

# Structural phase transitions of ionic layered PbFX (X = Cl<sup>-</sup> or Br<sup>-</sup>) compounds under high pressure



Y.A. Sorb <sup>\*,1</sup>, D. Sornadurai, Condensed Matter Physics Division, Materials Science Group

Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India

## ARTICLE INFO

### Article history:

Received 21 June 2014

Received in revised form 30 September 2014

Accepted 20 December 2014

Available online 3 January 2015

### Keywords:

A. Layered compounds

C. High pressure

C. X-ray diffraction

D. Crystal structure

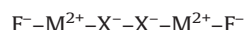
## ABSTRACT

The PbFX (X = Cl<sup>-</sup> or Br<sup>-</sup>) compounds crystallize in tetragonal structure with space group  $P4/nmm$ . High pressure X-ray diffraction studies carried out on PbFCl compound reveals that it undergoes pressure induced structural transitions at  $\sim 18$  GPa and  $\sim 38$  GPa to orthorhombic and monoclinic ( $P2_1/m$ ) phases respectively. Like PbFCl, a similar phase transition from tetragonal to orthorhombic phase is observed in PbFBr at intermediate pressure. These phase transitions seem to be similar to the transitions involving other matlockite structure compounds such as BaFX (X = Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>). PbFCl has a larger structural stability range compared to BaFCl and is attributed to the large anisotropic coordination of the Pb<sup>2+</sup> and Cl<sup>-</sup> ions.

© 2015 Published by Elsevier Ltd.

## 1. Introduction

Ionic layered compounds of the form MFX, where M is a divalent metallic cation (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup> or Eu<sup>2+</sup>) and X = Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>, crystallize in tetragonal structure with space group  $P4/nmm$  [1]. A typical unit cell of MFX has two formula units in which the arrangement of atomic layers perpendicular to the c-axis is in the following sequence



The unit cell of PbFCl compound (matlockite) is shown in Fig. 1. Apart from MFX compounds, two other families of compounds namely oxide halides [MOX] and hydride halides [MHX] crystallize in PbFCl-type structure. For example, in MOX compounds, the sequence of the layers is X–M–O–O–M–X [2], where the O layer is doubly occupied with respect to the M and X layers, which is similar to the sequence used by Yedukondalu *et al.* in BaFCl [3]. However, the phase transitions of matlockite compounds under high pressure can easily be understood if we assume the sequence of layers as F–M–X–X–M–F rather than X–M–F–F–M–X [3].

The matlockite compounds have interesting properties such as photoconductivity [4], photoluminescence [5,6] and anisotropic

ionic conductivity [7,8] and find application in various fields. For example, BaFBr doped with Eu<sup>2+</sup> (BaFBr: Eu<sup>2+</sup>) has been successfully applied for detecting X-rays as imaging phosphors due to the photo stimulated luminescence property [9]. Similarly, BaFCl: Sm<sup>2+</sup> has been used as a pressure sensor in high pressure experiments [10]. Based on a detailed luminescence study, pure PbFCl has been demonstrated to be an excellent scintillation detector material for neutrino detection [11]. Effect of pressure on scintillator materials can be used to elucidate the correlation between the intrinsic resolution and their electronic band structure thereby one can design newer and better storage phosphors. But more theoretical and experimental evidences are required to validate the above statement. The high pressure structural behavior of matlockite structure compounds such as BaFCl, BaFBr and BaFI have been extensively studied [12–20]. Using first principle calculation, the structural, electronic, and optical properties of the alkaline-earth halo fluorides, BaXF (X = Cl, Br and I) and their high pressure structural behavior is extensively studied [3,21]. These systems undergo a series of symmetry lowering structural transitions: tetragonal → orthorhombic → monoclinic and have been attributed to a gradual anisotropic distortion of the charge distribution in the planes perpendicular to the stacking direction [13–15]. Replacement of Ba<sup>2+</sup> with Pb<sup>2+</sup> can be expected to result in stronger attraction between the two adjacent Cl<sup>-</sup> or Br<sup>-</sup> layers on account of the larger electro negativity of Pb<sup>2+</sup> ion (Fig. 1). It is interesting, therefore, to see if PbFX (X = Cl<sup>-</sup> or Br<sup>-</sup>) exhibit a similar structural sequence induced by pressure and study their stability range. High pressure

\* Corresponding author. Tel.: +91 8022082963.

