Calculated high-pressure structural properties, lattice dynamics and quasi particle band structures of perovskite fluorides KZnF₃, CsCaF₃ and BaLiF₃

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Received 17 March 2016, revised 8 May 2016
Accepted for publication 11 May 2016
Published 14 June 2016

Abstract
A detailed study of the high-pressure structural properties, lattice dynamics and band structures of perovskite structured fluorides KZnF₃, CsCaF₃ and BaLiF₃ has been carried out by means of density functional theory. The calculated structural properties including elastic constants and equation of state agree well with available experimental information. The phonon dispersion curves are in good agreement with available experimental inelastic neutron scattering data. The electronic structures of these fluorides have been calculated using the quasi particle self-consistent GW approximation. The GW calculations reveal that all the fluorides studied are wide band gap insulators, and the band gaps are significantly larger than those obtained by the standard local density approximation, thus emphasizing the importance of quasi particle corrections in perovskite fluorides.

Keywords: lattice dynamics, electronic structure, structural properties, elastic constants

(Some figures may appear in colour only in the online journal)

1. Introduction

The large class of perovskite compounds, generally expressed as ABX₃, where A and B are cations and X is an anion, have received great attention from experimentalists and theoreticians due to their interesting properties from the fundamental physics and chemistry point of view. They possess a wide range of applications such as lenses without birefringence, and exhibit magnetism, piezoelectrics, ferroelectrics etc [1]. The physical properties of perovskites may also have implications toward understanding the Earth’s lower mantle [2, 3]. Fluoride perovskites constitute one particular subclass, which has found important technological applications in the field of optics. The main advantage is that these materials can be used as light emitting materials in the deep ultraviolet region [4]. In the present work the three technologically important fluoroperovskites KZnF₃, CsCaF₃ and BaLiF₃ are considered. They all crystallize in the cubic perovskite structure. KZnF₃ is a promising candidate for application as a radiation detector [5]. Several experimental studies have focused on synthesis, lattice dynamics, high-pressure structural stability, elastic constants, optical absorption and photoluminescence [6–12]. In addition, several theoretical studies of KZnF₃ have investigated its electronic structure and optical properties, lattice dynamics and thermodynamic
properties, crystal fields and influence of 3d transition metal dopants [13–16]. Similarly to KZnF3, the CsCaF3 perovskite has also been investigated in several experimental and theoretical studies addressing the electronic structure and optical properties, low energy phonon dispersion curves, green luminescence upon Eu2⁺ doping, thermodynamics at low temperatures, and the equation of state [8], [17–23].

BaLiF3 has been of interest for application within lithography due to the short wavelength absorption edge at 123 nm (10.1 eV) [24]. In addition, BaLiF3 may also be used as an effective dopant to alter the dielectric properties of BaTiO3 [25]. The mechanism of ionic conductivity has also been investigated in BaLiF3 with the purpose of enhancing the ionic conductivity by means of intrinsic defects [26].

The infrared dielectric dispersion of BaLiF3 measured at several temperatures confirmed that this compound is one of the most stable fluoroperovskites [27]. This was further confirmed by inelastic neutron scattering measurements of the phonon spectrum [28]. The electron–phonon coupling in NiCl2 doped BaLiF3 has been measured and related to the change in bonding as manifested in the computed vibronic spectra [29]. The luminescence of BaLiF3:Eu2⁺ has been investigated under pressure [30]. High pressure studies on fluoride compounds have elucidated various interesting physical properties. A recent high pressure experimental and theoretical study on fluoride compound CaF2 reported super ionic behavior [31]. A recent high pressure experimental and theoretical study on fluoride compound CsCaF3, BaLiF3 and KZnF3 respectively. A double k-mesh partial waves for cesium, 3s, 3p, 4s, 4p, 4d partial waves for calcium, 5s, 5p, 5d, 6s and 6p partial waves for fluorine. The exchange correlation potential was calculated within the local density approximation (LDA) [37] as well as the generalized gradient approximation (GGA) scheme [38]. The charge density and electron potential inside the muffin-tin spheres were expanded in terms of spherical harmonics up to ℓmax = 6, while in the interstitial region, these quantities were expanded in plane waves, with 28 670 waves (energy up to 194.81 Ry) being included in the calculation. Total energies were calculated as a function of volume, for a (16 × 16 × 16) k-mesh, corresponding to 165 k-vectors in the irreducible wedge of the Brillouin zone (BZ), and the results fitted to the Birch equation of state [39] to obtain the ground state properties. The elastic constants were obtained from the variation of the total energy under volume-conserving strains, as outlined in [40].

