High pressure structural stability of BaLiF₃

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High pressure x-ray diffraction studies on inverse-perovskite BaLiF₃ show that this compound is structurally stable up to ~50 GPa. The bulk modulus of BaLiF₃ is determined to be 75.9 GPa which is in close agreement with that determined from a semi-empirical formulation. Our *ab initio* calculations show that among the three alkaline earth fluoro perovskites (ALiF₃, A = Ba, Ca, and Sr) which crystallize in the inverse-perovskite structure, BaLiF₃ is the least brittle at ambient conditions and also that the degree of brittleness decreases at high pressures. The behavior of the elastic constants at high pressure accompanied by a reduction in the bandgap indicates a decrease in the directional nature of the bonding. © 2011 American Institute of Physics. [doi:10.1063/1.3670036]

I. INTRODUCTION

Studies on perovskites having the formula ABX3 are important not only from a basic physics point of view but also due to their technological usage as piezoelectrics, lenses with no birefringence, neutron scintillators, ferroelectrics, relaxors, etc.¹ Under extreme temperature and pressure several of them undergo phase transformations to the post perovskite structures or decompose into their respective oxides, making them relevant to the understanding of geophysical phenomena.^{2,3} In particular, the studies on silicates, germanates, oxides, and fluorides suggest that the transformation to the post perovskite structure could be responsible for the seismic discontinuity at the earth's lower mantle-core boundary.⁴⁻⁶ Since these perovskites are made up of a network of corner linked polyhedra, tilt or distortion of the polyhedra at low/high temperatures or upon the application of pressure plays a crucial role in their stability. Based on an empirical formulation, Ross et al. have shown that the tilt of the octahedra at high pressures is related to the compressibility of the constituent polyhedra.

The BaLiF₃ crystallizes in the cubic inverse-perovskite structure. The high pressure structural stability of some group I-II fluoro perovskites has been investigated, but there is no experimental study on the structural stability of the I-II fluorides with the inverse-perovskite structure. In the only high pressure study (limited to 20 GPa) on BaLiF₃, Korba *et al.* have calculated its electronic structure, density of states, and optical properties using density functional theory based on the full-potential linear augmented plane wave method.⁸ With the help of their calculations they predicted that the valence bandwidth of BaLiF₃ monotonically increases with pressure. Recent experiments and *ab initio* calculations on perovskite structured KMgF₃ (Ref. 9) and CsCdF₃ (Ref. 10) show that they are structurally stable up to 40 and 60 GPa, respectively, and their pressure induced

bandgap variation is similar to that of BaLiF₃.¹¹ In BaLiF₃ the center of the F⁻ octahedron is occupied by the small Li⁺ ion, compared to the other cubic perovskites where this position is occupied by the bigger B^{+2} cation. The smaller size of the Li⁺ ion in the F⁻ octahedral cage results in a larger anharmonicity of the Li⁺ ion. Phase transitions in non-cubic NaMgF₃ have been attributed to the anharmonicity of the F⁻ ion. Hence, it is possible that even BaLiF₃ may become structurally unstable at pressures higher than 20 GPa. Recently, Xiaoa *et al.*¹² have shown that cubic perovskite $PbCrO_3$ transforms to an iso-structural cubic form at ~ 1.6 GPa. This transition may be attributed to the presence of the transition metal ion at the center of the octahedron. Hence, to determine and compare the structural stability of the cubic inverseperovskite fluoride with the perovskite structured fluorides we have carried out high pressure x-ray diffraction experiments (up to 50 GPa) and ab initio calculations (up to 84 GPa) on BaLiF₃. With the help of these calculations we have also determined and compared the elastic constants of all the three fluoro perovskites which crystallize or are predicted to crystallize in the inverse-perovskite structure.

