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Electronic, optical and luminescent properties of PbFCl single crystal

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Abstract

The first-principles calculation of energy band structure and density of states of the PbFCl crystal based on the plane waves and pseudopotential method in the frame of the generalized gradient approximation (GGA) were performed. Further, calculation with the *GW* approximation was used to correct the bandgap. The so-called *GW* approximation represents the lowest expansion of the self-energy, Σ , equal to the Green function *G* times the screened Coulomb interaction *W*. The calculated result shows that the direct bandgap is located at the Z point in the Brillouin zone with the gap of 3.5 eV in the GGA frame and 5.0 eV after *GW* correction. X-ray photoemission spectroscopy for the valence band (VB-XPS) was carried out to compare with the calculated density of states in the valence band, suggesting that the calculated result is in agreement with the experimental result. The reflection, excitation and emission spectra were measured using a synchrotron radiation light source in the energy region of 4–9.5 eV. The absorption and emission of the cation exciton was observed at 5.0 and 3.8 eV, respectively. The components of Pb 6p states and Pb 6s states located at the bottom of the conduction band and the top of the valence band, respectively, prove the possibility of the cation exciton of Pb²⁺. Violet band emission peaking at 3.1 eV was also observed, which may be due to the self-trapped exciton or the Pb²⁺ ion close to the Schottky-like defect.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

PbFCl crystal with the space group of $P4/nmm$ is the matlockite structure [1]. The properties of other matlockite structure compounds MFX ($M = \text{Sr, Ba}$; $X = \text{Cl, Br}$) have been extensively investigated because of the practical applications. For example, BaFX ($X = \text{Cl, Br}$):Eu is used as an x-ray phosphor for medical imaging [2, 3]. SrFCl:Sm can be used as a sensor to measure the pressure in diamond anvil cells at high temperature [4, 5].

Recently, the study of PbFCl is attracting more attention because the potential application as a scintillator has been found. High quality PbFCl crystals were grown by a modified Bridgman method in the Shanghai Institute of Ceramics, China [6, 7]. The scintillation light yield is about 20% of that of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) scintillator at room temperature [8]. The scintillation light with decay constants of 4 and 35 ns was obtained. This is the first time that considerable luminescence intensity has been achieved at room temperature, in contrast to the previous reports [9, 10]. The PbFCl single crystal is a promising scintillator to substitute lead perchlorate solution in neutron detection due to many advantages [8].

The theoretical study of electronic properties on the matlockite structure compounds MFX ($M = \text{Sr, Ba, Pb}$, $X = \text{Cl, Br}$) can be found in the past two years [11, 12]. Kanchana *et al* calculated the structural and electronic properties of SrFBr, SrFI and CaFBr using the self-consistent tight binding linear muffin tin orbital method (TB-LMTO) [11]. Hassan *et al* theoretically studied the electronic properties of MFX ($M = \text{Sr, Ba, Pb}$; $X = \text{Cl, Br, I}$) using the full potential linear-augmented plane wave method (FP-LAPW) [12]. Unfortunately, no experimental results except for the lattice constants were obtained and compared with the calculated results. Therefore, the research combined with theoretical calculation and experiment is still necessary for our understanding of the electronic and optical properties and checking the validity of theoretical calculation.

In this paper, electronic structure calculations for PbFCl are performed. For a comparison, we present the result of x-ray photoemission spectroscopy for the valence band (VB-XPS) on PbFCl. The luminescence spectra under the excitation of VUV-UV synchrotron radiation and the reflection spectrum were measured. A discussion on the experimental results and theoretical calculations is presented.

2. Method of calculations

First-principles total-energy calculations of PbFCl were performed using the ABINIT code [13, 14], which is based on pseudopotentials and plane-waves. It relies on an efficient fast Fourier transform algorithm [15] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate gradient method [16] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [17]. Exchange and correlation were treated in the generalized gradient approximation (GGA) [18] based on the density functional theory (DFT) [19]. The pseudopotentials have been generated thanks to the FHI98PP code [20]. The electronic wavefunctions were expanded in plane waves up to a kinetic energy cut-off of 15 Ha ($1 \text{ Ha} = 27.21 \text{ eV}$). A $4 \times 4 \times 4$ k -point grid based on the primitive vectors of the reciprocal space was applied. The density of states as well as partial density of states on Pb, F and Cl was calculated using the tetrahedron method. The calculation of band structure for PbFCl along the high symmetry directions in the BZ was performed. GW calculations for the correction of the bandgap at the Z point for the highest occupied and the lowest empty bands were also carried out.

