Optical Materials xxx (2016) 1–6

Contents lists available at ScienceDirect

Optical Materials

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

First-principles calculations of electronic and optical properties of $LiCaAlF_6$ and $LiSrAlF_6$ crystals as VUV to UV solid-state laser materials

Mui Viet Luong [a, *], Melvin John F. Empizo [a], Marilou Cadatal-Raduban [b], Ren Arita [a], Yuki Minami [a], Toshihiko Shimizu [a], Nobuhiko Sarukura [a], Hiroshi Azechi [a], Minh Hong Pham [c], Hung Dai Nguyen [c], Yoshiyuki Kawazoe [d], Krista G. Steenbergen [b], Peter Schwerdtferger [b]

[a] Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka 565-0871, Japan
[b] Centre for Theoretical Chemistry and Physics, Institute of Natural and Mathematical Sciences, Massey University, Albany, Auckland 0632, New Zealand
[c] Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan, Ba Dinh, Hanoi, Viet Nam
[d] New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form
27 July 2016
Accepted 22 September 2016
Available online xxx

Keywords:
First-principles
Electronic band structure
Colquiriite-type fluoride crystals
Laser host materials
VUV

ABSTRACT

We report the density functional calculations of the electronic and optical properties of perfect $LiCaAlF_6$ (LiCAF) and $LiSrAlF_6$ (LiSAF) crystals. The calculations are based on the Perdew-Burke-Ernzerhof (PBE) functional employing 35% exact exchange. Using optimized unit crystal volumes and equilibrium lattice constants, both LiCAF and LiSAF are found to have indirect band gaps of 12.23 and 11.79 eV, respectively. The band gap energies of these fluoride crystals are also observed to increase upon application of pressure by uniform volume compression. Moreover, their bulk moduli are determined to be 108.01 (LiCAF) and 83.75 GPa (LiSAF), while their static dielectric constants are 1.27 (LiCAF) and 1.26 (LiSAF). Considering the dielectric functions, refractive indices, and absorption coefficients, both perfect LiCAF and LiSAF crystals are viable vacuum ultraviolet (VUV) to ultraviolet (UV) laser host media. With knowledge of the different optical transitions and pressure dependence, our results yield helpful insights on the use of these fluoride compounds as effective solid-state laser materials in the VUV region.

1. Introduction

Lithium calcium hexafluoroaluminate ($LiCaAlF_6$, LiCAF) and lithium strontium hexafluoroaluminate ($LiSrAlF_6$, LiSAF) crystals are widely used as vacuum ultraviolet (VUV) and ultraviolet (UV) laser host media [1–5]. These fluoride materials can be stimulated by the fourth harmonics of a Nd:YAG laser, i.e. 266 nm [6–8]. When doped with trivalent cerium (Ce^{3+}, Ce), the crystals become attractive UV solid-state laser hosts with a central emission wavelength of 290 nm and with a practical tuning range from 288 to 315 nm. The slope efficiencies of Ce:LiCAF and Ce:LiSAF have also been reported to reach as high as 39 and 29%, respectively. The broad gain-bandwidth of the crystals in the UV region has made them appealing for ultrashort pulse generation and amplification. Aside from being a laser material, LiCAF can be used as a lens in VUV photolithography because of its optical transmission and low thermal lensing distortion [9]. The absorption edge of LiCAF is measured to be 112 nm, while that of LiSAF is 116 nm [10,11]. Although the properties of LiCAF and LiSAF crystals have been previously studied, most reports focus on the experimental investigations thereby limiting the findings by sample quality, characterization technique, or scientific instrumentation [12–14]. Theoretical and computational investigations are necessary to supplement these experimental results to accelerate the development of compact, solid-state, and tunable laser systems. Computational simulations, such as first-principles calculations, also aid towards a better understanding of the properties of multielemental and complex materials such as these fluoride crystals. We have initially compared the electronic band structures of LiCAF and LiSAF from numerical simulations [15]. Using the ABINIT program package based on pseudopotential and plane-wave expansion methods, we initially employed local density approximation (LDA) calculations within the framework of density functional theory (DFT). We have obtained results close to some experimental values, but LDA

* Corresponding author.
E-mail address: luong-vm@ile.osaka-u.ac.jp (M.V. Luong).

http://dx.doi.org/10.1016/j.optmat.2016.09.062
0925-3467/

underestimates band gap energies as one expects from this method. On the other hand, the Perdew-Burke-Ernzerhof (PBE) functional has been used successfully in the past to investigate the electronic structure and defects of LiCAF [16]. A better approximation than LDA is needed not only for the electronic but also for the optical properties of these materials, especially when LiCAF and LiSAF will be utilized in applications through doping with Ce or other trivalent rare-earth ions such as europium (Eu^{3+}, Eu), erbium (Er^{3+}, Er), and neodymium (Nd^{3+}, Nd). We therefore perform first-principles calculations for the electronic and optical properties of perfect LiCAF and LiSAF crystals. The PBE exchange-correlation functional employing 35% exact exchange is used within the framework of DFT to calculate electronic band structures, density of states (DOS), and band gap energies. Optical properties such as dielectric functions, refractive indices, and absorption coefficients are also obtained for both fluoride crystals.

