Computational Materials Science 143 (2018) 403–410

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

First principles investigation on pressure induced phase transition and photocatalytic properties in $RbPbCl_3$

Huang Yan, Hu Ziyu *, Li Kaiyue, Shao Xiaohong *

College of Science, Beijing University of Chemical Technology, Beijing 100029, China

A R T I C L E I N F O

Article history:
Received 5 July 2017
Received in revised form 3 October 2017
Accepted 11 November 2017

Keywords:
High pressure
Phase transition
First-principles
Electronic structure properties
Photocatalytic properties

A B S T R A C T

We present a theoretical study on new phase searches, structural stability, pressure induced phase transition and photocatalytic properties in $RbPbCl_3$ using first-principle calculations guided by the developed crystal structure analysis by particle swarm optimization (CALYPSO) methodology. Four new phases of *P4/mmm, C2mm, I4mm* and *Cm* of $RbPbCl_3$ are predicted and the phonon spectra show that all the four phases are thermodynamically and dynamically stable. The calculated results indicated that the four phases are semiconducting and the contribution of edge states mainly comes from the Pb—Cl chains. Besides, the comparison of the band gaps show that pressure can regularly modulate the electronic structures properties for a certain phase. More importantly, the much stable structures and band alignments show that *C2mm*, *I4mm* and *Cm* phases are promising candidates for the properties of photocatalytic water splitting.

1. Introduction

Inorganic–organic halide perovskites (ABX_3, where A = alkali/organic cation, B = Sn, Ge and Pb, and X = halide anion) have attracted enormous attention in the fundamental understanding of materials properties and device development because of its excellent optoelectronic properties of the most compelling candidate for the next generation of low-cost and high efficiency solar cells [1–13]. With the organic-inorganic hybrid perovskite rapidly development, an all-inorganic structure without a volatile organic component exhibits higher stability than the organic ones, and it has huge potential in optoelectronic applications [14–21]. Among the tremendous researches, crystal structure and phase transition are the most fundamental issue in understanding and designing new perovskites to improve the efficiency. Experimentally, some earlier studies reported that lead halide perovskites with the formula $APbX_3$, where $A = Cs^+/Rb^+$ and $X = Cl^-, Br^-$, or I^- shows various phases under different temperatures [15–19], and all possess a cubic perovskite structure (space group: *Pm3m*) at high temperature with desirable band gaps and electronic properties for photovoltaic and detector applications [17,19,22–29]. Umemoto et al. [27] investigated the phase transitions of ABX_3-type compounds by ultrahigh pressure up to 250 GPa by first-principles calculations. Since Rb and Cs belong to the same IA main group, $RbPbX_3$ (X = Cl, Br, I) may be have the similar phase transition behaviors to that of $CsPbX_3$ compounds. Monzel et al. [30] conducted a redetermination of the phase diagram $RbCl/PbCl_2$, and found that $RbPbCl_3$ would not form a single perovskite phase at room temperature but instead forms a two-phase mixture of $Rb_6Pb_5Cl_{16}$ and $RbPb_2Cl_5$. The $Rb_6Pb_5Cl_{16}$ phase adopts a non-perovskite tetragonal structure (space group *P4/mbm*), whereras for $RbPb_2Cl_5$, it has the monoclinic structure type with space group *P21/c*. Later, a perovskite phase $RbPbCl_3$ (space group *Pm3m*) is observed at temperatures above 340 °C. By conducting variable temperature measurements on $RbPbCl_3$, the symmetry and structural phase transitions are determined.

Since several work focused on the structure and phase transition at different temperature, an interesting problem that naturally arises is whether pressure can induce new phases, which is rarely involved. In this work, we focus on the new crystal phases of $RbPbCl_3$ induced by pressure and investigate the structural distortions and phase transitions under different pressures to explore the potential applications in $RbPbCl_3$. Luckily, we predicted four new phases of *P4/mmm*, *C2mm*, *I4mm* and *Cm* in $RbPbCl_3$ using first-principle calculations guided by the developed crystal structure analysis by particle swarm optimization (CALYPSO) methodology. The phonon spectra show that the four new phases are all dynamically stable. Based on this, the bandgaps and moderate positions of the valence band maximum (VBM) and the conduction band minimum (CBM) respect to the water redox level are investigated, and

---

* Corresponding authors.
E-mail addresses: huziyu@mail.buct.edu.cn (Z. Hu), shaoxh@mail.buct.edu.cn (X. Shao).

https://doi.org/10.1016/j.commatsci.2017.11.020
0927-0256/© 2017 Elsevier B.V. All rights reserved.

the results indicate the *C2mm*, *Cm* and *I4mm* phase halides are promising candidates for water splitting from visible to ultraviolet light regions.

