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Density functional studies of cubic elpasolites Cs_2NaYX_6 (X=F, Cl, Br) at ambient and elevated hydrostatic pressure

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ABSTRACT

Density functional calculations are presented for various properties of the elpasolite crystals Cs_2NaYX_6 (X=F, Cl, Br) using the CASTEP module, either in the generalized gradient approximation (GGA) or in the local density approximation (LDA). Specifically, the calculated properties are lattice parameter, density, band gap, elastic constants, bulk modulus, sound velocity, Debye temperature, Grüneisen constant, phonon frequencies and phonon dispersion. The variations of some of these properties with applied pressure have also been calculated. Comparison with experimental data is made where available.

1. Introduction

The name elpasolite derives from the location *El Paso*, where the K_2NaAlF_6 mineral was found. Elpasolites form a large group of compounds whose general chemical formula can be written as M_2ALnX_6, where M and A denote the univalent cations of the alkali metals, Ln stands for a trivalent metal (which can be one of the rare-earth elements, actinides, transition elements, or aluminum), and X^- is a halide anion. These systems crystallize in the cubic space group Fm3m or a subgroup of this. In the highest symmetry, considered herein, the Ln^{3+} and A^+ ions are hexa-coordinated to the halide ions X^-, being situated at octahedral sites with O_h site symmetry. The M^+ ions are 12-fold coordinated to the X^- ions at T_d symmetry sites [1]. These crystals can be easily doped with guest trivalent ions, which then would occupy the Ln^{3+} site without any need for charge compensation, thereby minimizing possible crystal lattice deformations. Thus, the elpasolites are excellent model systems to study the energy levels of impurities and their interaction with crystal lattice vibrations in the ideal octahedral crystal field, which conveys high level degeneracies and strict transition selection rules. Literature concerning the spectroscopic and crystallographic properties of rare earth ions in cubic elpasolites is available [2–11]. The neat elpasolite materials have, as a rule, a relatively wide band gap, which allows for their applications as X-ray storage phosphor materials [2] and scintillators [3,4]. At the same time, little attention was paid to the studies of the electronic, elastic and thermodynamic properties of neat elpasolites.

In the present paper we focus our attention on three representatives of the large elpasolite group: Cs_2NaYX_6 (X=F, Cl, Br) and provide detailed investigations of the structural, electronic and elastic properties of these materials performed in the framework of the density functional theory (DFT) approaches. Information on the band structure, elastic constants, compressibility etc., for these materials is still lacking, which to a certain extent inhibits the areas of applications of these crystals, especially at extreme conditions.

The paper is organized as follows: in the next section the details of calculations are described. The results of the structural optimization are then presented and the electronic, optical and elastic properties of these three studied elpasolites are elucidated.

2. Details of calculations

The present calculations were performed using the CASTEP module [12] of Materials Studio in two independent computational runs, either in the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional [13] or in the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA-PZ) functional [14,15]. The plane-wave basis energy cutoff was chosen to be 370 eV for structure optimization and 850 eV for the phonon calculations. The Monkhorst–Pack scheme *k*-points grid sampling was set at $4\times4\times4$ for the Brillouin zone for the geometry optimization and $5\times5\times5$ for the calculations of the density of states and optical properties. The convergence parameters were set as follows: total energy

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tolerance -2×10^{-5} eV atom^{-1}; maximum force tolerance 0.03 eV nm^{-1}; maximum stress 0.05 GPa; and maximum displacement 0.002 Å. The electronic configurations for all involved chemical elements were as follows: $5s^25p^66s^1$ for Cs, $2s^22p^63s^1$ for Na, $4d^15s^2$ for Y, ns^2np^5 for F ($n=2$), Cl ($n=3$) and Br ($n=4$).

3. Results of calculations

3.1. Structural and electronic properties

As the first step towards description of the physical properties of Cs_2NaYX_6 (X=F, Cl, Br) elpasolites, their crystal structures were optimized at the ambient pressure. The calculated lattice parameters are listed in Table 1 and it is observed that the LDA(GGA)-obtained results are under(over)-estimated when compared to the experimental data [5,16–18]. By contrast, the calculated densities are over(under)-estimated by LDA(GGA)-results and fall about mid-way between these.

