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Lattice Dynamics and Electronic Structure of Mixed Halofluoride Scintillators under High Pressure

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Abstract. We report the structural, lattice dynamics and electronic structure of mixed halo-fluoride scintillators MClF (M = Ca, Sr) based on density functional theory within generalized gradient approximation. The pressure dependent structural parameters and zone centered phonon frequencies are in reasonable agreement with the available experimental data. Both the structures are dynamically stable up to 50 GPa. MClF compounds are found to have a direct band gap along Γ–Γ direction at ambient as well as under pressure. It is found that these materials can serve as good storage phosphors in the low pressure region from the calculated electronic structure and optical spectra.

Keywords: Scintillators, Storage phosphors, Lattice dynamics, TB-mBJ, Electronic structure.
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INTRODUCTION

The alkaline-earth halo-fluoride scintillators MXF (M = Ca, Sr, Ba and X = Cl, Br, I) are interesting host materials. In scintillators, ionizing radiation produces an electron-hole pairs; they recombine radiatively at scintillation centers to emit light. The efficiency of emitting light depends upon transfer of energy to the scintillation site in the form of electron-hole pair. Eu^{+2}:MXF compounds are used for X-ray storage phosphors for medical imaging via photo stimulated luminescence as they are less capable in transferring energy to the scintillation center. While, Eu^{+2}:BaIBr and SrI_2 are highlight output scintillators, Alkaline-earth di-halides such as SrI_2, CaI_2, $SrBr_2$, BaX_2, BaIBr are optically isotropic materials in spite of strong anisotropy from their orthorhombic crystal symmetry. To understand their physical properties, extensive theoretical studies (Ref. 1 and references there in) have been reported on structural, electronic, optical, vibrational and thermodynamic properties of alkaline-earth halo-fluorides. Raman spectra analysis of SrClF, BaClF, and BaBrF single crystals were carried out at ambient conditions[2]. To the best of our knowledge there are no theoretical studies available in exploring the lattice dynamics and electronic structure of CaClF and SrClF compounds under high pressure. So, it is worthwhile to perform the structural, electronic and vibrational properties under high pressure.

Method of Calculation

The structural and lattice dynamical calculations were performed using PWSCF code within PBE-GGA functional. Ultra soft pseudo potentials are used to treat the electron-ion interactions. Electronic structure and optical properties were calculated using WIEN2k package. The calculations were converged with the integration in the Brillouin zone of 9×9×5 k-mesh and size of the plane wave basis set is 60 Ry.

Structural Properties

In order to obtain the equilibrium crystal structure, we have optimized both lattice geometry and ionic positions to get a fully relaxed structure. The calculated lattice constants are overestimated and bulk modulii are underestimated as expected trend using the PBE-GGA functional (see TABLE 1). Overall there is a good agreement between theory and experimental data[3] under studied pressure range (see FIGURE 1).

TABLE 1. Calculated ground state properties of CaClF and SrClF compared with the experimental data[4] given in parenthesis.

Material	a	c	u	v	B_0	B_0^1
CaClF	3.904	6.958	0.6459	0.1930	52.8	4.6
	(3.894)	(6.818)	(0.6432)	(0.1962)	(97)	(2)

SrClF	4.164	7.052	0.6438	0.2001	48.3	4.5
	(4.126)	(6.958)	(0.6429)	(0.2015)	(53.7,61)	(5)
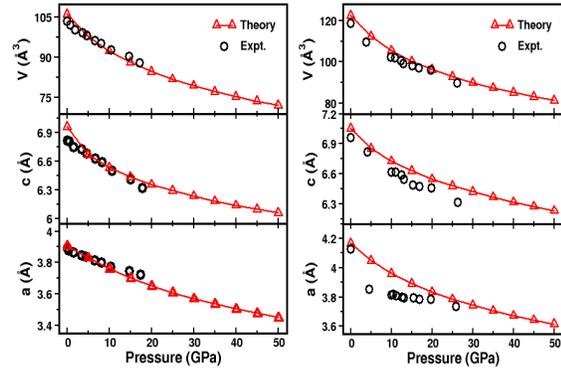
FIGURE 1. The calculated structural properties as a function of pressure for CaClF (left) and SrClF (right). Experimental data is taken from the Ref. 3.