2. Computational methods

The crystal structural calculations were performed by CALYPSO methodology [31,32]. The significant feature of this methodology is capable of predicting the stable and metastable structures at given pressure with only the knowledge of the chemical composition. The underlying ab initio structural relaxations and electronic properties calculations are performed by the projector augmented plane-wave (PAW) method [33] within the framework of density functional theory (DFT) in the Vienna Ab Initio Simulation Package (VASP) [34,35]. The exchange and correlation potential are described by generalized gradient approximation in the Perdewe Burkee Ernzerhof (GGA-PBE) and the Heyd, Scuseria, and Ernzerhof (HSE) functional forms [36–41]. The spin-orbit coupling (SOC) effect is considered and the calculations of PBE and HSE with SOC are also performed comparatively for $RbPbCl_3$. The projector augmented wave (PAW) pseudopotential is treated as $5s^15p^63d^{10}$, $6s^26p^2$, and $3s^23p^5$ for Rb, Pb and Cl, respectively. The plane-wave kinetic energy cutoff is set at 600 eV. Unit cells containing a single perovskite formula unit are treated with Γ-centered k-point mesh [42]. All the structures are fully relaxed with a force tolerance of 0.01 eV/Å. The phonon calculations were carried out by a supercell approach [43] as implemented in the PHONOPY code [44]. To obtain the absolute band positions of $RbPbCl_3$ phases, the VBM was normalized by the average electrostatic potential (Φ) obtained from the constructing slab calculations, which are the respective structures using a half-filled $1 \times 1 \times 6$ supercell. The ionization energy (I) was calculated according to $I = \Phi - E_F$, where Φ is the difference between the potential energy of the empty (approaching the vacuum) and filled (approaching the bulk material) sections of the supercell used, and E_F is the fermi energy of the single unit cell. The VBM was set to $-I$, and the CBM was calculated by the equation of $CBM = VBM + E_g$ [45,46].

3. Results and discussion

3.1. Structure predictions

The crystal structures of $RbPbCl_3$ searches are performed by using the CALYPSO code, which contains 1-4 formula units per simulation cell at 0, 10, 50 and 70 GPa. After the full structure searching, four thermodynamically stable high-pressure phases of *P4/mmm*, *C2mm*, *I4mm* and *Cm* are obtained. The ground-state phase of *P4/mmm* structure is shown in Fig. 1a, clearly, a Rb atom is in the center, and there is a corner-linked octahedral structure (one Pb atom surrounded by six Cl atoms) in it. The calculated lattice parameters are a = 4.275 Å, b = 4.275 Å and c = 9.068 Å in a unit cell. Above 10 GPa, a stable structure of tetragonal *C2mm* phase was obtained (shown in Fig. 1b), which contains three $RbPbCl_3$ f.u. in a unit cell and the lattice parameters are a = 16.069 Å, b = 3.837 Å, c = 3.921 Å, in which the corner-sharing $PbCl_6$ octahedral structure is distorted and the length of Pb—Cl is stretched about 1 Å at *a* direction and 0.1 Å along *b, c* directions. Upon further compression to 50 GPa, a novel structure of space group of *I4mm* phase appears, which comprises alternately a stacked structure of PbCl-$RbCl_2$ as a monolayer along its crystallographic axis, as is shown in Fig. 1c. Moreover, this orthorhombic structure contains a polyhedra $PbCl_4$ and an octahedral $RbCl_8$ structure with the lattice constants of a = 3.361 Å, b = 3.361 Å, c = 14.748 Å. Up to 70 GPa, a new crystal structure (space group: *Cm* phase) was predicted to be a stable monoclinic phase (shown in Fig. 1d). The lattice constants at 70 GPa are a = 8.809 Å, b = 4.006 Å, c = 6.308 Å, and α = γ = 90.0°, β=131.9°, in which almost all Pb—Cl and Rb—Cl bonds have the same bond length of 2.803 Å. All crystal structural information and atomic coordinates are shown in Table 1, which are fully optimized at different pressures.

