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Crystal structure of the high-pressure phase of BaFCl

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The structural stability of the layered matlockite compound BaFCl has been studied under pressure to ~35 GPa. BaFCl is observed to undergo a reversible structural transition at about 22 GPa and the high-pressure phase has been identified to be monoclinic with space group $P2_1/m$. The structural identification of the high-pressure phase was carried out by taking into account the fact that the interlayer bonding between the two similar Cl^- layers is relatively weak compared to those between the other layers and intralayer bondings, thereby rendering the low-pressure structure unstable against the deformation under pressure. [S0163-1829(98)50226-3]

INTRODUCTION

BaFCl belongs to the class of layered compounds crystallizing in the tetragonal PbFCl-type (also called matlockite type) structure at ambient conditions with space group $P4/nmm$.[1] These materials are of technological importance due to their x-ray image storage properties upon dilute doping with rare-earth ions.[2–8] A knowledge of their structural and optical behavior under pressure would be useful to design newer and better storage phosphors. Single crystals of BaFCl were first studied under pressure by Beck *et al.*[9] up to ~6.5 GPa using x-ray diffraction method and no structural transition was observed. They have observed that above ~2 GPa the system exhibits anisotropic compressibility with increasing c/a ratio. Recently, Shen *et al.*[10] have reported a structural transition in BaFCl under pressure, but have not determined the structure of the high-pressure phase. A Brillouin spectroscopy study of layered PbFCl-type compounds under pressure by Decremps and co-workers[11,12] up to ~20 GPa has revealed that the various layers in the unit cell are mainly bonded by weak forces thus explaining the observed anisotropic compressibility behavior as a consequence of the anisotropic bonding scheme. Further, the study confirms that the stability of the BaX (X=Cl, Br, I) structures in general is closely linked to the high polarizability and large size of the anion X. Systems like BaFCl are known to show interesting physical properties as a consequence of their layered nature.[13] Therefore it will be of interest to study the effect of pressure on their structural stability *per se.* Such studies also gain importance in the context of these materials holding good promise as luminescent pressure calibrants in diamond-anvil cell experiments upon doping with rare-earth ions. The present work was aimed at determining the pressure range of the ambient pressure crystal structure (matlockite) in BaFCl, the nature of the observed structural transition, and identifying the crystal structure of the high-pressure phase.

EXPERIMENTAL

Samples of BaFCl were prepared by direct solid-state reaction of the individual halides BaF_2 and $BaCl_2$ in a nitrogen atmosphere and characterized by powder x-ray diffraction (XRD). The samples were found to be in single phase with lattice parameters $a=4.388(1)$ Å and $c=7.215(5)$ Å, subscribing to the space group $P4/nmm$ and compare well with the Joint Committee for Powder Diffraction Standard (JCPDS) values of $a=4.391(3)$ Å and $c=7.226(4)$ Å.[14]

High-pressure x-ray diffraction (HPXRD) in the angle dispersive mode was carried out on the powder samples up to ~35 GPa with a Mao-Bell-type diamond anvil cell (DAC) using a Guinier diffractometer described in detail by Sahu *et al.*[15] and Yousuf *et al.*[16] This diffractometer is in vertical configuration and symmetric transmission mode with a Seeman-Bohlin focusing circle of diameter 114.6 mm. The DAC is mounted such that the sample inside it is also positioned on the Seeman-Bohlin circle. A linear position sensitive detector (PSD) of length 50 mm that can simultaneously record the diffraction pattern over an angle span of 10° is also mounted on the Seeman-Bohlin circle. Diffraction is performed using monochromatic Mo $K\alpha_1$ x-ray beam (with a concurrent $K\alpha_2$ component of ~6%)[17] derived from a quartz curved crystal monochromator mounted on the line source window of a RIGAKU 18 kW rotating anode x-ray generator. The overall resolution $\Delta d/d$ of this system is better than ~0.01.