Zone-centre phonon frequencies

We have calculated the zone centre phonon frequencies for CaClF and SrClF. According to group theory, the symmetry decomposition of *P4/nmm* space group 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. The calculated zone center frequencies (Raman and IR active modes including TO/LO splitting) are in good agreement with the experimental data as given in TABLE 2.

TABLE 2. Calculated Raman and IR active modes of CaClF and SrClF at ambient pressure.

	Modes	CaClF[5]	SrClF[2,6]
Raman	Eg	137.9, 164.6, 318.9	99.1, 147.0, 277.7
	(1,2,3)	(156, 209, 336)	(107, 167, 298)
	A1g	172.8, 255.5	149.9, 184.2
	(1,2)	(192, 265)	(155, 196)
	B1g	232.7(252)	220.3 (243)
IR	Eu (TO/LO)	123.1/153.7	113.1/145.0 (143)
	(1,2)	224.9/362.6	206.5/302.9 (255)
	A2u(TO/LO)	138.9/221.1	130.4/197.6 (182)
	(1,2)	327.3/418.0	295.6/353.6 (340)

The Eg(3) and Eu(2) modes correspond to in plane motion of F atoms, the frequency of Eu(2) mode is less than that of Eg(3) due to vibration of F atoms in the same direction, which reduces the electrostatic repulsion between the F atoms and it is the strongest intense band in the IR spectrum. The out of plane motion of F atoms along c-axis resembles the B1g and A2u(2) modes, the A2u(2) mode has higher frequency because of strong polarization of the crystal. Eg(2), Eu(1) and A1g(2), A2u(1) modes represent the motion of halogen (Cl, Br, and I) ions in phase and out of phase, respectively. The Eg(2) mode generates repulsion between halogen ions because of the movement of these ions in opposite direction, while the A1g(2) mode causes more interlayer effect in halogen ions than fluorine modes. The Eg(1) mode

corresponds to relative motion between two MXF units of the unit cell in xy-plane, whereas the A1g(1) mode is mainly due to anti-symmetric stretching of halogen and metal atoms along c-axis.

Phonon dispersion and phonon density of states

To study the dynamical stability of the layered materials, we also calculated the complete phonon dispersion along the whole Brillouin zone and the corresponding density of states at 0 and 50 GPa pressures for CaClF and SrClF are given in FIGURE 2 and 3. As illustrated in the FIGURE 2 and 3, no imaginary frequencies were found over the studied pressure range for both of the materials. Also, the phonon frequencies are increasing and phonon bands become more dispersive with increasing pressure which indicates hardening of the lattice under compression. This clearly shows the dynamical stability of both the materials at ambient and under pressure at 50 GPa.
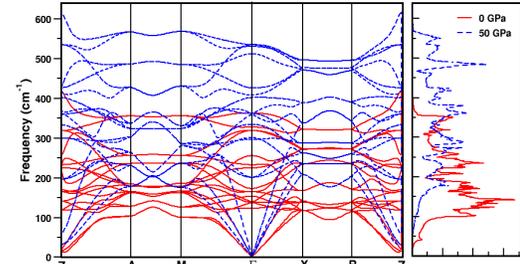
FIGURE 2. The calculated phonon dispersion and phonon density of states at 0 and 50 GPa pressure for CaClF.
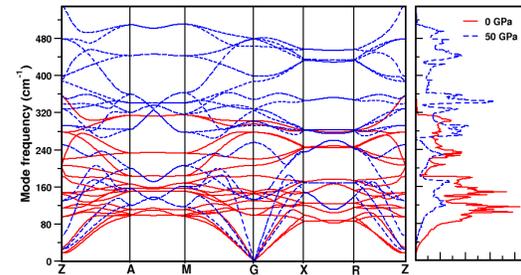
FIGURE 3. The calculated phonon dispersion and phonon density of states at 0 and 50 GPa pressure for SrClF.