3. Method of experiment

PbFCl single crystals were grown by the modified Bridgman method developed in the Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS). PbF_2 (99.999%) and PbCl_2 (99.5%) powders were used as starting materials. The detailed growth method was described in [6]. A piece of PbFCl single crystal with 1.0 mm thickness was prepared for this study.

The XPS spectra were obtained with a monochromatized Mg $K\alpha$ x-ray source (1253.6 eV) at room temperature using an Escalab mark II electron spectrometer. The energy resolution is 0.9 eV. The pressure in the vacuum chamber during the measurement was less than 2×10^{-8} mbar. Ar^+ sputtering was used to clean the sample surface. The spectrum was recorded until the contamination of C and O had been removed.

The reflection, excitation and emission spectra at 20 K were measured at the VUV station of the National Synchrotron Radiation Laboratory (NSRL), Hefei, People's Republic of China. The typical spectral resolution of the primary monochromator (1 m Seya-Namioka) and the secondary monochromator (Spectrapro-275) is 0.4 and 2 nm, respectively. The pressure in the vacuum chamber during the measurements was 1×10^{-4} Pa. The excitation and emission spectra were detected by a Hamamatsu H5920-01 photomultiplier. The reflection spectrum was recorded by a 9402B photomultiplier (Electron Tubes Limited), which is mainly sensitive to VUV but does not respond to visible light. The excitation spectra were corrected for the photo flux of the excitation beam using the excitation spectrum of sodium salicylate as standard. The reflection spectrum was corrected for the spectral distribution of the incident light detected by the same detector as the reflection spectrum measurement.

4. Results and discussion

4.1. Structural properties

PbFCl crystal belongs to the matlockite structure. Matlockite structure with space group $P4/nmm$ (D_{4h}^7 , no 129) is characterized by the tetragonal layered structure which consists of planes perpendicular to the c -axis [21], shown in figure 1. The Pb ions are on one side coordinated by a plane of four fluorine ions and on the other side coordinated by five Cl ions, of which one is on the c -axis out of the plane formed by the others. There are two molecules per unit cell. The atomic positions of PbFCl are given as the following.

$$\text{Pb: } 0 \quad 0.5 \quad 0.2; \quad \text{F: } 0 \quad 0 \quad 0; \quad \text{Cl: } 0 \quad 0.5 \quad 0.65.$$

The experimental lattice constants of $a = b = 4.106 \text{ \AA}$, $c = 7.23 \text{ \AA}$ [22], were used as the initial input during the optimized calculation for each lattice constant. The calculated lattice constants are $a = b = 4.156 \text{ \AA}$, $c = 7.319 \text{ \AA}$, which is in good agreement with the experimental results. The calculated lattice constants are 1.2% larger than experimental values because the GGA is known to often overestimate the lattice constants [23].

4.2. Band structure and density of states

The band structure of the PbFCl crystal along the high-symmetry lines of the Brillouin zones (BZ) is shown in figure 2. The total and partial density of states of PbFCl is shown in figure 3. The Fermi level is set to be zero. The band structure belongs to a typical ionic insulator with the relatively large bandgaps of 3.5 eV and a flat-topped valence band (VB). The real bandgap is somewhat larger than the calculated value because the GGA in the DFT framework often underestimates the bandgap. The top of the VB and the bottom of the conduction band (CB) are both located at the Z point, suggesting that the PbFCl is direct bandgap material. The top

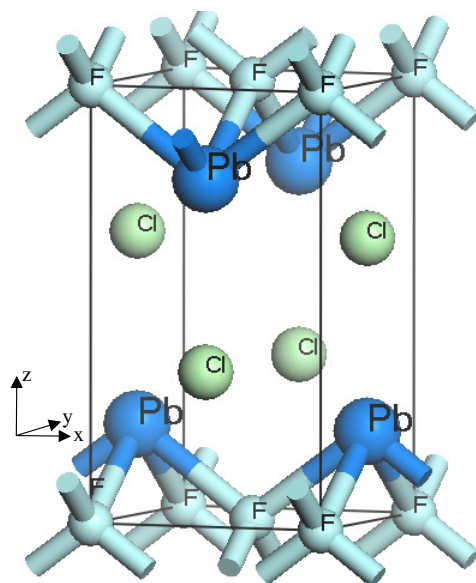


Figure 1. The crystal structure of PbFCl.