II. EXPERIMENTAL DETAILS

Stoichiometric amounts of dried LiF (Riedel de Haen, 99%) and BaF₂ (Alfa, 99.9%) were homogenized and pelletized in an inert atmosphere. The pellets were wrapped in a platinum foil and were sealed in a fused quartz tube in an argon atmosphere and were heated at 750 °C for 4 h. The heating and cooling was carried out very slowly (5 °C/min). The BaLiF₃ thus obtained was characterized using powder x-ray diffraction. In agreement with earlier studies, its structure was found to be cubic inverse-perovskite with (space group no. = 221, Pm $\overline{3}$ m) lattice parameter 'a' = 3.995 Å.¹³

For the high pressure experiments, a finely powdered sample of BaLiF₃ along with a few specks of copper was loaded into a hole $\sim 100 \,\mu\text{m}$ in diameter, drilled in a preindented ($\sim 80 \,\mu\text{m}$ thick) tungsten gasket of a diamond-anvil cell. A methanol: ethanol (4:1) mixture was used as a

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pressure transmitting medium. The pressure was determined from the known equation of state of copper.¹⁴ High-pressure angle dispersive x-ray-diffraction experiments were carried out up to ~50 GPa at the 5.2 R (XRD1) beamline of the Elettra Synchrotron source using monochromatized x-rays of $\lambda = 0.6888$ Å. The diffraction patterns were recorded using the MAR345 imaging plate detector kept at a distance of ~20 cm from the sample. Two-dimensional x-ray diffraction patterns were transformed to one-dimensional diffraction profiles by the radial integration of diffraction rings using the FIT2 D software.¹⁵

A. Computational details

Ab initio density functional theory calculations were carried out on $ALiF_3$ (A = Ba, Sr, and Ca), using the VASP code.^{16,17} The electronic wave functions were expanded on a plane wave basis set and ionic core states were approximated by the projected augmented wave method.¹⁸ We applied a generalized gradient approximation (GGA),^{19–21} to the exchange correlation functional. To check for convergence, we repeated the relaxation calculations at ambient pressure for different values of energy cut-off and k-mesh. A 500 eV cutoff for plane waves and a Monkhorst-Pack grid of $11 \times 11 \times 11$ was found to give lattice constants accurate up to 0.1%.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Figure 1 shows the x-ray diffraction patterns of BaLiF₃ at a few representative pressures. There is a monotonous shift in the diffraction peaks toward higher 2θ values up to 20 GPa. Beyond ~27 GPa it appears as if the (111) and (211) XRD peaks have split, transforming the higher symmetry cubic structure to a lower symmetry one. However, careful Rietveld analysis (using GSAS²²) indicates that this peak splitting is due to the separation of overlapping peaks of the sample and the gasket and BaLiF₃ remains cubic up to 50 GPa.

The linear compressibility (1/l)(dl/dP) of Ba-Ba and Ba-Li at low pressures is 3.17×10^{-3} /GPa and is similar to



FIG. 1. (Color online) Diffraction patterns of $BaLiF_3$ at a few representative pressures. The gasket and copper pressure marker peaks have been marked as 'W' and 'Cu,' respectively. The diffraction patterns of the released runs have been marked with 'r.'

that of Li-F and Ba-F which implies that the constituent polyhedra do not become distorted with pressure. Linear compressibilities of different cation-anion bonds in the cubic perovskite CsCdF₃ were also found to be equal $(2.6 \times 10^{-3}/$ GPa) indicating that the cation-anion bonds of the perovskites and inverse-perovskites have similar compressibilities. On the basis of the relative compressibilities of the AX₁₂ and BX₆ polyhedra, Ross *et al.*⁷ have formulated some general rules for predicting phase transitions in oxide perovskites. Assuming that the additional valence sum mismatch²³ induced by pressure at both the A and B cation sites is the same, they have stated that if

 $\begin{cases} \frac{\beta A}{\beta B} = \frac{MB}{MA} > 1 \text{ the tilt angle of the polyhedra are reduced and the perovskite structure becomes more symmetric,} \\ < 1 \text{ the tilt angle of the polyhedra increases resulting in symmetry lowering phase transitions,} \\ = 1 \text{ the degree of distortion of the structure would not change with pressure,} \end{cases}$

(where β represents the compressibility of the two polyhedra and M represents the variation of the bond valence sum at the cation of the polyhedra, due to the change in the average bond distance).