With this system a HPXRD pattern with reasonably good signal-to-noise ratio could be obtained in ~2 h for BaFCl at an x-ray power level of 50 kV×200 mA. The HPXRD pattern which was taken up for structural analysis was recorded for ~8 h to obtain good statistics and thereby good signal-to-noise ratio. The equation of state of silver was used for pressure calibration and a 16:3:1 mixture of methanol, ethanol, and water was used as the pressure transmitting medium.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of BaFCl recorded using the above setup at several pressures. It is seen that beginning at about 22 GPa, the following changes occur in the XRD pattern. The (101)-(002) peak of the ambient pattern can be observed to broaden and split progressively into a triplet with a large reduction in intensity. The intensity of the (102) peak decreases and subsequently, this peak vanishes completely at ~28 GPa, marking the completion of the structural transition. A new peak is seen to appear at a θ value of ~8.74° in the 22 GPa pattern, which gradually de-

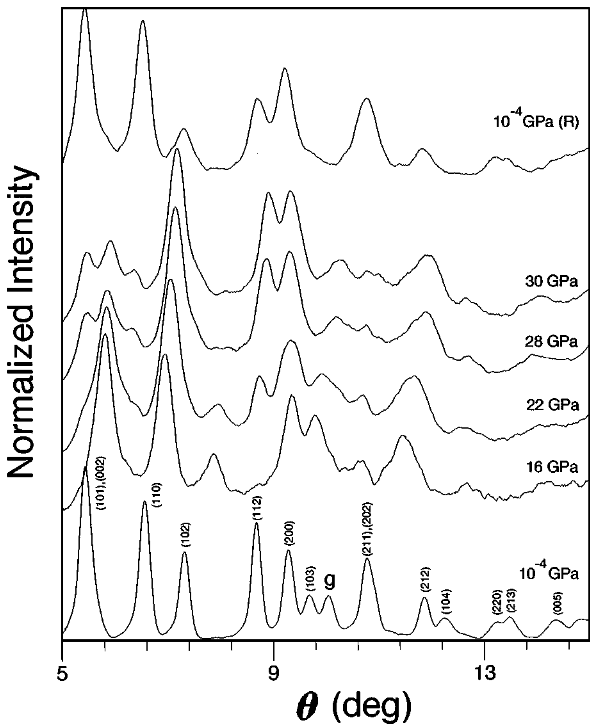

FIG. 1. HPXRD patterns of BaFCl at various pressures. The pattern marked ''(R)'' is the XRD pattern of the sample after release of pressure. The peak marked ''g'' in the ambient pattern is the gasket peak.

velops into a high intensity peak at higher pressure. The intensity of the (110) peak of the ambient XRD pattern remains basically unchanged even across the transition and up to ~35 GPa, the highest pressure to which the sample has been studied. The transition is reversible in nature and the width of the transition is ~6 GPa. This transition has first been reported by Shen *et al.*[10] at ~21 GPa, who studied this material up to ~35 GPa using energy dispersive x-ray diffraction (EDXD) technique with synchrotron radiation source. They have rationalized the high-pressure behavior in terms of an elegant hard-sphere model and geometric considerations, but were unable to identify the high-pressure structure in spite of their highly resolved data, probably because of the presence of very few peaks and interference of Ba $K\alpha$ and $K\beta$ lines. The HPXRD patterns presented in Fig. 1 show clearly a few more peaks with finer features, apart from the new peaks observed by Shen *et al.*[10] This was as a consequence of the truly focusing geometry of our Guinier HPXRD system coupled with high detection efficiency of the PSD (Refs. 15 and 16) and proved to be of importance in performing the crystal structure analysis of BaFCl.

The above observations, viz. splitting of peaks and appearance of new peaks in the HPXRD patterns, apparently point to the reduction in symmetry upon going from the ambient to the high-pressure structure. Therefore, a good candidate for the high-pressure phase can be a monoclinic or triclinic lattice.

The 28 GPa HPXRD pattern was taken up for analysis and several possible low-symmetry structures were attempted. The best fits (with a figure of merit $F_{10}>11$ and with no lines unindexed) were obtained for two monoclinic lattices $M1$ and $M2$ with the following lattice parameters:

$$a=7.0603 \text{ Å}; \quad b=4.3894 \text{ Å}; \quad c=4.0336 \text{ Å};$$

$$\beta=100.33° \quad (\text{for } M1)$$

$$a=4.6651 \text{ Å}; \quad b=4.4332 \text{ Å}; \quad c=5.7242 \text{ Å};$$

$$\beta=94.39° \quad (\text{for } M2)$$

In order to pinpoint the correct structure, the intensities of the Bragg peaks had also to be calculated with the ionic positions and above lattice parameters as the basic input. Hence the problem at hand was to first determine the ionic positions for the high-pressure phase. This is a nontrivial task in analyzing any data from HPXRD experiments and becomes especially difficult in the absence of any single crystal data or calculations that reveal the possible ionic positions at such high pressures. Therefore, approximate methods have to be resorted to for obtaining the ionic positions. One of the ways in which this problem has been overcome is to start with the ambient ionic positions themselves as input to refinement programs and keep adjusting the positions until a good agreement between the calculated and experimental patterns is obtained.[18]