of the VB mainly originates from the Cl 3p states, below which F 2p states are mainly located between -4.1 and -2.6 eV as well as -6.9 eV. Pb 6s states and Cl 3s states are mainly located at -6.9 and -12.9 eV, respectively. The sharp and strong contribution of Pb 6d states lies at -15 eV. The CB is comprised of Pb 6p states at 3.8 – 7.0 eV and a small number of Cl 3p states at 6.5 eV. The band structure and density of states in the present paper are consistent with the results calculated using the FP-LAPW method [12], indicating that the calculated results are reasonable. Furthermore, the *GW* approximation calculation was performed to obtain the more precise bandgap with the experimental result. The result of *GW* calculation shows the bandgap at the Z point to be 5.0 eV, which is very close to the experimental result of 5.2 eV based on the reflection spectrum.

The VB-XPS for the PbFCl single crystal is shown in figure 4. For comparison the calculated total density of states are also displayed. The profiles of VB-XPS are in agreement with the calculated density of states. It should be mentioned that the experimental result cannot present as many details as the calculated result because of the background and broadening factor responsible for the experimental energy resolution of VB-XPS. In the VB-XPS, the valence band in the region of -4.2 to 0 eV belongs to the F 2p and Cl 3p components. Three peaks with binding energy at about 7.7 , 14.6 and 15.4 eV appear in the VB-XPS, which is ascribed to the (Pb 6s, F 2p orbitals), Cl 3s orbitals and Pb 6d orbitals respectively. The agreement of VB-XPS with calculated density of states indicates that the present calculation based on first principles is reliable.

4.3. Optical and luminescent properties

The reflection and excitation spectra at 20 K are shown in figure 5. The reflection spectrum exhibits an absorption peak at 5.0 eV and interband transition absorption in the energy higher than 5.2 eV. It is estimated that the bandgap is 5.2 eV. This experimental value of the bandgap is in good agreement with the *GW* calculated value. The emission spectra at 20 K, shown

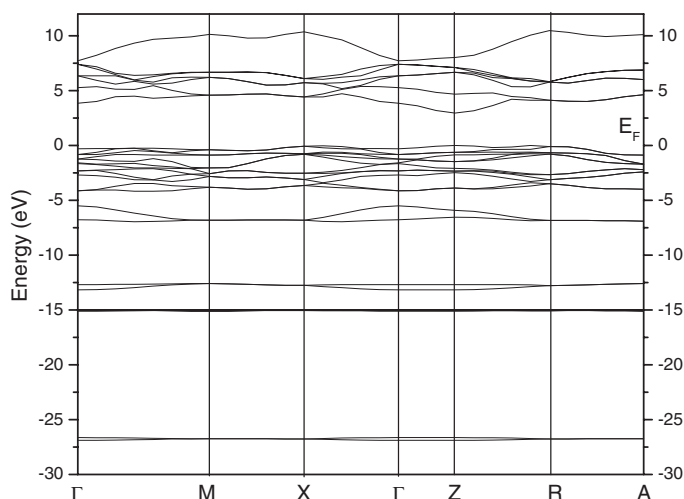


Figure 2. The band structure of PbFCl.

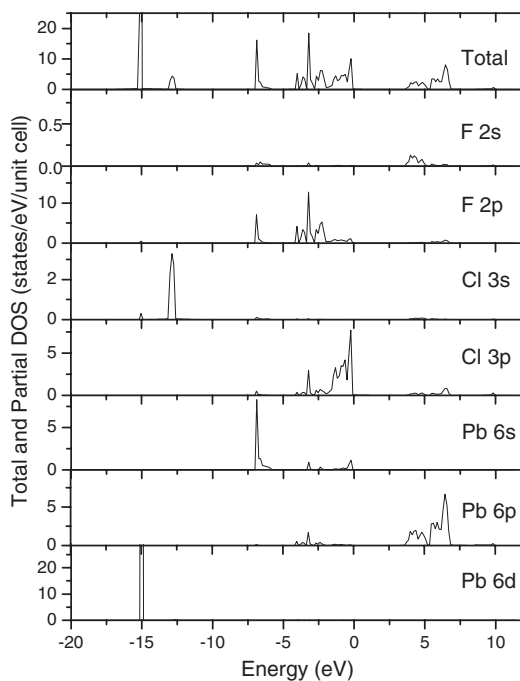


Figure 3. The total and partial density of states of PbFCl.