The phonon frequencies were calculated based on the density functional linear-response approach [41] within the GGA [38], combined with the plane-wave pseudopotential method as implemented in the Plane Wave Self Consistent Field (PWSCF) package [42]. Norm-conserving pseudopotentials were used to describe the valence electrons. The BZ integrations were carried out with a (6 × 6 × 6) Monkhorst–Pack (MP) grid [43]. Kinetic energy cutoffs of 90 Ry, 90 Ry and 120 Ry were used for CsCaF3, BaLiF3 and KZnF3 respectively. A (4 × 4 × 4) q mesh in the first BZ was used for the interpolation of the force constants needed for the phonon dispersion curve calculations. The theoretical equilibrium lattice constants of 4.096 Å, 4.604 Å, and 4.085 Å for KZnF3, CsCaF3 and BaLiF3 respectively, were obtained by total energy minimization and used in the phonon calculations.

The electronic structures of KZnF3, CsCaF3 and BaLiF3 have been calculated with the quasiparticle self-consistent GW (QSGW) (where G denotes the Green’s function and W denotes the screened Coulomb interaction) approximation [44, 45], in the FP-LMTO implementation of [46]. This calculation also included a double k×k LMTO basis set (ℓmax = 6), however additionally including the F 3s and 3p partial waves (treated as local orbitals [46]) for better description of the unoccupied band states. An (8 × 8 × 8) MP k-mesh was used for the calculation of the screened interaction, which is evaluated in the random-phase approximation. Convergence tests showed only minor changes compared to a (6 × 6 × 6) mesh. The most common type of GW calculations use a selfconsistent LDA or GGA band structure as input for the evaluation of the G and W operators. The special feature of the quasiparticle self-consistency in the QSGW method is that the one-particle band structure, which is used as input for the evaluation of the Green’s function, is iterated in a further selfconsistency loop so as to come as close as possible to the output GW band structure [44, 45]. Though appealing from a theoretical point of view, this procedure has a tendency to slightly overestimate semiconductor gaps [47], a fact traceable to the neglect of vertex corrections. As a simple remedy for this, Chantis et al [47] suggested the hybrid QSGW (h-QSGW), by which the LDA and

The calculations include 3s, 3p, 4s, 4p and 3d partial waves for potassium, 4s, 4p and 3d partial waves for zinc, 5s, 5p, 6s and 5d partial waves for cesium, 3s, 3p, 4s, 4p, 4d partial waves for calcium, 5s, 5p, 6s, 6d and 4f partial waves for barium, and 2s and 2p partial waves for fluorine.
Table 1. Calculated lattice constants (in Å), bulk moduli $B_0$ (in GPa) and its pressure derivatives $B'_0$, of KZnF$_3$, CsCaF$_3$ and BaLiF$_3$.