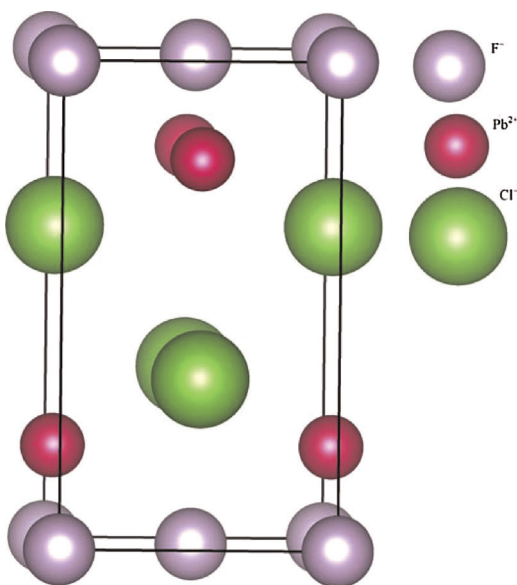
E-mail address: [sorbya@jncasr.ac.in](mailto:sorbya@jncasr.ac.in) (Y.A. Sorb).

<sup>1</sup> Presently at Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur 560 064, India.

X-ray diffraction studies have been reported on the PbFBr compound by Decremps *et al.* and have not observed any phase transition up to  $\sim 30$  GPa [22]. Our recent high pressure work on PbFCl shows that two interlayer ‘rigid layer’ modes, namely  $A_{1g}$  and  $E_g(1)$ , of the parent tetragonal layered phase, suffer from instability above  $\sim 24$  GPa as a result of pressure induced change of bonding nature from layer to non-layer type [23]. This work has focused only on the dynamics of phonon modes of the PbFCl compound under pressure. Here, we present the detailed XRD studies of the PbFCl compound to understand the pressure induced structural behavior of PbFCl and also our results on PbFBr at  $\sim 15$  GPa.

## 2. Experimental details

The PbFX ( $X = Cl^-$  or  $Br^-$ ) compounds were synthesized by the stoichiometric mixtures of  $PbF_2$  and  $PbX_2 \cdot nH_2O$  ( $n \sim 2$ ) in nitrogen atmosphere using the solid state reaction method. Powder X-ray diffraction pattern of PbFCl showed that the compound was in a single phase with tetragonal matlockite structure ( $P4/nmm$ ). The lattice parameters obtained from the powder pattern were:  $a = 4.097$  (3) Å and  $c = 7.224$  (2) Å and these values were matched well with the Joint Committee for Powder Diffraction Standard (JCPDS) values of  $a = 4.1104$  (2) Å and  $c = 7.2325$  (5) Å [24]. Similarly, the lattice parameters obtained for PbFBr were:  $a = 4.189$  (4) Å and  $c = 7.597$  (1) Å and were matched well with the JCPDS values of  $a = 4.191$  Å and  $c = 7.591$  Å [25]. A Mao-Bell type diamond anvil cell (DAC) with culet size of  $\sim 500$   $\mu m$  in diameter was used for high pressure experiments. A stainless steel gasket was preindented to a thickness of 50  $\mu m$ ; a hole of diameter 200  $\mu m$  was drilled in its center and finely powdered sample was loaded into the gasket hole. A 4:1 mixture of methanol and ethanol was used as pressure transmitting medium. Pressure was determined using the equation of state of gold and Pt which were loaded along with PbFCl and PbFBr compounds respectively. HPXRD experiments were performed on the samples in angle dispersive geometry using Mo  $K\alpha_1$  X-ray radiation obtained from an 18 kW rotating anode X-ray generator and was monochromatized by a graphite monochromator. The sample to detector distance was calibrated using  $LaB_6$ . The diffraction patterns were