The band structure of the three systems was calculated using the above-mentioned two approximations. The electronic structure of Cs_2NaYX_6 is shown in Fig. 1(a)–(c), and the calculated band gaps of the three compounds are listed in Table 1. All compounds have a direct band gap. The calculated band gap values decrease for halides with larger atomic number, which can be attributed to the increased lattice constants and interatomic separations. There is a certain difference between the electronic properties of these crystals: the calculated conduction band (made of the Y 4d states mainly) is the widest in Cs_2NaYF_6 (about 5 eV) and is only about 4 eV wide in the remaining two elpasolites. The valence band (composed of the p states of halogen ions) exhibits a dip between −2 and −3.5 eV in Cs_2NaYF_6, whereas in other two crystals such a dip is absent. As usual for DFT calculations, the calculated band gap values are much smaller than the experimental values, by between 2.2 and 3.9 eV, although the correct trend is observed. The variation of the band gap with pressure is depicted in Fig. 1 (d) and the relevant equations are shown. Both approximations predict a linear increase with increasing pressure.

3.2. Elastic properties

Table 2 collects the results of the elastic constant calculations performed using the GGA and LDA runs. The elastic tensor for cubic crystals is determined by three independent constants: C_{11}, C_{12}, and

Table 1
Calculated structural and electronic properties of Cs_2NaYX_6 (X=F, Cl, Br) elpasolites.

Compound	Lattice constants (Å)			Density kg m^{-3}			Band gap (eV)		
	Expt.	LDA	GGA	Expt	LDA	GCA	Expt	LDA	GGA
Cs_2NaYF_6	9.075 [16]	8.806	9.404	4382 [5]	4782	3927	10.3 [7]	7.30	6.37
Cs_2NaYCl_6	10.672 [17]	10.411	11.014	3173 [5]	3476	2935	7.1 [19]	4.88	4.66
Cs_2NaYBr_6	11.305 [18]	10.967	11.593	3943 [5]	4316	3654	6.7 [20]	4.04	3.95

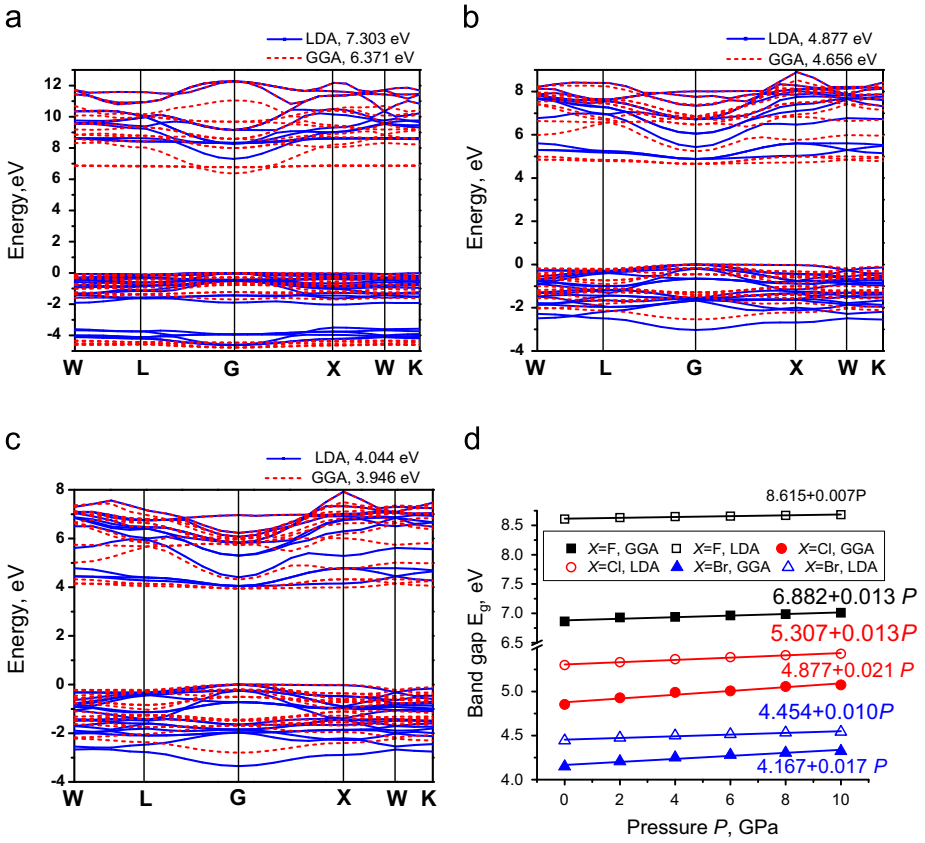

Fig. 1. Calculated band structure of Cs_2NaYX_6 (X=F, Cl, Br) elpasolites (a)–(c) and band gap variation with pressure (d) as calculated by GGA and LDA. In the fitting equations P is pressure in GPa and the calculated result is energy in eV.