| Compounds   | Lattice constant | $B_0(V_0^{th})$ | $B_0(V_0^{exp})$ | $B'_0$ |
|-------------|------------------|-----------------|------------------|--------|
| KZnF$_3$    |                  |                 |                  |        |
| LDA$^a$     | 4.017            | 95.2            | 83.5             | 4.4    |
| GGA$^a$     | 4.154            | 72.3            | 99.8             | 4.3    |
| Expt.       | 4.053$^b$, 4.060$^c$ | 77.6$^b$, 54.8$^c$ | 11$^c$          |        |
| Other theory| 4.021$^d$, 4.072$^e$, 4.07$^f$ | 89.2$^d$         | 4.51$^d$        |        |
|             | 3.797$^g$, 3.897$^h$, 4.1499$^i$ | 66.4$^i$         |                  | 4.22$^i$ |
| CsCaF$_3$   |                  |                 |                  |        |
| LDA$^a$     | 4.401            | 73.5            | 47.8             | 4.6    |
| GGA$^a$     | 4.545            | 55              | 58.2             | 4.5    |
| Expt.       | 4.526$^a$        |                 | 50.9$^a$         |        |
| Other theory| 4.569$^a$, 4.579$^a$, 4.5885$^m$ | 50.2$^a$, 50.9$^a$, 45.8$^m$ | 4.27$^a$, 4.6$^m$, 3.8$^l$ |
| BaLiF$_3$   |                  |                 |                  |        |
| LDA$^a$     | 3.892            | 98.2            | 65.8             | 4.6    |
| GGA$^a$     | 4.028            | 75.6            | 80.7             | 4.5    |
| Expt.       | 3.999$^a$        |                 | 79.3$^a$, 75.9±1.3$^o$ | 5.35±0.15$^o$ |
| Other theory| 4.050$^o$        | 64.5$^o$        |                 | 4.6$^o$ |

$^a$ Present work; $^b$ [49]; $^c$ [11]; $^d$ [15]; $^e$ [50]; $^f$ [51]; $^g$ [52]; $^h$ [53]; $^i$ [54]; $^j$ [55]; $^k$ [23]; $^l$ [22]; $^m$ [21]; $^n$ [28]; $^o$ [32]; $^p$ [56].

Note: The bulk moduli have been calculated both at the experimental and theoretical volumes ($B_0(V_0^{th})$ and $B_0(V_0^{exp})$, respectively). The experimental bulk modulus reported for KZnF$_3$, CsCaF$_3$ and BaLiF$_3$ are obtained from high pressure structural measurements [11] and [32], or derived from the elastic constants: $B = (C_{11} + 2C_{12})/3$ [28, 49] and [55].

QSGW self energies are mixed in the proportions 20%–80%. See [48] for a detailed description. Here we also apply the h-QSGW method to the fluoride perovskites to monitor its effect for this class of wide-gap insulators.

3. Ground state, elastic properties and phonon dispersions

The calculated structural properties such as lattice parameters, and bulk moduli of KZnF$_3$, CsCaF$_3$ and BaLiF$_3$ are presented in table 1 along with available experimental information and results of other calculations. In the case of KZnF$_3$ the calculated lattice parameter within LDA is 0.9% lower when compared with the experimental value and the corresponding bulk modulus is 23% overestimated. In contrast, the calculated lattice parameter using GGA overestimates the experimental value by 2.4%, and the bulk modulus is 6.8% too low. This is the usual trend observed in the LDA and GGA schemes. In the case of CsCaF$_3$ the LDA calculated lattice constant is lower by 2.8% when compared to experiments, and the corresponding bulk modulus is 44% higher. Similarly, the GGA lattice parameter is 0.4% lower and the corresponding bulk modulus is 8% too large. A similar situation is seen in the case of BaLiF$_3$. The calculated bulk modulus is in excellent agreement with the two reported experimental values, which is, however, a bit fortuitous. Since the calculated equilibrium volume is overestimated (by about 0.8%) with GGA (and underestimated by about 2.6% with LDA), an error solely depending on the error in volume is introduced in the calculated bulk modulus. Therefore we recalculated the bulk modulus also at the experimental volume in a manner similar to our earlier work [33] (see table 1). This diminishes the discrepancies between the LDA and GGA results, as expected. In addition, the LDA bulk modulus now becomes smaller than the GGA for all the three compounds, and both functionals are seen to actually overestimate the bulk modulus. For KZnF$_3$ two experimental determinations of the bulk modulus are at variance. In particular the high value for the pressure derivative of the bulk modulus ($B'_0 = 1$) reported by [11] is at odds with the general range $B'_0 ~ 4$–5 found for the fluoride perovskites by both experiment and theory. The authors suggest that the limited pressure range covered in their study may be the cause of their high fit value for $B'_0$. In figure 1 the GGA and LDA equations of state of KZnF$_3$, CsCaF$_3$ and BaLiF$_3$ in the pressure range from 0 to 50 GPa are compared with the available experimental data [11, 32]. The agreement between theory and experiment is excellent for BaLiF$_3$ in figure 1(c), while the agreement is less satisfactory for KZnF$_3$ in figure 1(a). A special feature in KZnF$_3$ is the role of the Zn 3d states, which occur as a narrow resonance within the F valence bands, reflecting their semi-localized character. Their bonding properties are usually ill described in LDA/GGA and this may be the cause of the discrepancy here.
increase in temperature generally tends to reduce the elastic constants because of thermal expansion.