While making these formulations Zhao *et al.*²⁴ have assumed that the additional valence sum mismatch induced by pressure is the same at both the A and B cation sites and, therefore, $\beta_A/\beta_B = M_B/M_A$. However, since β_A/β_B for both compounds is equal to 1, but M_A/M_B is ~2.828 and ~0.7 for BaLiF₃ and CsCdF₃, respectively, the relation, $\beta_A/\beta_B = M_B/$

 M_A , does not hold for this class of compounds. In addition, as seen in Fig. 2, the additional valence sum mismatch, ΔV_i (i = A, B), due to the application of pressure is not equal at both of the cation sites for BaLiF₃ (here, $M_i = (-R_i (dV_i/dR_i)$ where R_i is the average bond distance, $\langle V_i \rangle$ is the total bond valence sum at the central cation 'i' calculated on the basis of the average bond length). This indicates that the assumptions made by Zhao *et al.*²⁴ (i.e., the additional valence sum mismatch induced by pressure is the same at both the A and B cation sites) cannot be extended to the perovskites and inverseperovskites crystallizing with the cubic structure and hence,



FIG. 2. (Color online) The additional valence sum mismatch at both (Ba, Li) cation sites (ΔV_i (i = A, B)) as a function of pressure.

the ratio of M_A/M_B cannot be used as a reliable predictor of their compression behavior.

The bulk modulus, $K_0 = 75.9 \pm 1.3$ GPa, and its pressure derivative, $K' = 5.35 \pm 0.15$, were determined by fitting the third order Birch-Murnaghan equation of state²⁵ to the observed pressure induced variation of volume (Fig. 3). Using the elastic constants measured by Shimamura *et al.*²⁶ the bulk modulus is calculated to be $K_0 \sim 74.3$ GPa, which is close to our experimental value.

B. Bulk modulus by empirical methods

The bulk modulus of a material depends on the bulk moduli of the constituent polyhedra and the network structure linking these polyhedra. In the case of corner linked structures, the bulk moduli are known to be significantly less than their constituent polyhedra because of the bending of linkages and not due to compression of the polyhedra. However, in spinels and garnets where there is extensive edge sharing of the polyhedra, the bulk modulus of the minerals is similar to those of the constituent polyhedra. As in BaLiF₃ constituent polyhedra are face sharing, it is understandable that the bulk moduli of the constituent octahedra and dodecahedra are similar to that of the compound. Upon plotting the V/V_o of the dodecahedra of different fluoro perovskites,^{27,28} (Fig. 4) we find that irrespective of whether the center of the dodecahedra is a group I or II element (i.e., K or Ba) the compressibility of these dodecahedra are the same. However, the dodecahedra are less compressible if an atom of transition metals, such as Co, occupies its central position. This difference in compressibility could be due to the presence of 'd' electron bonding in the Co-F bond.

Hazen *et al.* derived a semi-empirical formula (using the data for several metal oxides and silicates) for estimating the bulk moduli of polyhedral compounds²⁹ by relating it to the cation charge density of its constituent polyhedra. For these compounds, the polyhedral compressibilities are proportional to the average polyhedral volumes divided by the formal charges of the cations. Hazen *et al.*²⁹ found that K_0 (in GPa) is (750 * Z_i)/ d^3 , where Z_i is the cationic formal charge and 'd' is the mean cation–anion distance (in Å). However, fitting the experimentally determined bulk moduli of several scheelite-structured compounds as a function of the 'A' cationic charge per unit volume of the AO₈ polyhedra, Errandonea *et al.* found that K_0 (GPa) is (610* Z_i)/ d^3 .³⁰ The difference in the coefficients of the above two formulations





FIG. 3. (Color online) The observed P-V variation fitted with the third order Birch-Murnaghan equation of state for $BaLiF_3$. The closed and open circles represent the compression and decompression data, respectively, while the red solid line is the fitted curve with the B-M equation of state. The dot-dashed blue line shows the equation of state obtained from our *ab initio* calculations.

FIG. 4. Pressure induced variation of normalized volume of KF_{12} and BaF_{12} polyhedra for several fluoro-perovskites. For $KZnF_3$ and $KMgF_3$ the data are from Ref. 27, while for $KCoF_3$ the data was taken from Ref. 28. The $BaLiF_3$ data is from the present high pressure x-ray diffraction experiments.

