 shows the electron density corresponding to the valence band states of $PbWO_4$.

The plot labeled I shows the contours corresponding to the narrow Pb $6s$ states below the valence band. With the exception of the small region of high density near the Pb site, most of the contours shown in the diagram correspond to oscillations about the 0.1 e/Å^3 level around the Pb site and near the O site. Plots labeled II and III correspond to the lower and upper portions of the valence band, divided at the minimum in the density of states located 3.2 eV below the valence band maximum. From these plots, it is evident that the lower bands (II) are dominated by σ bonding states formed from the O $2p$ and the W $5d$ states, while the upper bands (III) are dominated by π bonding states formed from the O $2p$ with somewhat less density associated with the W $5d$ states. This result is consistent with the density of states analysis discussed above. The sum of the densities II and III correspond to the density shown in the 3-dimensional plot shown in Fig. 1.

Fig. 11 shows the electron density corresponding to the valence band states of $CaMoO_4$. Plots labeled II and III correspond to the lower and upper portions of the valence band, divided at the minimum in the density of states located 3.0 eV below the top of the valence band maximum. These plots show very similar distributions to those of $PbWO_4$, showing the dominance of the O $2p\sigma$ states in the lower portion and the O $2p\pi$ states in the upper portion of the valence band.

Figures 12 and 13 show the electron density distributions in the unoccupied bands of $PbWO_4$ and $CaMoO_4$, respectively. The bottom portion of the conduction bands (labeled IV) is dominated by states of e symmetry about the tetrahedral site formed from the W $5d$ or Mo $4d$ states with a small antibonding contribution from the O $2p\pi$ states. The upper portion of the conduction bands (labeled V) is dominated by states of t_2 symmetry formed from the W $5d$ or Mo $4d$ states with a small antibonding contribution from the O $2p\pi$ and $2p\sigma$ states. For $CaMoO_4$, the upper most portion of the conduction band ($E > 6.7$ eV) is plotted separately (labeled VI) showing the contributions from the Ca $3d$ states.

V. DISCUSSION AND CONCLUSIONS

The results presented here represent an accurate self-consistent evaluation of the Schrödinger equation for the ground state of the system within the density functional formalism. The total energy of the system and the corresponding electron density are determined variationally. However, the band structure and the corresponding densities of states are only qualitatively related to the "quasiparticle" states[14] which are accessible experimentally. Within this caveat, it is useful to relate the present results to some of the experimental and theoretical results in the literature. For the purpose of the present qualitative discussion, we first relate our results to the ligand field model used extensively in the literature and then present a tentative comparison with some spectroscopic results.

A. Ligand field model

For the purpose of this analysis, it is helpful to visualize the formation of these materials in the following way. Imagine that one could place the neutral atoms at the correct atomic positions in the crystal. First allow the neutral spherical atoms to self-consistently transfer charge to produce spherical $A^{+\alpha}$, $B^{+\beta}$, and $O^{-\gamma}$ ions as described in Sec. II. If the valence bands were formed only from O $2p$ states, the band filling would indicate that $\gamma = 2$, $\beta = 6$, and $\alpha = 2$. Now apply degenerate perturbation theory to describe the splittings of the valence states of the spherical ions.[15] The splitting of the O $2p$ states is dominated by the Coulomb attraction of the electron to the nearest neighbor $B^{+\beta}$ ion. The first order σ and π energy shifts are given, respectively, by:

$$E^1_{p\sigma} = -\frac{2\beta e^2 < r_p^2 >}{5R^3_{BO}} \quad \text{and} \quad E^1_{p\pi} = +\frac{\beta e^2 < r_p^2 >}{5R^3_{BO}}. \tag{2}$$

Here, R_{BO} is the Mo–O or W–O bond length and $< r_p^2 >$ is the expectation value of the squared radius of the O $2p$ orbital. Using the estimated values of the parameters $\beta = 6$, $R_{BO} = 3.4$ Bohr, and $< r_p^2 >= 2$ Bohr^2 (estimated from numerical integration using neutral O $2p$ wavefunctions), we find $E^1_{p\pi} - E^1_{p\sigma} \approx 5$ eV.