The calculated phonon dispersion curves at the optimized theoretical lattice parameters are shown in figure 2. The available experimental inelastic neutron scattering frequencies [8, 28] are included and good agreement between theory and experiment is found. The dynamical stability of the cubic structures is confirmed by the absence of any imaginary modes in the calculated dispersions. There are 15 phonon branches in the full phonon dispersion since the unit cell consists of five atoms, which give rise to three acoustic and twelve optical phonon branches. The agreement with experiment is excellent for BaLiF₃, and for the few frequencies determined for CsCaF₃, while there is some discrepancy to be seen for KZnF₃ around the lowest frequencies at the M and R points. The calculations find a noticeable gap between the lowest optical mode and the highest acoustic mode in the calculations for BaLiF₃ and CsCaF₃, which does not appear in KZnF₃. In addition, in CsCaF₃ a large second gap appears at high frequency. The experiments have only managed to map the lowest frequencies and thus cannot confirm or discard this prediction. Evidently, it would be of great interest to obtain experimental phonon frequencies in the higher end of the spectrum for all three compounds, in particular to test the theoretical prediction that the phonon spectrum for CsCaF₃, BaLiF₃ and KZnF₃ contain two, one and zero gaps respectively.

Table 2. Calculated elastic constants and shear modulus (G), all expressed in GPa, for KZnF₃, CsCaF₃ and BaLiF₃ at the theoretical equilibrium volume.

| Compounds  | C₁₁   | C₁₂   | C₄₄   | G     |
|------------|-------|-------|-------|-------|
| KZnF₃      |       |       |       |       |
| LDA        | 175.7 | 55.0  | 47.2  | 52.5  |
| GGA        | 134.8 | 41.1  | 44.1  | 45.2  | Present |
| GGA        | 99.2  | 38.0  | 29.1  | 29.7  | [54]    |
| GGA        | 111.8 | 49.8  | 31.4  | 31.2  | [16]    |
| Expt.      | 134.5 ± 1 | 52.7 ± 0.5 | 38.1 ± 0.2 | 39.2 | [49]    |
| Expt.      | 146   | 54    | 39    |       | [10]    |
| CsCaF₃     |       |       |       |       |
| LDA        | 166.2 | 27.3  | 29.2  | 45.3  | Present |
| GGA        | 121.0 | 22.1  | 29.4  | 37.4  | Present |
| GGA        | 98.5  | 24.8  | 27.6  | 31.0  | [23]    |
| GGA        | 99.9  | 23.6  | 25.0  | 29.6  | [22]    |
| Expt.      | 102 ± 1 | 25.3 ± 0.5 | 25.5 ± 0.5 | 30.6 | [55]    |
| BaLiF₃     |       |       |       |       |
| LDA        | 232.3 | 31.2  | 42.2  | 65.5  | Present |
| LDA        | 163.8 | 50.8  | 50.0  |       | [56]    |
| GGA        | 149.2 | 33.1  | 58.0  | 58.0  | Present |
| Expt.      | 130 ± 1 | 46.5 ± 0.5 | 48.7 ± 0.5 | 45.9 | [28]    |

The phonon partial densities of states are also included to the right of figures 2(a)–(c). The acoustic modes in BaLiF₃ and
CsCaF$_3$ are dominated by the motion of the heavy Ba and Cs respectively, while in KZnF$_3$ the atomic masses are more similar, and the atomic vibrations are fully coupled to each other as shown in figure 2(a). Furthermore, the acoustic band width is smaller in CsCaF$_3$ than in BaLiF$_3$, which reflects the larger lattice constant of CsCaF$_3$, while the second gap (between 8 and 11 THz) in the phonon spectrum of CsCaF$_3$, which does not find a counterpart in BaLiF$_3$, reflects the different masses of Ca and Li. Thus, there is a significant Li component to the highest frequencies in BaLiF$_3$, while no Ca weight is found in the highest CsCaF$_3$ frequency range.