In the case of BaFCl, we have followed a different approach in which the ionic positions in the high-pressure phase were obtained, as a first approximation, by transforming the ambient ionic positions in accordance with the lattice transformations to $M1$ and $M2$ structures, respectively. The equations given below were used to effect these transformations.

$$x_i'=x_i-(c'/c)z_i\tan(\beta-90°);$$

$$y_i'=(b'/b)y_i; \quad z_i'=(c'/c)z_i.$$

In the above equations, $b(=a),c,\beta,x_i$, y_i and z_i correspond to the lattice parameters and ionic coordinates (of ions of type i, where $i=$Ba/F/Cl) for the ambient tetragonal cell whereas the primed quantities stand for similar parameters for the high-pressure monoclinic structures ($M1$ or $M2$). For example, for the $M1$ phase, the approximate positions of Ba^{2+}, F^- and Cl^- are (0.2291, 0.2504, 0.1146), (0.75, 0.2504, 0), and (0.1841, 0.2504, 0.3618), respectively. These ion positions are the raw (unrefined) transformed coordinates from the tetragonal cell. Although the ionic positions determined thus may not be accurate, they can be very reliable input parameters for structure refinement programs. For the present work, however, these approximate positions were used for intensity calculations with the principal aim of identifying the correct structure from among $M1$ and $M2$. The Bragg peaks were calculated using the above information and broadened into Lorentzians with an average linewidth of 0.2°. Strictly, one should consider the variation of linewidth W with θ as $W^2(\theta)=a+b\tan\theta+c\tan^2\theta$.[19] However, in HPXRD patterns, where the line broadening due to (a) nonhydrostatic effects, (b) pressure inhomogeneities, (c) overlapping of nearby peaks owing to the low resolution as a consequence of using short wavelength x-rays,[20] etc. predominate over that yielded by the expression for $W(\theta)$ at high pressures, it is reasonable to assume an average line-

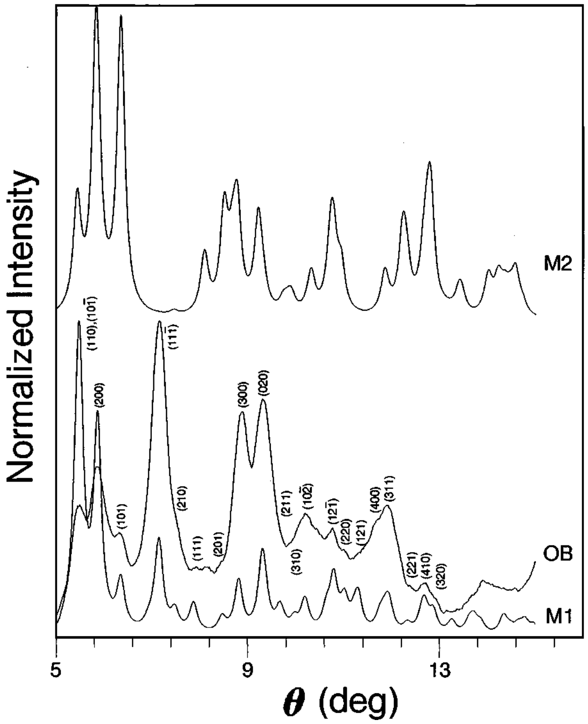

FIG. 2. HPXRD patterns of BaFCl at 28 GPa. ''OB'' is the observed pattern while ''$M1$'' and ''$M2$'' are the calculated patterns (refer text for description).

width for the purpose of calculation. The space group in case of both $M1$ and $M2$ is $P2_1/m$.