The splitting of the $4d$ or $5d$ states of the B ion is dominated by the Coulomb repulsion of the electron from the four tetrahedral nearest neighbor $O^{-\gamma}$ ions. The first order energy shift for states of "t_2" and "e" symmetries are given, respectively, by:

$$E^1_{t_2} = -\frac{8\gamma e^2 < r_d^4 >}{27 R_{BO}^5} \quad \text{and} \quad E^1_e = \frac{4\gamma e^2 < r_d^4 >}{9 R_{BO}^5}. \tag{3}$$

Here $< r_d^4 >$ is the expectation value of the fourth power of the radius of the d orbitals of the B ions. Using the estimated values of the parameters $\gamma = 2$, $R_{BO} = 3.4$ Bohr, and $< r_d^4 >= 9$ Bohr^4 (the average value from numerical integration using Mo^{+6} $4d$ or W^{+6} $5d$ wavefunctions), we estimate $E^1_e - E^1_{t_2} \approx 1$ eV.

Finally, following the approach of Ballhausen and Liehr[16] we allow the t_2 and e orbitals on the B sites to hybridize with linear combinations of $p\sigma$ and $p\pi$ ligand orbitals, symmetrized for the tetrahedral geometry, forming bonding and anti-bonding combinations which approximate the eigenstates of the $BO_4^{-\alpha}$ ions. The 4 ligand $p\sigma$ orbitals are compatible with the tetrahedral representation of symmetry a_1 and t_2, while the 8 ligand $p\pi$ orbitals are compatible with the tetrahedral representation of symmetry t_1, t_2, and e. From our partial densities of states analyses, we can roughly guess the ordering which would correspond to the molecular orbitals for the $BO_4^{-\alpha}$ clusters. These are shown in Fig. 14, where we have also indicated in the same diagram the positions of the atomic-like bands that we have identified in our calculations — Pb $6s$ states and the Ca $3d$ states. This qualitative picture (apart from the ordering of the lower molecular orbital states) is consistent with the early semi-empirical molecular orbital calculations for WO_4^{-2} and MoO_4^{-2} by several authors.[16–18] In particular, the early calculations recognized that the top occupied state has t_1 symmetry formed from the O $2p\pi$ states and the lowest unoccupied state has e symmetry formed from an antibonding combination of Mo $4d$ e or W $5d$ e state with O $2p\pi$ states. In fact, this model has been used more generally to describe the class of tetrahedral $BO_4^{-\alpha}$ anions.[19]

The fact that there is hybridization between the d orbitals of the $B^{+\beta}$ ions and the O $2p$ orbitals means that there is some covalent character to the bonding. From the ratio of occupied to unoccupied charge density within the muffin tin spheres of the $B^{+\beta}$ ions, we estimate $\beta \approx 3$ for all four materials.

B. Comparison with optical spectra

A large portion of the interest in these materials is due to their intrinsic luminescence spectra.[1,2] While a detailed understanding of the luminescence processes goes far beyond the scope of the present study, we can make some qualitative comments. For each of the four materials, the intrinsic luminescence spectrum has been interpreted in terms of a molecular diagram such as Fig. 14, similar to that given by Ballhausen and Liehr[16]. The ground state of the system corresponds to filling all one-electron states below the band gap, resulting in a many-electron state of ${}^1A_1$ symmetry. The lowest excited states involve one hole in the t_1 (primarily O 2pπ) states and one electron in the e (primarily Mo 4d or W 5d) states, corresponding to the many-electron states ${}^1T_1$, ${}^3T_1$, ${}^1T_2$, and ${}^3T_2$. Of these states only the transition ${}^1A_1 \leftrightarrow {}^1T_2$ is a dipole allowed transition. However, it is the lower ${}^3T_1$ or ${}^3T_2$ states which were shown to account for the intrinsic luminescence by a spin-forbidden transition to the ground ${}^1A_1$ state in optically detected electron paramagnetic resonance experiments on $CaMoO_4$ and $PbMoO_4$.[20,21]

While the molecular orbital model describes the general features of the excitation and luminescence of these materials, a more accurate description corresponds to a Frenkel-type exciton[22–26] having energies within the band gap of the one-electron states.[27] Since the present study has calculated the one-electron states only, we have no detailed information about the excitons. However, having information about the band states, we can comment on the qualitative differences between the excitons in the Ca and Pb materials. In particular, several authors[23,25,26] have suggested that the Pb 6s and 6p states contribute in a significant way to the excitation and luminescence spectra of $PbWO_4$. One experimental impetus for this suggestion is that an exciton peak is found at considerably lower energy in $PbWO_4$ (4.2 eV) than in $CaWO_4$ (5.9 eV), despite the fact that both crystals have the same $WO_4^{-\alpha}$ complex anion and the same scheelite structure.