Electronic structure and optical properties

The electronic structure of mixed halofluoride compounds were obtained using Tran Blaha-modified Becke Johnson (TB-mBJ) potential at ambient and under pressure. The obtained electronic structures show that CaClF and SrClF are direct band gap insulators along Γ-Γ direction with band gap values of 7.18 and 7.72 eV, respectively and the corresponding values with PBE-GGA are 5.72 and

5.95 eV at ambient pressure. The TB-mBJ functional improves band gaps over standard DFT functionals[7]. The band gap values decrease with pressure for both of the compounds as shown in Fig. 3 and they exhibit insulating behavior at high pressure.
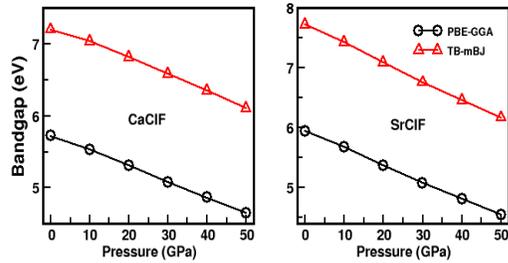
FIGURE 4. Calculated band gap as a function of pressure for CaClF (left) and SrClF (right).

As illustrated in Fig. 5, the valence bands of alkaline-earth halo-fluorides at ambient pressure show an important difference from alkaline-earth dihalides, which is reflected in the response of alkaline-earth halo-fluorides to ionizing radiation. The holes will be created on halogen (X) derived valence bands, since the halogens are anions and the holes are positively charged between the X-M-F-F-M-X layers (see Fig. 1 of Ref. 1), leads to hole self-trapping, and hence the recombination of electron-hole pairs occurs radiatively with less probability at the scintillation site. This might be the reason for alkaline-earth halo-fluorides being used as storage phosphors rather than highlight output scintillators. As pressure increases the electronic bands become more dispersive and they are direct band gap (Γ–Γ) insulators even at 50 GPa as shown in Fig. 6.
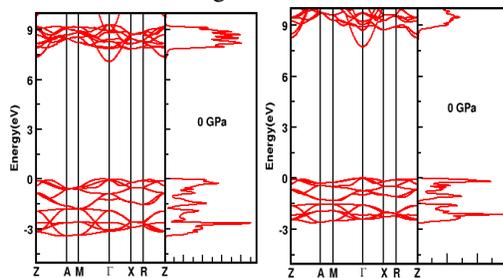
FIGURE 5. The calculated electronic band structure and DOS of CaClF (left) and SrClF (right) at 0 GPa.
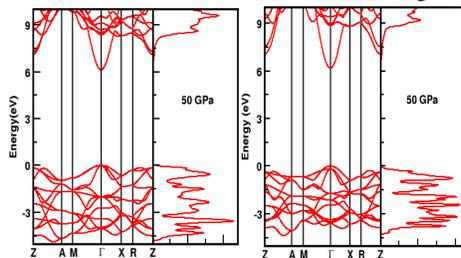
FIGURE 6. The calculated electronic band structure and DOS of CaClF(left) and SrClF (right) at 50 GPa.

One of the key requirements for a ceramic scintillator is optical isotropy to avoid light scattering at misoriented grain boundaries. It was found from the refractive index that the optical anisotropy is weak in both CaClF and SrClF up to 8-10 eV at ambient pressure. As pressure increases the anisotropy increases and these materials show a weak anisotropy up to 6 eV at 50 GPa. Therefore, we confirm that these materials serve as good storage phosphors at low pressure rather than at high pressure region.
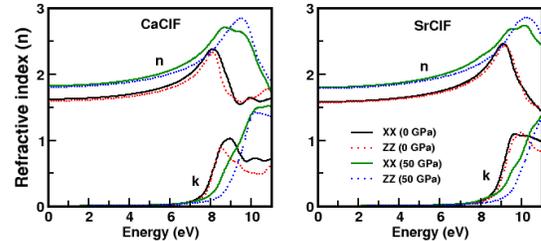
FIGURE 7. The calculated complex refractive index of CaClF (left) and SrClF (right) at 0 and 50 GPa.

Conclusions:

In summary, structural, dynamical and electronic structure calculations were performed for CaClF and SrClF at ambient and high pressure. The calculated structural properties and Γ-point phonon frequencies are in reasonable agreement with the experiments. Both the structures are dynamically stable up to 50 GPa. MClF (M = Ca, Sr) are direct and wide band gap insulators along Γ–Γ direction at ambient and high pressure. From the electronic structure and optical properties it was concluded that these materials can be used as storage phosphors in the low pressure region.

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