TABLE I. Bulk moduli of various fluoro-perovskites determined from x-ray diffraction data and from the known elastic constants of these compounds. Bulk moduli calculated using the semi-empirical formulation of Hazen *et al.* (Ref. 29) and Errandonea *et al.* (Ref. 30) are shown. Since both the octahedra and dodecahedra have the same compressibilities, the bulk moduli have been calculated using the polyhedral cation formal charge and mean cation-anion distance (in Å) of both the polyhedra (shown in columns 7-10 of this table). It can be seen that the bulk moduli calculated from our fit to Scott's formulation (Ref. 32) { $K_0 = (Y - Z\lambda)(V_0)^n$ where n = 0.1387, Y = 25.28, and Z = -42.57} gives the closest agreement with the experimental values.

Compound	Lattice parameter (Å)	K ₀ (expt.) (GPa)	K ₀ ′	Bulk moduli (GPa) (from elastic constants) (Ref. 40)	Bulk moduli (calculated using our fit to Scott's formulation) (Ref. 32)	Calculated K ₀ (Ref. 29) (octahedra)	Calculated K_0 (Ref. 30) (octahedra)	Calculated K ₀ (Ref. 29) (dodecahedra)	Calculated K ₀ (Ref. 30) (dodecahedra)
CsCdF ₃	4.4669 ^a	79 ^a	3.8	62.9	74.7	135	110	67	55
KMgF ₃	3.989 ^b	71.2 ^b	4.7	70.4	75.3	189	154	95	77
BaLiF ₃	3.995 (#)	75.9 (#)	5.4	74.3	75.4	94.9	77.2	67	54
KZnF ₃	4.053 ^b	77.6 ^b		79.9	75.8	180	147	90	73
NaMgF ₃	3.833 ^b	75.6 ^b		*	74.1	213	173	107	87
RbCaF ₃	4.455 ^b			50.4	78.7	135	110	68	55
CsCaF ₃	4.526 ^b			50.8	79.2	129	105	23	19
KMnF ₃	4.182 ^b			64.7	76.7	164	133	29	24
KFeF ₃	4.120 ^c			*	76.3	172	140	30	25
KCoF ₃	4.071 [°]			78.7	75.9	178	145	31	26
KNiF ₃	4.012 ^c			85.1	75.9	186	151	33	27

Note: (#) denotes this work and * indicates unavailability of elastic constants data.

^cReference 42.

arose because Errandonea *et al.* included only scheelite and scheelite-like structures, while Hazen *et al.* included a more diverse set of compounds. In both of these formulations the more compressible polyhedron was used for determining the bulk modulus.

Since the fluoro-perovskites are also made up of a network of polyhedra, we tried to determine the bulk modulus of lithium barium fluoride using the formulations of both Errandonea et al. and Hazen et al. Since both of the polyhedral units of this compound have the same compressibility, the bulk modulus determined by using either of the polyhedra should give us the same result. However, as can be seen from Table I, the bulk modulus calculated using the octahedra is very different from that determined from the experiments. These results imply that we cannot use the semiempirical formulation of Hazen²⁹ and Errandonea³⁰ to predict the bulk moduli of fluoro perovskites. Hence, in order to predict the correct bulk modulus with the help of a semiempirical formulation we used the fact that the bulk moduli can be related to the ambient pressure molar volume as suggested by Ming et al.³¹ Using this correlation and the semitheoretical formulation of Scott *et al.*,³² we have fitted the relation, $K_0 = (Y - Z\lambda)(V_0)^n$, where λ is the Cohen polarization factor,³³ V_0 is the molar volume (cm³ mol⁻¹), and Y, Z, and n are the parameters obtained by fitting the known experimental values of different fluoro-perovskites. The fitted values of n, Y, and Z are 0.1387, 25.28, and -42.57, respectively. Using our fitted values we have calculated the bulk moduli of several fluoro-perovskites (tabulated in the sixth column of Table I). The values of the bulk moduli appear to be in agreement with the earlier experimentally observed values. To date, the bulk moduli of a very few fluoroperovskites have been determined using the equation of state. However, since the elastic constants of several of these compounds were known³⁴ we calculated their bulk moduli, which are shown in column 5 of Table I.

