Vibrational properties of BaClF, BaBrF and BaIF under high pressure

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Abstract. We have studied the Raman active optical phonons of layered BaClF, BaBrF and BaIF scintillators at ambient as well as at high pressures. The calculations were carried out using density functional perturbation theory within the local density approximation. We observed the softening of low and high frequency modes $E_g(1)$ and $E_g(3)$ under pressure. The calculated optical dielectric and Born effective charge tensors are found to be isotropic even though the crystal structures are anisotropic.

1. Introduction
Mixed barium halofluorides BaXF (X = Cl, Br, I) crystallize in the primitive tetragonal PbClF-type (matlockite) structure. The materials can act as host lattices for rare earth ions[1,2]. Europium activated BaClF and BaBrF are used for X-ray storage phosphors for medical imaging via photo stimulated luminescence[3-5]. Our recent investigation also revealed that these materials can act as storage phosphors[6]. BaClF : Sm$^{2+}$ can be used as a luminescence sensor in the pressure range of 5 GPa[7]. The electronic structure determines the physical and chemical properties of materials. Extensive theoretical studies have been devoted to understand the structural, electronic and optical properties of MXF (M = Ca, Sr, Ba, Pb and X = Cl, Br, I) compounds [8-14]. In addition to that high pressure X-ray diffraction study has been performed by several groups [15-17], in which they observed structural phase transitions in BaClF and BaBrF at 21 and 27 GPa respectively. High pressure phase transition in BaClF is also studied by using molecular dynamics[18]. The thermal expansion coefficients of BaClF and BaBrF were determined by Kurobori et al [19]. Ultrasonic pulse echo and Brillouin scattering techniques have been used for the measurement of elastic constants for BaClF[20].

The reported lattice dynamical calculations using shell model[21], provide a theoretical understanding of elastic constants, equation of state, phonons, and thermo dynamic properties of MXF (M = Sr, Ba, Pb and X = Cl, Br, I) compounds. Raman spectra analysis of BaClF, BaBrF and BaIF single crystals were carried out at ambient conditions[22,23], in which the polarizations and frequencies of the vibrations are interpreted in terms of symmetry co-ordinates. High pressure Raman spectroscopic measurements on BaClF[24] and BaIF[25] revealed that ambient tetragonal structure of BaClF transforms to a mixture of tetragonal and orthorhombic structures at 10.8 GPa and both of these phases coexist up to 21.1 GPa, at which a new monoclinic phase is observed and all three phases coexist up to 25.6 GPa. While the ambient phase of BaIF found to be extremely stable and it undergoes a gradual layer to non-layer transition under high pressure. To the best of our knowledge there are no theoretical calculations exploring the vibrational properties of the above mentioned compounds under...
pressure. So, it is worthwhile to perform the phonon calculations under pressure in order to understand the structural phase transitions in these series of compounds. In the present study, we report the Raman active optical phonons of layered BaClF, BaBrF and BaIF at ambient as well as at high pressures.

2. Method of calculation

First principles calculations were performed using the CAmpbridge Series of Total Energy Package[26] based on the density functional theory (DFT). We used norm conserving pseudo potentials [27] for the electron-ion interactions to calculate the total energies as they are well suited for the calculation of phonons. The exchange correlation potential of Ceperley and Alder[28] parameterized by Perdew and Zunger[29] in the local density approximation for electron-electron interactions are used. The following plane wave basis orbitals were used in the calculations, Ba:5s2 5p6 6s2, F:2s 2 2p5, Cl:3s 2 3p5, Br:4s 2 4p5, I:5s 2 5p5. To conform the convergence of the calculations for the Brillouin-zone sampling, we tested the plane wave cut off energy and K-mesh according to the Monkhorst-pack grid scheme[30]. From which, we fix the cut off energy as 450 eV and K-mesh are 8x8x6, 8x8x6 and 6x6x4 for BaClF, BaBrF and BaIF respectively. We used a criterion for self-consistency that the energy is converged to 5x10^-7 eV/atom and the force to 10^-4 eV/Å.

3. Results and Discussion

3.1. Raman active modes

In our recent investigation[6], we studied the structural (under pressure), electronic, bonding and optical properties of BaClF, BaBrF and BaIF. In the present work, we have calculated the zone centre phonon frequencies of BaClF, BaBrF upto 30 GPa with a step size of 5GPa, and for BaIF upto 60 GPa in steps of 10 GPa. The BaXF(X = Cl, Br and I) crystallizes in the primitive tetragonal symmetry D_{4h} or P4/nmm PbClF type structure with two formula units (six atoms) per unit cell. The barium and halogen (Cl, Br and I) atoms are located at C_{4v} (or 4mm) whereas the fluorine atoms are at D_{2d} (or 2/m) symmetry site. According to group theory, the symmetry decomposition of modes is as follows:

\[ \Gamma_{18} = 2A_{1g} + B_{1g} + 3E_{g} + 3E_{u} + 3A_{2u}, \]

in which six are Raman active (2A_{1g}, B_{1g}, 3E_{g}) and four are IR active (2A_{2u}, 2E_{u}) modes. E_{g}(1,2,3) modes correspond to atomic motion of Ba, Cl and F along b-axis respectively. The anti symmetric vibration of Ba and Cl belongs to the modes of A_{1d}(1,2) along c-axis. The B_{1g} mode corresponds to the anti symmetric vibration of F-atoms along c-axis. The calculated Raman active optical modes are given in Table.1 along with experimental values, they agree quite well with the experiments for BaClF[22,24], BaBrF[22], BaIF[23,25].