Figure 2. Calculated phonon dispersion curves of (a) KZnF$_3$ and (b) CsCaF$_3$ and (c) BaLiF$_3$ at the theoretical lattice parameter. The experimental data are shown by dots and taken from: KZnF$_3$: ([8]); CsCaF$_3$: ([8]); BaLiF$_3$: ([28]).

Figure 3. Calculated LDA (red (gray thin) lines) and QSGW (black thick lines) band structures of (a) KZnF$_3$, (b) CsCaF$_3$, and (c) BaLiF$_3$ at the experimental lattice constants. The zero of energy is situated at the valence band maximum. The BZ special points are $\Gamma$; (0, 0, 0); X: (1, 0, 0); M: (1, 1, 0) and R: (1, 1, 1) in units of $2\pi/a$.

4. Quasiparticle band structures

The QSGW band structures of KZnF$_3$, CsCaF$_3$ and BaLiF$_3$ are presented in figure 3. All three compounds exhibit large
The conduction band minimum occurs in all cases at the Γ point, while the valence band maximum (VBM) also falls at Γ for BaLiF₃, i.e. this is a direct gap insulator. The three top valence states at Γ, M, and R are rather close, with M (R) at −0.17 eV (−0.20 eV) relative to the VBM in BaLiF₃. In contrast, for CsCaF₃ and KZnF₃ the gap is indirect. In CsCaF₃ the VBM occurs at the M point while the topmost valence state at Γ is about 0.25 eV lower in energy. In KZnF₃ the VBM occurs on the line connecting the M and R points, and the topmost valence state at Γ is 1.5 eV lower in energy.

The F band widths are 4.0 eV, 2.1 eV and 3.2 eV in KZnF₃, CsCaF₃ and BaLiF₃ respectively. The low band width of CsCaF₃ reflects its larger lattice constant. KZnF₃ and BaLiF₃ have similar lattice constants, however in KZnF₃ the Zn 3d bands fall at the bottom of the F bands, partially hybridizing and thus effectively enhancing the F band width. The semicore states are slightly shifted toward higher binding energies by the GW approximation compared to their LDA positions, by about 2 eV for the K 3p states of KZnF₃ (located at 12 eV below VBM), by about 0.1 eV for the Cs 5p states in CsCaF₃ (located at 4.5 eV below VBM), and by about 0.6 eV for the Ba 5p states of BaLiF₃ (located at 9 eV below VBM). Thus the most significant effect of the GW approximation is the more or less rigid shift of the conduction bands with respect to the valence bands, which is of the order of 5−7 eV for the three fluorides considered.

5. Conclusions

The electronic structures and vibrational properties of the KZnF₃, CsCaF₃ and BaLiF₃ perovskite fluorides have been investigated with density functional methods. The calculated phonon frequencies are in good agreement with experimental values—which, however, are limited to the lowest part of the spectrum, and a full experimental mapping of the phonon dispersion curves is desirable. The calculated pV-curve of BaLiF₃ is in excellent agreement with experiment, while the agreement between theory and experiment is less satisfactory for KZnF₃, and no experimental data exist for CsCaF₃.

The QSGW quasiparticle band structures reveal significant insulating gaps in the fluorides studied, which are about 6 eV larger than predicted by the LDA/GGA. Most of this effect may be seen as a rigid shift of the conduction bands with respect to the valence bands. The F valence bands are only slightly wider in QSGW than in LDA, while some shifts towards higher binding energies are found for the secondary (semi-core) valence states. All of these effects are usual trends of the GW method, which are also observed in comparison of Hartree–Fock and LDA band structures, hence they may be ascribed to the non-local character of the electron–electron interaction.

Acknowledgments

GV acknowledges CMSD-University of Hyderabad for providing the computational facility.

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