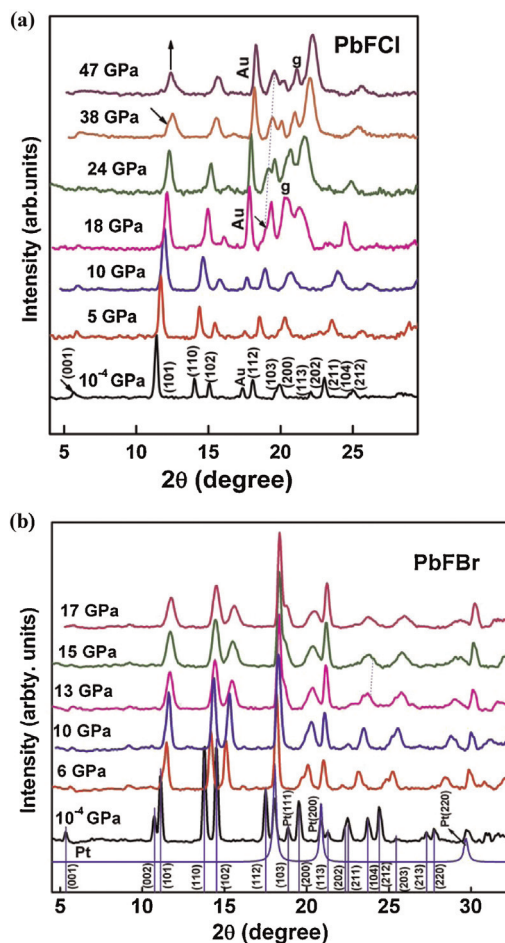


**Fig. 1.** Unit cell of PbFCl compound. The spheres with the labels  $F^-$ ,  $Pb^{2+}$  and  $Cl^-$  represent the type of ions.

collected using a mar345dtb diffractometer with an overall resolution of  $\delta d/d \sim 0.001$  and the average acquisition time was 2 h. The 2D XRD diffraction images were integrated using FIT2D software which produces patterns of intensity versus the diffraction angle  $2\theta$  [26]. The HPXRD patterns of these compounds were analyzed using Powd [27] and NBS-Aids\*83 programs [28] to obtain the lattice parameters. Peak positions were determined by a Gaussian fitting of the diffracted lines.

## 3. Results and discussions

The representative XRD patterns of PbFCl and PbFBr compounds at various pressures are shown in Fig. 2a and b respectively. In PbFCl compound, the XRD pattern at  $\sim 18$  GPa shows the emergence of a new peak at  $2\theta \approx 19^\circ$  and the intensity of this peak is seen to increase with pressure. For instance, the intensity of (102) peak decreases, while that of (200) peak increases drastically as shown in Fig. 2a. The analysis of the HPXRD pattern at  $\sim 21$  GPa shows that the new structure is orthorhombic with lattice parameters  $a = 7.751$  (1) Å,  $b = 3.346$  (5) Å and  $c = 3.838$  (3) Å. The starting tetragonal phase is seen to coexist with the high pressure orthorhombic phase up to



**Fig. 2.** (a) The angle dispersive X-ray diffraction spectra of PbFCl at various pressures. The slanted arrow indicates the emergence of new peaks, whereas the upward arrow indicates the intensity enhancement of the new peaks. Au is the pressure marker. ‘g’ is the gasket peak. The intensity enhancement of the peak (301)<sub>o</sub> with pressure is represented as a dotted line. (b) X-ray diffraction pattern of PbFBr at various pressures. The stick patterns from JCPDS match with the ambient pattern of PbFBr. Pt (111), Pt (200) and Pt (220) are the peaks obtained from ‘Pt’ which is used as pressure calibrant.

Download English Version:

<https://daneshyari.com/en/article/1487664>

Download Persian Version:

<https://daneshyari.com/article/1487664>

[Daneshyari.com](https://daneshyari.com)