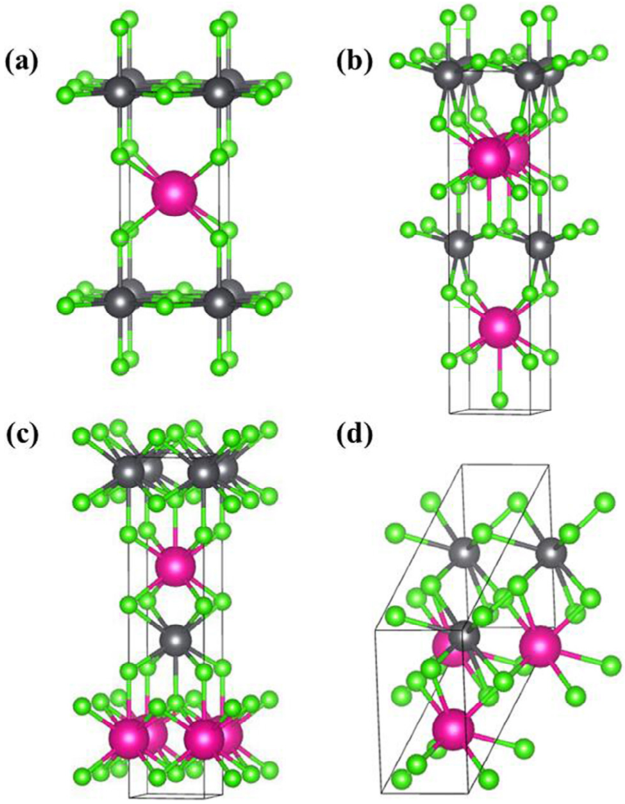

Fig. 1. Structures of the predicted $RbPbCl_3$ phases: (a) *P4/mmm*, (b) *C2mm*, (c) *I4mm*, and (d) *Cm*. Red (large), gray (middle), and green (small) spheres denote Rb, Pb, and Cl atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Enthalpies as a function of pressure for the four new phases of $RbPbCl_3$ (space group: *P4/mmm*, *C2mm*, *I4mm* and *Cm*) are presented in Fig. 2a. To our knowledge, CsCl-type RbCl and cotunnite-type $PbCl_2$ have not yet been seen experimentally at room temperature. According to the previous work, the ternary halides has revealed that reactions of the type: $nACl + MCl_2 = A_nMCl_{n+2}$, (A = alkaline metal, M = Ca, Sr, Ba, Pb) [47–49], and other materials such as $MgSiO_3$ [50,51] perovskite (PV with *Pbnm* symmetry) and $NaMgF_3$-type [27] postperovskite (PPV with *Cmcm* symmetry) are also adopted the same reaction to discuss the pressure-induced transitions. Similarly, the formation enthalpies of $RbPbCl_3$ compounds can be considered as the decomposition into the constituents of RbCl and $PbCl_2$ and it could be synthesized in experiment. The formation enthalpies of $RbPbCl_3$ are calculated by the following equation: $\Delta H_{RbPbCl_3} = H_{RbPbCl_3} - H_{RbCl} - H_{PbCl_2}$, in which ΔH is the formation enthalpy, H_{RbPbCl_3}, H_{RbCl} and H_{PbCl_2} are the energies of the four phases, the cubic phase of RbCl (space group: *Pm3m*) [51–53], and the orthorhombic phase of $PbCl_2$ (space group: *Pnma*) [51,54], respectively. For comparison, the *P4/mmm* phase remains metastable structure up to 8.25 GPa, above which the *C2mm* structure is the most stable structure. Furthermore, the *I4mm* phase in $RbPbCl_3$ is stable ranging from 20 to 65 GPa. Up to 65 GPa, only the *Cm* phase maintains stable crystal structure and it can be existed at the pressure range of 30–100 GPa. These results suggest that the successive transition pressures are 8.25 GPa,