in figure 6, exhibit two bands peaking at 3.1 (violet band) and 3.8 eV (UV band) under the excitation at 5.3, 5.0 and 7.0 eV. From figure 5(b), the excitation spectrum with 3.1 eV emission exhibits a band peaking at 5.0 eV and a shoulder at 4.8 eV below the bandgap region and some bands peaking at 5.3, 6.0, 7.0 and 7.4 eV beyond the bandgap region in which the properties of the valence band and the conduction band are exhibited. The excitation spectrum of 3.8 eV emission shows the similar characteristics to the excitation spectrum of 3.1 eV emission except

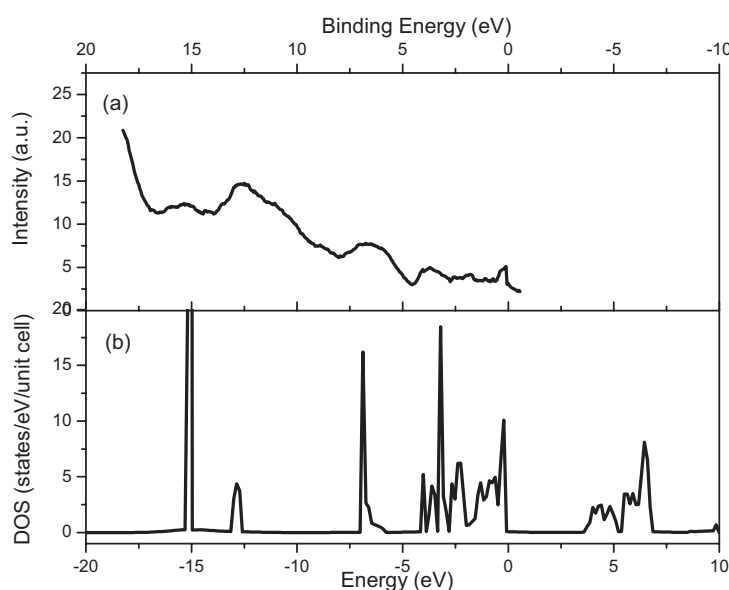


Figure 4. The VB-XPS spectrum (a) and the density of states (b) of PbFCl.

that the shoulder at 4.8 eV disappears, suggesting that the excitation band at 4.8 eV can only excite the 3.1 eV emission. The UV emission band peaking at 3.8 eV can be ascribed to the cation exciton of Pb^{2+} with the transition of $(6s6p) \ ^3P_1 \rightarrow (6s^2) \ ^1S_0$ on Pb^{2+} . In the earlier report on the luminescence of PbFCl [9, 10], the violet band emission was also observed but the UV band emission was absent. The absence of UV band emission is probably due to the poor crystal growth technology resulting in the quenching of cation exciton emission. The peak at 5.0 eV in the reflection and excitation spectra is due to the absorption of the cation exciton of Pb^{2+} with the transition of $^1S_0 \rightarrow ^3P_1$. There is a considerable Stokes shift of 1.2 eV between the absorption and emission of the cation exciton. The energy of the Stokes shift may originate from the splitting of 3P_1 by the pseudo-Jahn-Teller effect into $^3P_1^{(1)}$ and $^3P_1^{(2)}$. Such a cation exciton of Pb^{2+} was observed in $\beta\text{-PbF}_2$ [24], PbCl_2 [25] and PbBr_2 [25]. From the calculated partial density of states, one can find that the conduction band consists of Pb 6p states and part of the F 2s states participate in the formation of the top of valence band. Slightly below the bottom of the conduction band, there exist some localized Pb 6p states in the bandgap. Similarly, there should be some Pb 6s states at the top of the valence band. The radiative transition takes place from a localized exciton state, not a free one [26]. Additionally, such a cation exciton exhibits a significant thermal quenching effect above 60 K for PbX_2 ($X = \text{F}, \text{Cl}, \text{Br}$) [26] and PbFCl [27]. In this sense, this luminescence process from Pb^{2+} is analogous to exciton luminescence in alkali halide crystals [28], thus we call it a cation exciton. In fact, the cation exciton emission in the PbFCl crystal has been observed for the first time in our recent investigation. This is partly because of the significant progress in crystal growth using the modified Bridgman method, which can greatly reduce the oxygen contamination. The violet band emission peaking at 3.1 eV is also reported in previous articles [9, 10]. Although the origin of the violet band is not very clear, its luminescence centre may be the self-trapped exciton, which is a common luminescence centre in halides [26], or the Pb^{2+} ion close to the Schottky-like defect based on the result of computer simulation [29, 30].