Thus, Belsky *et al.* suggested that the first sharp reflectance peak in $PbWO_4$ at 4.17 eV is associated with Pb $6s \rightarrow 6p$ transitions.[23] In advance of an available band structure calculation, they speculated that a narrow Pb^{+2} $6p$ sub-band at the bottom of the conduction band should be expected. However, the partial density of states ($N^a(E)$) calculations presented in figures 3 and 6 do not exhibit a narrow Pb peak at the bottom of the conduction band nor at the top of the valence band. Rather, a nearly uniform density of Pb states is distributed throughout the conduction and valence bands. The only distinct narrow Pb $6s$ band is located *below* the valence bands. We will return later to the discussion of partial Pb character in the lowest exciton. Comparing second ionization potentials of Ca and Pb, Mürk *et al.* suggested another exciton model for $PbWO_4$ in which a hole residing mainly on the tungstate group is paired with an electron described as being in the Pb^+ state.[26]

The peak energies of intrinsic recombination luminescence in the four scheelite materials under consideration are listed in Table IV. The intrinsic luminescence energy E_{lum} is about 2.9 eV in both tungstates and about 2.3 eV in both molybdates, consistent with the view that the intrinsic luminescence mainly involves the tungstate (molybdate) complex anion. We have already seen that the exciton energy depends strongly on whether Ca or Pb is the cation. In contrast, the luminescence energy is almost independent of this factor.[28] The luminescence peaks are broad, having full width at half maximum (FWHM) around 0.7 eV at temperature T = 295 K. The intrinsic luminescence energy is Stokes-shifted about 3 eV below the exciton reflectance peak in $CaWO_4$, and about 1.3 eV below the exciton in $PbWO_4$. Since the 2.9 eV luminescence in tungstates has been satisfactorily identified as intrinsic recombination luminescence, the large Stokes shift and broad band imply that excitons self-trap before emitting luminescence photons.[25,29,30] This conclusion is further supported by the Urbach slope parameter $\sigma_0 = 0.9$ measured for $PbMoO_4$ by van Loo.[31] According to Toyozawa's theory,[32,33] $\sigma_0 < 1$ implies an exciton- phonon coupling constant strong enough to induce self-trapping. This has been confirmed by observations reported for a wide variety of crystals.[30] Because of the significant local lattice distortion that accompanies self-trapping, the states giving luminescence can be described reasonably well as molecular orbitals of the single distorted atomic group on which the exciton localizes. Van der Waals and co-workers have used optically detected electron paramagnetic resonance to study the excited state responsible for the intrinsic green luminescence in $CaMoO_4$[20] and $PbMoO_4$.[21] The luminescence was found to originate from a spin triplet excited state localized on a MoO_4^{-2} ion distorted by a Jahn-Teller instability. In $PbWO_4$, the complex shape of the spectrum of the blue luminescence band was attributed by Polak *et al.*[34] to Jahn-Teller splitting of the nearly degenerate localized excited states of a WO_4^{-2} complex anion. In contrast, it is the delocalized exciton band states which determine the near- edge excitation spectrum.

The band gaps of $PbWO_4$ and $CaWO_4$ can be assigned on the basis of excitation spectra of thermoluminescence[26,29] or phosphorescence.[35] Excitation of thermoluminescence or trap-mediated recombination phosphorescence implies charge separation followed by capture in traps. Such excitation spectra may be considered to yield information similar to photoconductivity spectra, without the need to apply an external field. We have chosen the threshold for production of free carriers, E_{fc} , as the beginning of the steep rising edge of the thermoluminescence excitation spectrum in $PbWO_4$ single crystals measured at 80 K by Mürk et al.[26] It is listed as $E_{fc} = 4.7$ eV in Table IV. Estimating the free-carrier threshold for a single crystal of $CaWO_4$ at a roughly corresponding point on its thermoluminescence excitation spectrum[26], we find $E_{fc} \approx 7$ eV. Gurvich *et al.*[35] assigned $E_{fc} \approx 6.5$ eV for calcined powder samples of $CaWO_4$ at 295 K and Nagirnyi *et al.*[29] recently found $E_{fc} \approx 6.8$ eV for single crystals of $CaWO_4$ at 8 K. We will adopt $E_{fc} \approx 6.8$ eV as the band gap for data comparisons below.