Figure 2 shows the observed and calculated HPXRD patterns for both $M1$ and $M2$ phases at 28 GPa. The pattern $M2$ does not match at all the observed pattern in the sense that the 100% main peak itself is not present and a number of new peaks are also seen. On the other hand, the pattern $M1$ agrees reasonably well with the observed pattern except for the intensities of some peaks. Table I lists the observed and calculated θ values ($M1$) and d spacings for the 28 GPa pattern for all the major peaks. It can be seen from Fig. 2 that even most of the minor observed peaks not presented in Table I can be found in the calculated pattern. The mismatch between the observed and calculated intensities in Fig. 2 can be reduced by refining the atom positions as also taking the rather strong preferred orientation effects into account. Such discrepancies in the intensities is indeed a perennial problem with HPXRD experiments[20] and has been chiefly attributed to the small sample quantities (~μg) used in the DAC leading to significant preferred orientation effects. A comparison of the XRD pattern of BaFCl before application of pressure with that after release of pressure (Fig. 1) shows that though the transition is reversible, preferred orientation effects that have set in at high pressure continue to be present. Another point to note is the increased width of all the Bragg peaks of the pressure cycled sample as compared to the ambient peaks.

TABLE I. Observed and calculated θ and d values of the high-pressure phase of BaFCl at 28 GPa. The calculated values correspond to structure $M1$ (refer to text for details). $\lambda = 0.709\,26$ Å.

S. No.	θ_{Obs} (deg)	θ_{Cal} (deg)	d_{Obs} (Å)	d_{Cal} (Å)	hkl
1	5.43	5.43	3.7476	3.7476	10$\bar{1}$, 110
2	5.86	5.86	3.4734	3.4734	200
3	6.36	6.35	3.2014	3.2064	101
4	7.15	7.15	2.8492	2.8492	11$\bar{1}$
5	8.85	8.81	2.3051	2.3154	300
6	9.32	9.30	2.1898	2.1944	020
7	10.18	10.19	2.0065	2.0045	10$\bar{2}$
8	10.77	10.79	1.8978	1.8943	12$\bar{1}$
9	11.93	11.95	1.7155	1.7127	311
10	12.70	12.69	1.6131	1.6143	410

The distortion of the ambient tetragonal structure to monoclinic structure $M1$ at high pressure can be rationalized in the following manner. The unit cell of BaFCl has two molecular units with planes of identical ions in the sequence F^--Ba^{2+}-Cl^--Cl^--Ba^{2+}-F^- stacked along the c axis.[1,10–12] As the bonding between the two adjacent Cl^- layers is relatively weak, the unit cell is susceptible for deformation under pressure leading to the above transition. Previous studies have indicated that the stability of the ionic layer compounds of type BaFX are closely related to the high polarizability and large size of the halogen X.[12] The effect of pressure is to basically affect the weak bonds leading to a redistribution of the electronic density of the highly polarizable anion X. It can therefore be expected that the deformation will be of continuous nature, leading to a gradual changeover to a low-symmetry structure, rather than a sharp structural transition. This point is elucidated by seeing the pressure evolution of the 100% line of the ambient phase in Fig. 1. At ~16 GPa, the line can be seen to be considerably broadened and at ~22 GPa, the multiplet structure can be seen to be on the verge of emerging. Finally, at ~28 GPa it becomes a well pronounced triplet. There is no discernible volume change across the transition in our case. In case of sharp structural transitions, such a behavior is not seen usually.

A comparison of the lattice parameters of $M1$ with the ambient values shows consistency with the picture that with increasing pressure there can be an expected large compression of the electron charge density of the Cl^- ions between the adjacent weakly bonded Cl^- layers along the c axis, while simultaneously it can get redistributed more in the a-b plane with anisotropy along the a axis owing to the large polarizability. We believe that it is this anisotropic elongation of the charge cloud under pressure that is responsible for the distortion of the unit cell itself. The c/a ratio for the 28 GPa phase is 0.5711, compared to a value of 1.6443 for the ambient phase, and is qualitatively consistent with earlier observations on the large decrease of c/a ratio in BaFCl under pressure.[10]

The argument can be extended further to predict that the high-pressure phase of BaFCl may show relatively a large electrical conductivity in the a-b plane. Electrical resistivity measurements under pressure on BaFCl remain to be done to support this point. In this context, recent electronic structure calculation done by Kalpana *et al.*[21] using the tight-binding linear muffin-tin orbital (TB-LMTO) method has shown an interesting possibility of the BaFCl metallizing at high pressures. The metallization pressure has been found to be ~21 GPa, close to the structural transition pressure. This again gives a hint that the observed structural transition may be electronically driven. Detailed electronic structure and total energy calculations are being done on the high-pressure monoclinic phase to provide more details about the above aspect. We are also studying other related BaFX (X=Br,I) systems using the HPXRD technique to check whether the high-pressure behavior is akin to that of BaFCl described in this work.

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