From this table, we can see that though there is a large difference (25%) in the bulk moduli, determined from the elastic constants and the equation of state for CsCdF₃, the difference from our calculated value is small i.e., ~5%. This gives us confidence that we can predict the bulk moduli of different fluoro-perovskites using our fit to Scott's semiem-pirical formulation.³² Since there is a large discrepancy in the bulk moduli of CsCaF₃ and RbCaF₃ (Table I), we feel that x-ray diffraction experiments should be carried out on these compounds to determine their bulk moduli.

C. Ab initio calculations

Starting from the experimental structural parameters we optimized the ionic coordinates and lattice parameters, keeping the volume fixed. The calculations were repeated for lower volumes to understand the behavior of BaLiF₃ under pressure. Calculations were performed for SrLiF₃ and CaLiF₃ for comparison. Due to their structural similarity, we used the BaLiF₃ structural parameters as starting structures for these materials. Our calculations on BaLiF₃ are found to agree well with the experimental observations. However, since GGA calculations are known to overestimate the equilibrium volume, 4% difference from experimentally determined volume seems reasonable. The bulk modulus determined from the equation of state (69.4 GPa) and calculated elastic constants (73.9 GPa) is close to the experimental value. The bulk moduli of SrLiF₃ and CaLiF₃ (Table II)

^aReference 10.

^bReference 41.

	$\begin{array}{c} \mathrm{K}_{0} {=} 1/3 \; (\mathrm{C}_{11} {+} 2\mathrm{C}_{12}) \\ (\mathrm{GPa}) \end{array}$	EOS ^a	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)	C12/C44	G (GPa)	K/G ^b	$\nu = (3 \text{ K/G} - 2)/(6 \text{ K/G} + 2)$
BaLiF ₃	73.9	69.4	136.4 130 ^c	42.8 46.5 [°]	47.1 48.7 [°]	0.91	47.02	1.57	0.24
CaLiF ₃	85.31	75.9	179.5	38.2	45.8	0.83	54.55	1.56	0.236
SrLiF ₃	72.07	68.1	157.2	38.5	48	0.80	52.2	1.49	0.227

TABLE II. Ambient pressure elastic constants and moduli of $ALiF_3$ (A = Ba, Sr, Ca) determined from GGA *ab-initio* computations. For comparison, the experimentally determined elastic constants of $BaLiF_3$ have also been tabulated (Ref. 43).

^aBulk modulus determined from EOS obtained by *ab-initio* density functional calculations.

^bK is bulk and G is shear modulus.

^cElastic constants taken from experimental data of Reference 43.

indicate that all three inverse-perovskites have similar compressibilities.

The variation in the elastic constants under pressure can provide useful information about changes in the stability and stiffness of the material. Cubic lattices have only three independent constants, namely C_{11} , C_{12} , and C_{44} . The calculated values at ambient pressure are given in Table II. It can be seen that for BaLiF₃ these are in close agreement with experimentally determined values.⁸ For all three compounds, the ratio C_{12}/C_{44} is almost close to unity, as predicted by Cauchy's law and this indicates that the short range potentials are almost spherically symmetric.

Table III shows that the calculated elastic constants for the perovskite fluorides are found to obey the modified stability criterion³⁵ (given below) for cubic crystals under finite strain corresponding to pressures of \sim 84 GPa i.e.,

$$M_1 = (C_{11} + 2C_{12})/3 + P/3 > 0, \tag{1}$$

$$M_2 = C_{44} - P > 0, \tag{2}$$

$$M_3 = (C_{11} - C_{12})/2 - P > 0.$$
(3)

The angular character of atomic bonding can be described by the Cauchy pressure (C_{12} - C_{44}). If this pressure is negative then the material is nonmetallic with directional bonding and if it is positive then the material is expected to be metallic.³⁶ This has been verified for ductile materials such as nickel and aluminum and also for brittle materials such as silicon.³⁷ The fluorides that we have studied have a negative Cauchy pressure at an ambient condition, which increases toward positive values upon the application of pressure (Fig. 5).