We have made use of E_{fc} in order to overlay the valence band density of states from the present calculation with spectra of reflectivity and luminescence excitation near the interband edge in $PbWO_4$ (Fig. 15) and in $CaWO_4$ (Fig. 16). Although it is not expected that optical spectra should be directly comparable to the valence band density of states in general, our rationale for the present comparison is that the main differences in band structure which we want to compare between $CaWO_4$ and $PbWO_4$ occur near the top of the valence band, whereas the conduction band edge is similar in both materials. Furthermore, as long as we confine attention to transitions near the interband edge, overlapping optical transitions should not complicate the spectra so much as to obscure basic valence structure.

With these caveats in mind, we have aligned the top edge of the valence band density of states, $N^T(E)$, with the photon energy $(h\nu)$ corresponding to the experimental band gap E_{fc} , such that deeper valence states correspond to the higher photon energies needed to excite them. The implied assumption is that the important spectroscopic features near the interband edge represent mainly transitions from successively deeper valence states to just the conduction band edge, and that a rough comparison to the density of initial states may be made without treating transition matrix elements explicitly. In future work, we will calculate optical constants from the band structure for a more accurate comparison over a larger photon energy range.

We focus now on the $PbWO_4$ reflectance and luminescence excitation spectra measured at liquid helium temperature by Kolabanov *et al.*[24] and reproduced in Fig. 15 with the aligned and overlaid valence band density of states.[36] It is obvious that the lowest-energy peak in reflectivity lies within the band gap, in agreement with the previous identification of the 4.2 eV peak as an exciton.[26,24,23,22,25] The exciton binding energy is 0.5 eV if the band gap is $E_{fc} = 4.7$ eV. The rise of reflectivity on the high energy side of the exciton line coincides with the onset of interband transitions out of the highest valence states in the overlaid $N^T(E)$, starting at 4.7 eV on the photon energy scale. The luminescence excitation spectrum, which should have some correspondence to the absorption spectrum in this region, exhibits a shoulder roughly matching the shoulder at the top of the calculated valence $N^T(E)$. The strong O $2p$ peaks in the valence $N^T(E)$ spectrum rise sharply at about 6 eV on the aligned photon-energy scale, just where the experimental excitation spectrum turns sharply upward. The deeper group of valence bands accessible by photons above 8 eV seem a little mis-aligned with the valley at 8.6 eV and the peak at 10 eV in the excitation spectrum. This may indicate that we are getting too far from the interband edge for this simplistic comparison to valence structure to be faithful. Another reason for the apparent mis-alignment with the 10-eV peak in the excitation spectrum is that at least parts of the peaks at 10 eV and 15 eV probably correspond to excitation multiplication[37,29] at photon energies 2 and 3 times the band gap. We note that the isolated narrow Pb 6s peak in the calculated $N^T(E)$ at $h\nu = 12$ eV ($E =$ -7.2 eV) aligns well with the bump in the excitation spectrum at the corresponding energy.

Similar comparisons can be made for $CaWO_4$ reflectivity and the overlaid valence $N^T(E)$ in Fig. 16. With the band gap taken to be $E_{fc} \approx 6.8$ eV as discussed above, the exciton reflectance peak at 5.9 eV implies a 0.9 eV binding energy of the exciton. Furthermore, we find reasonable qualitative correspondence between both the energy location and width of the valence $N^T(E)$ structure aligned in this way and the region of main reflectivity structure above the exciton, measured by Grasser *et al.*.[22]