2. Crystal structure and calculation methods

LiCAF and LiSAF are colquiriite-type fluorides with a hexagonal crystal structure belonging to the P-31c space group (group number 163). Both are optically uniaxial crystals with two formula units per unit cell. Six fluorine (F) atoms surround a lithium (Li), calcium (Ca)/strontium (Sr), or aluminum (Al) atom. Each Li, Ca/Sr, and Al cation occupies a deformed octahedral site as shown in Fig. 1 (a) [17,18]. DFT calculations were completed to obtain the optimized volume, electronic band structures, total and partial DOS, and band gap energies of the LiCAF and LiSAF crystals. These calculations employed the projector-augmented wave (PAW) method as implemented within the Vienna Ab Initio Simulation Package (VASP) [19–24], with a plane-wave basis cutoff of 500 eV and the hybrid PBE density functional using 35% exact exchange [25,26]. The addition of exact exchange presents a definite improvement over the LDA description of the system properties as it improves the description of the structural, electronic, thermal, and chemical properties of wide band gap solid-state systems [27]. A previous report on LiCAF crystal implemented a hybrid functional with 38.5% exact exchange [16]. In this work, various amounts of exact exchange were initially tested, leading to the optimized value of 35% which yielded a band gap energy close to the experimental reference. The same amount of exact exchange was then used for the LiSAF crystal computations.

The perfect crystals of LiCAF and LiSAF were used with a unit cell composed of 18 atoms. The unit cell was initially optimized by using the Murnaghan equation of state to fit the curve of the total energy as a function of volume [29]. The lattice constants were then obtained from the optimized volumes to compute the band structures, DOS, complex dielectric functions, refractive indices, and absorption coefficients of the fluoride crystals. In order to generate the charge density and wave function for the first run, a 3 × 3 × 1 Monkhorst-Pack k-point grid was utilized. For the band structure and DOS diagrams, the k-points were chosen following the Brillouin zone in Fig. 1 (b) with the symmetry points: Γ (0,0,0), M (1/2,0,0), K (1/3,1/3,0), A (0,0,1/2), L (1/2,0,1/2), and H (1/3,1/3,1/2) [30]. All valence band maxima of the resulting diagrams were also shifted to zero. To identify the effects of high pressure on the material properties, the pressure dependence of crystal volume and band gap energy was also investigated. Moreover, since the dielectric function is related to the electronic band structure, the complex dielectric function formed the basis of the optical property calculations such as the refractive index and absorption coefficient. The complex dielectric function, $\varepsilon(\omega)$ can be expressed as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{1}$$

where the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts, respectively. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function is based on the Bethe-Salpeter equation and is given by Refs. [31–33]:

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2\omega^2}\right)\sum_{ij}\int \langle i|M|j\rangle^2 \left|f_i(1-f_i)\times\delta\left(E_f - E_i - \omega\right)d^3k\right. \tag{2}$$

where M is the dipole matrix, i and j are the initial and final states, respectively, f_i is the Fermi distribution for the i^{th} state, and E_i is the energy of electron in the i^{th} state. The real part $\varepsilon_1(\omega)$, on the other hand, can be calculated using the Kramers-Kronig relation

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}P\int_0^\infty \frac{\omega'\varepsilon_2(\omega')d\omega'}{(\omega'^2 - \omega^2)} \tag{3}$$

where P is the principal value of the integral. From the components of the dielectric function, the refractive index (n) and absorption coefficient (α) can be subsequently obtained by Equations (4) and (5), respectively [34,35].

$$n(\omega) = \left[\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)}{2}\right]^{1/2} \tag{4}$$

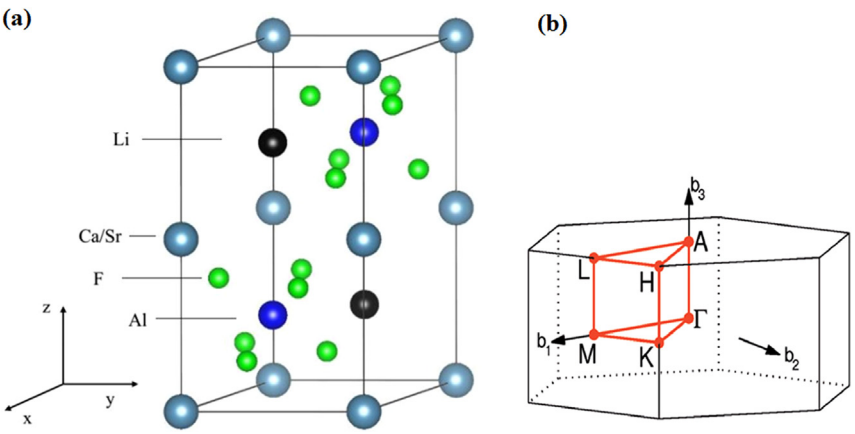

Fig. 1. (a) Colquiriite-type structure and (b) first Brilloiun zone of hexagonal unit cell of the LiCAF and LiSAF crystals.

Please cite this article in press as: M.V. Luong, et al., First-principles calculations of electronic and optical properties of $LiCaAlF_6$ and $LiSrAlF_6$ crystals as VUV to UV solid-state laser materials, Optical Materials (2016), http://dx.doi.org/10.1016/j.optmat.2016.09.062