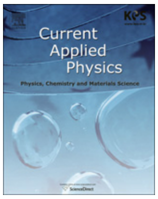
Current Applied Physics 10 (2010) 1286–1289

Contents lists available at ScienceDirect

Current Applied Physics

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



First-principles study of $LiBaF_3$ crystals containing interstitial fluoride☆

Hailing Qiao, Tingyu Liu*, Qiren Zhang, Fang Cheng, Xiuwen Zhou

College of Science, University of Shanghai for Science and Technology, 516JunGong Road, Shanghai 200093, China

ARTICLE INFO

Article history:
Received 24 November 2009
Received in revised form
22 January 2010
Accepted 25 February 2010
Available online 19 March 2010

Keywords:
$LiBaF_3$ crystal
Interstitial fluoride
CASTEP
Absorption spectra
Electronic structure

ABSTRACT

The positions of the interstitial fluoride atoms in $LiBaF_3$ crystal are simulated by GULP. It is found that the formation energy is low when interstitial fluoride atoms at the center of the edge of the cube formed by Ba ions. The electronic structures and absorption bands for the perfect $LiBaF_3$ crystal and the $LiBaF_3$ crystal containing interstitial fluoride have been calculated using density functional theory code CASTEP. It is predicted that the interstitial fluoride atom combine with a formal lattice fluoride ion forming H center causes the 320 nm absorption band.

1. Introduction

Since $LiBaF_3$ crystal has high light yield within a wide temperature range with a nanosecond range decay time, it has been found many applications as dosimeters, information storage devices, X-ray monochromaters and laser media [1–4]. This inorganic material is remarkable because of the presence of both core valence (CV) and self-trapped exciton luminescence (STE) under gamma-irradiation, whereas only the STE luminescence is present under neutron or alpha-irradiation. K. Shimamura and A. Bensalah [5] have grown pure $LiBaF_3$ using Czochralski method. Nishimatsu et al. [6] performed local density approximation based on ab initio calculations for band structure of $LiBaF_3$ crystal. S. Amara Korba et al. [7] studied the structural, electronic and optical properties of $LiBaF_3$ crystal using the full-potential linearized augmented plane-wave method (FP-LAPW). In $LiBaF_3$ crystal, X, γ or UV irradiation creates absorption band in VUV, UV or visible regions due to the creation of color centers. A. V. Chadwick et al. [8] applied extended X-ray absorption fine-structure (EXAFC) to the study of the local structure in pure and doped $LiBaF_3$ crystal. X-ray irradiation provides a useful means for studying the absorption band and color center.

Coloration of $LiBaF_3$ crystal under X-irradiation has been performed by I. Tale et al. [9]. The irradiated crystal exhibits five absorption bands peaks at 270, 320, 430, 660 and 705 nm, respectively. The 270 nm, 320 nm and 430 nm absorption bands have similar quenching temperature. It suggested that these three absorption bands correspond to electron transitions within the same radiation defect. Through thermally stimulated recombination processes in $LiBaF_3$ crystal, it is reported that the 320 nm absorption band may connected with H-centers [10]. Due to lack of direct experimental evidence or theoretical calculations, the origins of 320 nm absorption bands by X-irradiation are not clearly up to now.

Computer simulation provides a useful means for studying the properties of $LiBaF_3$ with various kinds of defects. R. A. Jackson et al. [11] study the properties of pure and doped $LiBaF_3$ with various kinds of defects by computer simulation. In order to investigate the existent form of interstitial fluoride ions in $LiBaF_3$ crystal, several possible defect models are studied using the general utility lattice program (GULP) and the corresponding electronic structures and the optical absorption bands of the $LiBaF_3$ crystal with interstitial fluoride calculated by the CASTEP code.

2. Calculation model and method

2.1. Calculation model

$LiBaF_3$ crystal has inverse perovskite structure (space group O_h^1 or P_{m3m}) with a lattice constant of 3.995 Å and there are no distortions even at low temperatures [12]. In the ‘inverse’ perovskite with cubic structure, the monovalent ion Li^+ is at the center of six F^- octahedrons and the Ba^{2+} divalent ions are in the 12-fold

---

☆ Supported by the Doctor Foundation of USST (X696). Project supported by the Scientific Development Foundation of Shanghai Municipal Education Committee, China (Grant No. 06EZ032).

* Corresponding author. Tel.: +86 21 55272483.
E-mail address: liutyyxj@163.com (T. Liu).

1567-1739/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2010.02.057

environment site, which is different from the classic perovskite structure [13].

When interstitial fluoride atom exists in the $LiBaF_3$ crystal, there are three different possible sites. The position (0.5, 0.0, 0.0) is at the centre of the edge of the cube formed by the Ba ions, the position (0.50, 0.25, 0.25) is at the centre of the edge of the octahedron of F ions and the position (0.25, 0.25, 0.25) is on the diagonal of the cube formed by the Ba ions.

2.2. *Calculation method*

The lattice simulations are performed using the GULP program that is based upon the Mott–Littleton methodology for accurate modeling of defective lattices. The program GULP optimizes the structure with respect to the asymmetric unit fractional coordinates and cell strains, using analytical symmetry-adapted first and second derivatives within a Newton–Raphson procedure starting from the exact Hessian matrix [14–17]. An important feature of these calculations is building the model of defects. The simplification of the Mott–Littleton method is to divide the crystal lattice that surround the defect into three regions known as I, 2a, and 2b. In the calculations, the region I sizes of 10 Å were used and the region 2a radius was 15 Å. The potential parameters used in the calculations are listed in Table 1.