The pressure dependence of Raman active optical modes of BaClF, BaBrF and BaIF are shown in Fig.1(a), Fig.1(b) and Fig.1(c) respectively. It can be clearly seen that the vibrational frequencies of A_{1g}(1), E_{g}(2), A_{1g}(2) and B_{1g} increases with pressure, which implies that the hardening of the modes in these three compounds. In BaClF, E_{g}(1) and E_{g}(3) modes have been soften upto 20 and 10 GPa respectively. This might be an indication for the structural phase transition that occurs in BaClF, which agrees with the tetragonal phase co-existing with orthorhombic phase at 10.8 GPa and further these two phases co-existing with monoclinic phase at 21.1GPa[17,24].

Table.1: The calculated and experimental (in parenthesis) Raman active optical modes of BaClF, BaBrF and BaIF at ambient pressure.

| Mode   | BaClF[22,24]   | BaBrF[22]   | BaIF[23,25] |
|--------|----------------|-------------|-------------|
| E_{g}(1)| 81.34(89,82)   | 74.46(76)   | 66.29(70,40)|
| A_{1g}(1)| 128.36(125,132)| 99.85(105)  | 76.34(79,81)|
| E_{g}(2)| 135.54(142,145)| 104.71(109)| 99.17(105,74)|
| A_{1g}(2)| 161.64(162,165)| 122.94(119)| 107.46(113,113)|
| B_{1g}  | 216.73(212,215)| 208.85(215)| 210.11(203,205)|
| E_{g}(3)| 308.72(247,255)| 315.90(240)| 315.90(240)|
The softening of $E_g(1)$ mode is also observed in BaBrF and BaIF upto 30 and 60 GPa respectively, this could be an evidence for the reported structural phase transition in BaBrF at 27 GPa[16] and in BaIF around 55 GPa[25]. $E_g(3)$ mode decreases within pressure range 10-20 GPa for BaBrF and 10-40 GPa for BaIF, this is due to enhancement of intramolecular interaction under pressure. $A_{1g}(1)$ and $E_g(3)$ modes of BaIF are present upto 60 GPa in our calculation, but these modes are absent in experiment[25] from 30 and 55 GPa respectively.

![Fig.1:](image)

(a) 

(b) 

(c) 

3.2. Born effective charge tensors 

Born effective charge($Z^*$) and optical dielectric($\varepsilon^\infty$) tensors are fundamental quantities for understanding the lattice dynamics in polar insulators. The form of $Z^*$ directly results from site symmetry of crystal. The Born effective charge tensor $Z^*_{ij,k}$ is defined as the linear change in the polarization per unit cell created along the direction $i$, when the atom $k$ is displaced along the direction $j$

$$Z^*_{ij,k} = V \frac{\partial p_i}{\partial r_j^k}$$

where, $V$ is volume of the unit cell, $p_i$ , macroscopic polarization along the $i$–axis, and $r_j^k$ is the displacement of the $k^{th}$ atom along $j$–axis. The effective charge tensors of Ba, X (X = Cl, Br and I) and F atoms and the dielectric constants of BaXF compounds are reported in Table 2. The effective charge tensors vanish, when they summed over all the atoms in the unit cell i.e $\sum_k Z^*_{ij,k} = 0$. The neutrality guarantees that the polarization remains invariant under rigid translation of the crystal and also
suggests that the calculations are well converged. Due to tetragonal symmetry of crystals the effective
charge tensors for each atom, which are diagonal and obey $Z^*(xx) = Z^*(yy)$, the $Z^*(xx), Z^*(zz)$
components of each atom in all these three compounds are very similar, indicating that the effective
charge tensor is nearly isotropic. This is even more true from dielectric tensor, where the differences
between $\varepsilon^{\infty}(xx)$ and $\varepsilon^{\infty}(zz)$ are very small, therefore the BaXF compounds are isotropic in view point
of dielectric and effective charge tensors. Our recent investigation also revealed that these are optically
isotropic materials even though strong anisotropy from structural and elastic properties[6]. We
observed that the accumulation of the effective charges for Ba and halogen ions along $a$ or $b$-axis is
more compared to $c$-axis. This is in good agreement with the experiment for BaClF[31]. It is also clear
from the Born effective charges, the fluoride ion seems to be rigid since its dynamical charge is less
deviation from its formal charge (-1). The accumulation of effective charges on Ba and F (except for
BaBrF along $a$-axis) increases whereas it is decreases on halogen ($X = Cl, Br, I$) from BaClF to
BaBrF then to BaF.

Table 2: The calculated effective dynamical charge tensors perpendicular $Z^*(xx)$ and parallel $Z^*(zz)$
to the $c$-axis and high frequency dielectric constants of BaCF, BaBrF and BaIf at ambient pressure.

| Parameter | BaClF | BaBrF | BaIF |
|-----------|-------|-------|------|
| $Z^*(xx)$ | 2.58  | -1.46 | -1.22| |
| $Z^*(zz)$ | 2.57  | -1.35 | -1.22| |
| $\varepsilon^\infty(xx)$ | 3.15  | 3.43  | 3.96 |
| $\varepsilon^\infty(zz)$ | 3.12  | 3.38  | 3.86 |

4. Conclusions
The vibrational properties of BaClF, BaBrF upto 30 GPa and BaIF upto 60 GPa have been studied
using density functional perturbation theory within the local density approximation. The calculated
Raman active optical modes at ambient pressure are consistent with the experimental results. The
softening in the $E_g(1)$ and $E_g(3)$ modes under pressure might be responsible for pressure-induced
structural phase transitions in BaClF, BaBrF and BaIF. The calculated optical dielectric tensor and
effective charge tensors show the isotropic nature inspite of strong anisotropy from their crystal
structures.

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