TABLE III. Derived elastic constants characterizing mechanical stability $(M_i: Eqs. (1)-(3))$ of BaLiF₃ at different pressures, calculated from GGA *ab initio* computations.

BaLiF ₃						
Pressure (GPa)	K/G	M_1	M_2	M ₃	$\nu = (3 \text{ K/G} - 2)/6 \text{ K/G} + 2)$	
0.0	1.57	73.90	47.13	46.79	0.24	
1.74	1.65	79.94	46.67	45.53	0.25	
9.09	1.59	100.56	53.49	50.86	0.24	
20.52	1.66	141.16	62.55	57.67	0.25	
38.58	1.73	201.03	74.45	63.94	0.26	
48.55	1.75	231.75	80.13	66.86	0.26	
67.74	1.79	290.98	90.03	71.74	0.26	
84.24	1.82	340.75	97.51	74.36	0.27	

Although the large bandgap of BaLiF₃ at high pressures shows that it is still an insulator, this change in sign of the Cauchy pressure could be indicative of a reduction in the angular character of the bonding. In fact, for BaLiF3 we have observed that its sign changes around 21 GPa, where the increase in the bandgap is very gentle and then beyond 38 GPa the bandgap starts decreasing, as shown in Fig. 6. It is noteworthy here that below 20 GPa the bandgap increases with pressure while in the region of 20-40 GPa the rate of increase of the bandgap with pressure shows a plateaulike behavior and beyond 40 GPa the bandgap starts decreasing. Upon calculating the density of states, it was found that the Ba 5d states dominate the bottom of the conduction band and F 2s and F 2p states dominate the top of the valence band. It was observed that upon increasing pressure, though, that the bands broadened the energy of the 5d states increased, thereby resulting in an increase in the splitting between the Ba 5d and F 2s and F 2p states, and hence, an increase in the bandgap. However, beyond 40 GPa the energy of the Ba 5d states started decreasing, resulting in a decrease of the bandgap. It has also been observed from band structure calculations that the bandgap continues to be direct up to the highest pressure studied. We know that the plastic properties of materials can be linked by their elastic moduli using the Pugh indicator (K/G) where the shear modulus (G) of materials represents the resistance to plastic deformation.³⁸ A K/G ratio greater than 1.75 and a Poisson's ratio greater than 0.33 are associated with the ductility of a material.³⁹ Our studies



FIG. 5. (Color online) The Cauchy pressure $(C_{12}-C_{44})$ as a function of pressure for all three inverse-perovskite fluorides. The solid lines are fits to the theoretically calculated data.



FIG. 6. (Color online) Pressure variation of the bandgap of $BaLiF_3$, calculated from *ab initio* calculations.

show that the Cauchy pressure (Fig. 5), K/G, and Poisson's ratio (ν) (Table III) of BaLiF₃ increases with pressure, indicating that the application of pressure reduces the brittleness and angular nature of the bonding of BaLiF₃. Our studies also indicate that the brittleness of BaLiF₃ < CaLiF₃ ~SrLiF₃.

IV. CONCLUSIONS

Our high pressure x-ray diffraction studies on BaLiF₃ show that this compound does not undergo any phase transition up to \sim 50 GPa. However, our *ab initio* calculations show that even though there may be a change in the nature of bonding at high pressure, the cubic structure of this fluoride is stable up to 84 GPa. Even calcium and strontium lithium fluoride were found to be stable at high pressures. Since these fluorides do not undergo any structural phase transitions at high pressures, they can be used as an alternative pressure marker. By fitting the observed pressure induced variation of volume with the third order Birch-Murnaghan equation of state K0 and K' were determined to be \sim 75.9 ± 1.3 GPa and 5.35 ± 0.15, respectively. We have shown that the compressibility of the perovskite and inverseperovskite fluorides is similar. Our studies also indicate that the ratio of MA/MB cannot be used as a reliable predictor of the compressional behavior of cubic inverse perovskites.

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