After the optimal defect cluster in the crystal has been determined by the GULP program, the lattice optimization for the $LiBaF_3$ crystal containing interstitial fluoride is performed using a plane-wave pseudopotential formulation with generalized gradient correction in the form of Perdew–Wang-91. The CASTEP code is used for the calculation of the ground-state electronic structure within the DFT method [18, 19]. Generalized gradient approximations were chosen for the theoretical basis of density function. In CASTEP, basic parameters were chosen as follows: kinetic energy cutoff 330 eV, space representation reciprocal and SCF tolerance 1.0×10^{-6} eV/atom.

Once an interstitial fluoride atom is introduced into the $LiBaF_3$ crystal, it would make the local lattice distortion. So the lattice relaxation should be taken into consideration. Optimal atomic positions are determined until satisfying the conditions: (1) the maximal force on them is smaller than 0.05 eV/Å; (2) the maximal change of energy per atom is smaller than 0.00001 eV; (3) the maximal displacement is smaller than 0.001 Å. It is well known that DFT calculations usually underestimate the band gap. To take this into account, a 'scissors operator' is used, allowing a shift of the bands situated above the valence band [20]. According to the calculated result, the band gap of perfect $LiBaF_3$ crystal is 6.4 eV and the experimental value is 9.8 eV, the shifting value of the scissors operator Δc is chosen as 3.4 eV.

3. Results and discussion

3.1. *Optimal position of interstitial fluoride atom*

In order to confirm the optimal positions of interstitial fluoride atoms in the $LiBaF_3$ crystal, the possible positions where the interstitial fluoride atom may exist are simulated. The calculated formation energies of (0.50, 0.25, 0.25) are not convergent, it means that interstitial fluoride ion is unlikely to exist in this site in crystal. Since this position is very close to two F positions, leading to strong repulsion. The formation energies of interstitial fluoride of (0.5, 0.0, 0.0), (0.25, 0.25, 0.25) are −0.853 eV and −0.349 eV respectively. According to the lattice energy minimization, the possible interstitial fluoride is at the center of the edge of the cube formed by Ba ions. This agrees with the result in Refs [10]. The structure of optimal position of interstitial fluoride atoms is illustrated in Fig. 1.

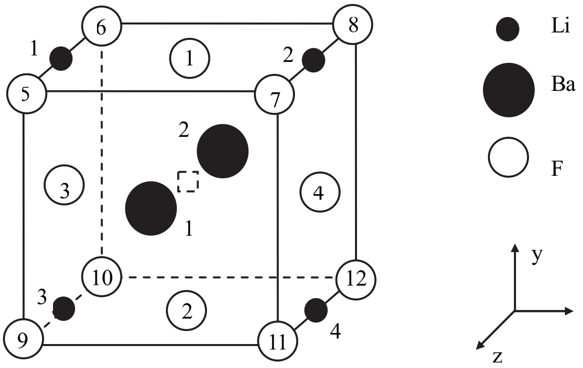


Fig. 1. The structure of optimal position of interstitial fluoride atoms, the hollow square is interstitial fluoride.

When the interstitial fluoride occurs at (0.5, 0.0, 0.0), the bond lengths between the interstitial fluoride and formal lattice ions for the non-optimized structure and the optimized structure are listed in Table 2. After structure optimized, it is found that the distance of cations Ba 1 and Li 3 with interstitial fluoride becomes smaller, the distance between other anions and the interstitial becomes larger. Because the electrical potential caused by the interstitial fluoride may attract the cations Ba^{2+}, Li^{+} and simultaneously repulses the anions F^{-}. However, the F10 and F12 are attracted and shifted towards interstitial fluoride. From Table 2, it is found that the distance between the interstitial fluoride and formal lattice F12 change 3.459 Å to 2.611 Å. In alkali halides, we know that an interstitial haloids atom can easily combine with a formal lattice haloids ion forming haloids molecule ion X_2^- [21], which is called H center. For example, the interstitial fluoride atom combines with the formal lattice fluoride occupying the fluorine site and oriented along [111] direction in LiF crystal. There is a similar situation in $LiBaF_3$ crystal that the interstitial fluoride atom combines with the formal lattice fluoride F12 ion forming a fluoride molecular ion, which can be expressed in the following equation:

$$F + F^{-} \rightarrow F_2^{-}$$

3.2. *Electronic structures and absorption bands*

The calculated total density of states (TDOS) of Li, Ba and F atoms for the perfect $LiBaF_3$ crystal are shown in Fig. 2. The calculated results are in good agreement with the results reported in Ref [6]. In this paper, all the curves related to the perfect $LiBaF_3$ crystal are plotted in dotted lines and the $LiBaF_3$ crystal containing interstitial

Table 1
Empirically derived potential parameters used in $LiBaF_3$ crystal.

Short-range potential parameters					Shell parameters			
Interactions	A(ev)	$\rho(10^{-10}$ m)	C($Å^6$ eV)	References	ions	Y(e)	K($Å^{-2}$ eV)	References
Li^{+}–F^{-}	113.720	0.3654	0.000	[11]	Li^{+}	1.0		[11]
Ba^{2+}–F^{-}	2190.01	0.3068	0.000	[11]	Ba^{2+}	2.0		[11]
F^{-}–F^{-}	1127.70	0.2753	15.83	[11]	F^{-}	−1.59	20.77	[11]