The shape of the optical spectra near the interband edge in $PbWO_4$ is suggestive of a weaker absorption threshold followed at higher energy by a stronger threshold in stair-step fashion, whereas in $CaWO_4$ there appears to be a main absorption threshold with which the exciton is associated. The "strong" absorption thresholds in both materials involve direct transitions at Γ starting from valence states with overwhelming O 2p character. The weaker threshold and associated exciton in $PbWO_4$ involve the topmost valence band which disperses upward away from Γ, extending about 1 eV higher than the dominant O 2p bands at Γ. According to Fig. 9 and Table III, there is a minimum-energy direct transition at about 0.5 along Σ and another direct transition 0.19 eV higher at about 0.5 along Δ. In this regard, it is interesting to note that the 4.2 eV reflectance peak in $PbWO_4$ was resolved as a doublet with a 0.1 eV splitting at 4.2 K by Kolobanov *et al.*[24]. An indirect gap from Σ to Δ lies about 0.1 eV lower in energy according to the present calculations. Since the exciton luminescence is emitted after self-trapping with 1.3 eV relaxation, luminescence spectra are unlikely to indicate whether an indirect edge lies 0.1 eV below the minimum direct edge. We know of no data yet available to support or rule out a minimum- energy indirect edge slightly below the direct edge.

We have seen in Fig. 3 that there is no peak in the partial density of states corresponding to Pb 6s orbitals ($N^{Pb}(E)$) at the energy of the top- most valence band. However, because

$N^O(E)$ dips sharply above the energy of the Γ critical point, the relative importance of the nearly constant $N^{Pb}(E)$ increases significantly in the top-most band. With respect to some of the earlier discussions on the involvement of Pb states,[26,23,25] the top-most valence band may be described as having Pb 6s character with a strong admixture of O 2p character. Even though the distinct Pb 6s band actually lies below the valence bands at about -7.2 eV, we conclude that the presence of Pb (rather than Ca) in the $PbWO_4$ scheelite-type material also causes a band with hybrid Pb 6s and O 2p character to disperse upward from Γ and establish the minimum gap. However, a "Pb 6$s \rightarrow$ 6p exciton" is not supported because no Pb^{+2} 6p discrete band was found at the bottom of the conduction band. The minimum-energy direct exciton in $PbWO_4$ should involve charge transfer from both lead and oxygen to mainly tungsten. In $CaWO_4$ and also in $PbWO_4$ at its second absorption threshold, the direct exciton at Γ involves charge transfer mainly from oxygen to tungsten.

C. Summary

For the four scheelite materials studied in this work, the results of the partial densities of states analyses (Figs. 3, 4, 5, and 6) and electron density contour plots (Figs. 10, 11, 12, and 13) together with the band structure plots (Figs. 8 and 9) are in qualitative agreement with the energy level diagram presented in Fig. 14. Namely, the main features of the valence and conduction band states near the energy band gap are well approximated by the molecular orbitals[16] of the tetrahedral molybdate or tungstate ions. The valence band accommodates 48 electrons per unit cell in one-to-one correspondence with the number of O 2p states. The shape of the valence band density of states has two main peaks, with the upper peak primarily composed of O 2$p\pi$ states and the lower peak composed of a combination of O 2p σ and π states together with contributions from the d states of Mo or W. The lowest conduction band is largely formed from e- symmetry states derived from d states of Mo or W and, in the Ca materials, is separated from the upper conduction band by a small gap. The upper conduction band is largely formed from t_2- symmetry states derived from d states of Mo or W. In the Pb materials, a narrow band of filled states is formed 1 eV below the valence bands as a result of the Pb 6s states. In the Ca materials, the 3d orbitals form a narrow band above the molybdate or tungstate conduction bands.

In addition to these general features, there is significant hybridization of the Pb 6s and 6p states throughout the valence and conduction bands of $PbMoO_4$ and $PbWO_4$, so that the band dispersions and splittings in the Pb materials are different from those of the Ca materials. In particular, the top-most valence band acquires significant Pb 6s character along with O 2p character and disperses upward away from the Γ point of the Brillouin zone. We have analyzed some of the optical properties of these materials as summarized in Table IV and have made a rough comparison of our densities of states with reflectance and excitation yield data in Figs. 15 and 16. In the future, we hope to use the present results as a basis for a more thorough analysis of the optical properties of these materials.

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magnitude of reflectance at the exciton peak versus the interband region above it. We have chosen the data of Ref. 24 for comparison to the calculated $N^T(E)$ in Fig. 15 mainly because it also includes a luminescence excitation spectrum.