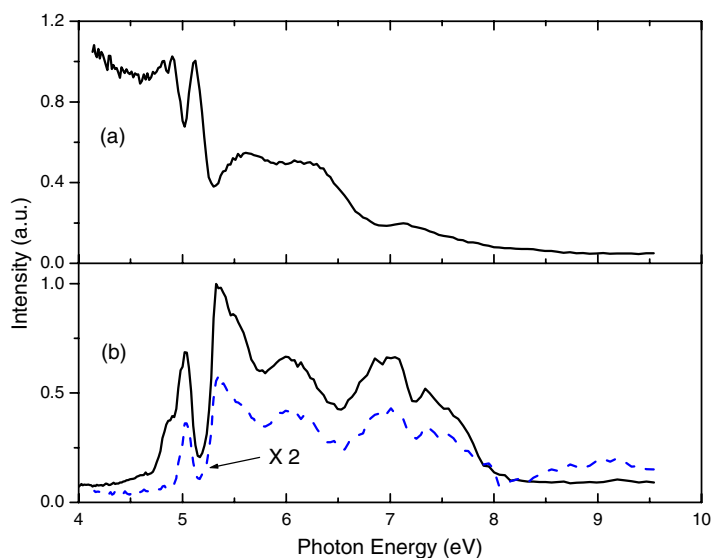


Figure 5. Reflection spectrum (a) and excitation spectra (b) with 3.8 eV (dashed line) and 3.1 eV (solid line) emission bands in PbFCl at 20 K.

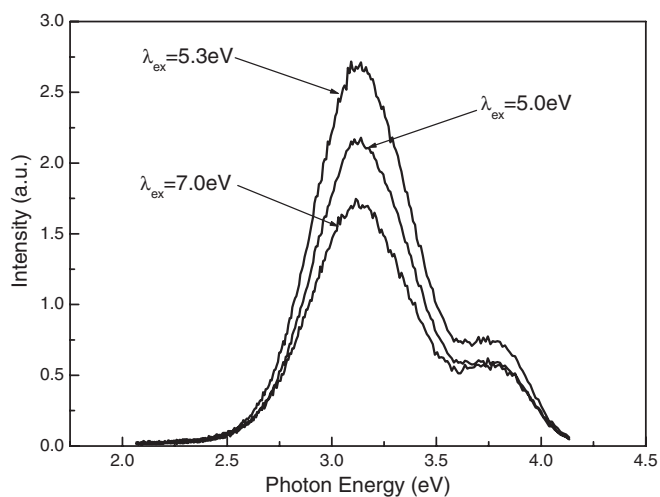


Figure 6. Emission spectra of PbFCl at 20 K under excitation at 5.0, 5.3 and 7.0 eV.

5. Conclusion

First-principles calculations of band structure and density of states of the PbFCl crystal indicate that the PbFCl is a direct bandgap material at the Z point in the BZ with a gap of 3.5 eV in the GGA frame. The calculation with the *GW* approximation at the Z point gives the corrected bandgap as 5.0 eV, which is in good agreement with the experimental result of reflection and excitation spectra. The density of states shows the top of the valence band consists of dominant Cl 3p states and a small number of Pb 6s and F 2p states, while the conduction band is comprised of Pb 6p states and a little of F 2s states. The calculated valence band is primarily

consistent with the VB-XPS. The absorption and emission of the cation exciton was observed at 5.0 and 3.8 eV, respectively. Violet band emission peaking at 3.1 eV was also observed, which may be due to the self-trapped exciton or the Pb^{2+} ion close to the Schottky-like defect.

Acknowledgments

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