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FIGURES

FIG. 1. Perspective drawing of the structure of $PbWO_4$ indicating the a and c axes. The atomic positions are indicated by spheres. The largest spheres (with no bonds) are the Pb sites; the middle size spheres at the W sites and the smallest spheres at the O sites are connected along nearest neighbor bonds. The shaded plane passes through two W–O bonds and one of the Pb sites. Contour levels corresponding to the occupied electron density in the valence band are indicated on this plane with lowest contour level at 0.1 e/Å^3 and with a spacing of 0.25 e/Å^3 between contours.

FIG. 2. Plot of total densities of states per unit cell for the four ABO_4 scheelite materials, evaluated using Eq. (1) with $\sigma = 0.1$ eV including upper core, valence, and conduction band states. The zero of energy is taken at the top of the last occupied states. The upper core states are labeled according to their dominant atomic behavior.

FIG. 3. Atomic partial densities of states per muffin tin sphere for the four ABO_4 scheelite materials, evaluated as described in Fig. 2. The partial densities were weighted by the charges within a muffin tin sphere for Ca or Pb (solid line), Mo or W (dashed line) and O (dotted line).

FIG. 4. Crystal field split O $2p$ partial densities of states per muffin tin sphere for the four ABO_4 scheelite materials, evaluated as described in Fig. 2. The partial densities were weighted by the σ-like (full line) and π-like (dotted line) charges within each O muffin tin sphere.

FIG. 5. Crystal field split $4d$ and $5d$ partial densities of states per muffin tin sphere for the four ABO_4 scheelite materials, evaluated as described in Fig. 2. The partial densities were weighted by the e- like (full line) and t_2-like (dotted line) charges within a Mo or W muffin tin sphere.

FIG. 6. Ca and Pb atomic orbital partial densities of states for the four ABO_4 scheelite materials, evaluated as described in Fig. 2. The partial densities were weighted by the s-like (full line), p-like (dashed line), and d-like (dotted line) charges within each Ca or Pb muffin tin sphere.

FIG. 7. Diagram of the Brillouin zone for a body-centered tetragonal crystal structure, based on Ref. 38.

FIG. 8. Band structure diagram for $CaMoO_4$ and $CaWO_4$ plotted in the range of 6 eV below and 10 eV above the valence band maximum (taken as the 0 of energy). The bands are plotted along the $\hat{\mathbf{z}}$ (c) axis from Γ to Z and within the a plane from its boundary at $\frac{\pi}{a}(1+(\frac{a}{c})^2)$ along the Σ direction to the Γ point and from the Γ point along the Δ direction to the X point, where the labels correspond to Fig. 7.

FIG. 9. Band structure diagram for $PbMoO_4$ and $PbWO_4$ plotted in the same energy range and along the same Brillouin zone directions as in Fig. 8.

FIG. 10. Contour plot of the electronic charge density associated with the valence band of $PbWO_4$, showing separately the narrow 0.5 eV band associated with the Pb $6s$ states which is separated from the valence band by 1.5 eV (labeled I), the bottom 2.3 eV of the valence bands (labeled II), and the top 3.2 eV of the valence bands (labeled III). The plane of the contour plot is the same plane as shown in Fig. 1, and passes through four atomic sites: 2 O sites, 1 W site, and 1 Pb site. The contour levels are uniformly spaced starting at 0.1 e/Å^3 with a spacing of 0.2 e/Å^3 between contours.

FIG. 11. Contour plot of the electronic charge density associated with the valence band of $CaMoO_4$, showing separately the bottom 1.9 eV (labeled II) and the top 3.0 eV (labeled III) portions. The plane of the contour plot and the contour levels are the same as in Fig. 10.

FIG. 12. Contour plot of the electronic charge density associated with the conduction bands of $PbWO_4$, showing separately the lower 2.1 eV portion (IV) and the next higher 3.4 eV portion (V) of the conduction band. The plane of the contour plot and the contour levels are the same as in Fig. 10, with the density calculated from full occupancy of these states.

FIG. 13. Contour plot of the electronic charge density associated with the conduction bands of $CaMoO_4$, showing separately the lower conduction band having a width of 1.2 eV (IV), the bottom 1.6 eV of the upper conduction band (which is 0.9 eV above the lower conduction band) (V), and the next 2.8 eV of the upper conduction band (VI). The plane of the contour plot and the contour levels are the same as in Fig. 10, with the density calculated from full occupancy of these states.

FIG. 14. Schematic diagram of the crystal field splitting and hybridization of the molecular orbitals of a tetrahedral $WO_4^{-\alpha}$ (or $MoO_4^{-\alpha}$) cluster using the notation of Ref. 16, with "*" indicating anti-bonding (unoccupied) states. The numbers in parentheses indicate the degeneracy (including spin degeneracy) of each cluster state. The ordering of the molecular orbitals in the diagram approximates the partial density of states analyses. The shaded boxes are included to emphasize the fact that the discrete states are broadened by neighboring cluster interactions in the solid material. The relative positions of the Pb $6s$ states (for $PbWO_4$ and $PbMoO_4$) and Ca $3d$ states (for $CaWO_4$ and $CaMoO_4$) are also indicated on this diagram.

FIG. 15. Experimental spectra of reflectance [R($h\nu$)] and excitation yield of intrinsic luminescence [Y($h\nu$)] measured for $PbWO_4$ at liquid helium temperature in Ref. 24 are overlaid with the calculated total density of states [$N^T(E)$]. The experimental free carrier excitation threshold $E_{fc} = 4.7$ eV, as discussed in the text, is used to align the top ($E = 0$ eV) of the valence density of states with the photon energy scale such that $h\nu$ is the energy from each plotted valence state to the conduction band edge.

FIG. 16. Reflectance spectra [R($h\nu$)] measured for $CaWO_4$ in Ref. 22 are overlaid with the calculated total density of states [$N^T(E)$]. The broken and solid reflectance spectra were measured at 77 K and 295 K, respectively. The experimental free carrier excitation threshold $E_{fc} \approx 6.8$ eV, as discussed in the text, is used to align the top ($E = 0$ eV) of the valence density of states with the photon energy scale such that $h\nu$ is the energy from each plotted valence state to the conduction band edge.

TABLES

TABLE I. Some representative experimental data for ABO_4 scheelite crystals at room temperature. Quoted values refer to the conventional unit cell structure with A sites at $\pm(0, \frac{1}{4}, \frac{5}{8})$; B sites at $\pm(0, \frac{1}{4}, \frac{1}{8})$; and O sites at $\pm(x, y, z)$, $\pm(\frac{1}{2}-x, -y, \frac{1}{2}+z)$, $\pm(-\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}+z)$, and $\pm(-\frac{1}{4}+y, -\frac{1}{4}-x, -\frac{1}{4}+z)$, where 12 additional lattice sites are generated by adding $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Some references use the alternative O site parameters $x \to \frac{1}{4}-y$, $y \to \frac{1}{4}-x$, and $z \to \frac{1}{4}-z$. Still other references choose the origin of the unit cell at the site of a B atom with the corresponding O positions described with parameters $x \to x$, $y \to \frac{1}{4}-y$, and $z \to \frac{1}{8}-z$. The experimental methods are abbreviated with "XP" for X-ray powder, "XC" for X-ray single crystal, and "N" for neutron diffraction. The starred rows indicate the parameters used in the present calculations.

Material	Year	Ref.	Method	a (Å)	c (Å)	c/a	x	y	z
$CaMoO_4$	1943	[8, 39]	XP	5.213	11.426	2.192	0.25	0.10	0.05
	1971	[40]	N	5.226	11.43	2.187	0.2428	0.1035	0.0424
	1972	[41]	XP	5.2256	11.434	2.188			
	*1985	[9]	XC	5.222	11.425	2.188	0.2431	0.1010	0.0411
$CaWO_4$	1943	[8, 39]	XP	5.230	11.348	2.170	0.25	0.10	0.05
	1964	[42]	XC	5.234	11.376	2.170	0.2415	0.0996	0.0389
	1964	[43]	N				0.2413	0.0989	0.0389
	1972	[44]	XP	5.2437	11.3754	2.169			
	1972	[41]	XP	5.2419	11.376	2.170			
	*1985	[9]	XC	5.2429	11.3737	2.169	0.2414	0.0993	0.0394
	1989	[45]	XP	5.24294	11.373	2.169			
$PbMoO_4$	1943	[8, 39]	XP	5.424	12.076	2.226	0.25	0.12	0.05
	*1965	[46]	N	5.4312	12.1065	2.229	0.2352	0.1143	0 .0439
	1972	[47]	XP	5.4360	12.1107	2.228			
	1972	[41]	XP	5.4355	12.108	2.228			

	1985	[9]	XC	5.4351	12.1056	2.227			
$PbWO_4$	1943	[8, 39]	XP	5.448	12.016	2.206	0.25	0.12	0.05
	1972	[41]	XP	5.4622	12.048	2.206			
	1985	[9]	XC	5.4595	12.0432	2.206			
	*1996	[48]	XC	5.456	12.020	2.203	0.2388	0.1141	0.0429
	1996	[49]	XC	5.4612	12.0452	2.206	0.2524	0.1364	0.0446

TABLE II. List of calculational and convergence parameters used for LAPW calculations

Muffin tin radii:	Ca, Pb	1.9 Bohr
	Mo, W	1.65 Bohr
	O	1.65 Bohr
Maximum $\lvert\mathbf{k}+\mathbf{G}\rvert$ for wavefunctions		6 Bohr $^{-1}$
Maximum $\lvert\mathbf{G}\rvert$ for charge density		14 Bohr $^{-1}$
Inequivalent **k**-points for BZ integrals		6
Convergence tolerance of total energy		0.001 eV

TABLE III. Band gaps determined from the band dispersion calculations shown in Figs. 8 and 9 are listed for various values of **k** for the valence and conduction bands (k_v and k_c, respectively).

Material	E_{gap} (eV)	k_v $\left(\frac{2\pi}{a}\right)$	k_c $\left(\frac{2\pi}{a}\right)$
$CaWO_4$	4.09	Γ	Γ
$CaMoO_4$	3.41	Γ	Γ
$PbWO_4$	2.96	0.51 (Δ)	0.47 (Σ)
	3.06	0.47 (Σ)	0.47 (Σ)
	3.25	0.47 (Δ)	0.47 (Δ)
	4.13	Γ	Γ
$PbMoO_4$	2.59	0.57 (Δ)	0.47 (Σ)
	2.71	0.47 (Σ)	0.47 (Σ)
	2.93	0.51 (Δ)	0.51 (Δ)
	3.62	Γ	Γ

TABLE IV. Optical parameters (in units of eV) measured and deduced from experimental spectra. In a few cases, multiple entries are listed in order to illustrate the variability of these parameters, depending on temperature (T), sample preparation, and other factors.

	$CaWO_4$	$PbWO_4$	$CaMoO_4$	$PbMoO_4$
Luminescence peak (E_{lum})	2.9[a]	2.9[b]	2.3[a]	2.2[c]
Luminescence width (FWHM)	0.8[a]	0.8[b]	0.6[a]	0.6[c]
		0.7[b,d]		0.5[e]
Exciton reflectance peak (E_{exc})	5.9[f]	4.2[g,h]	5.0[f]	
Luminescence Stokes shift (ΔE_S)	3.0	1.3	2.7	
Free-carrier threshold (E_{fc})	7.0[i]	4.7[i]		
	6.5[j]			
	6.8[k]			
Exciton binding energy (E_b)	0.9	0.5		
Luminescence excitation threshold (Y_{th})	5.1[l]	4.1[g]	4.6[l]	3.4[c,e]
	4.7[m]	4.0[m]		

[a]Ref. [50], T = 295 K.

[b]Ref. [51], T = 295 K.

[c]Ref. [31], 1.6 K < T < 144 K.

[d]Ref. [52], T = 4.2 K.

[e]Ref. [53], at T = 4.2 K (luminescence spectrum); at T = 77 K (excitation spectrum).

[f]Ref. [22], T = 295 K.

[g]Ref. [24], T = 4.2 K, 295 K.

[h]Ref. [23], T = 295 K.

[i]Deduced from the thermoluminescence excitation spectra of Ref. [26], T = 80 K.

[j]Ref. [35], calcined powder sample, T = 295 K.

[k]Ref. [29], single crystal, T = 8 K.

[l]Ref. [54], T = 295 K.

[m]Ref. [26], T = 80 K.