Structural transition of BaF_2 nanocrystals under high pressure*

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Abstract: The structural transition of BaF_2 nanocrystals is studied by in situ high pressure synchrotron radiation X-ray diffraction measurements up to about 21.2 GPa at ambient temperature. Two phase transformations were observed at 5.8 and 14.4 GPa, and the two high pressure phases are identified as orthorhombic (Pnma) phase and hexagonal ($P6_3/mmc$) phase by Rietveld refinement. Upon decompression, the α-$PbCl_2$-type metastable phase is retained when the pressure is released. Two phase transformations of the BaF_2 nanocrystals are higher than that in bulk BaF_2. It is proposed that the size effects are found to influence the BaF_2 nanocrystals high-pressure behaviors and the surface energy plays a significant role in the structural stability.

Key words: nanocrystals, BaF_2, synchrotron radiation, phase transition

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1 Introduction

The alkaline earth fluorides have attracted much attention due to their unique properties, such as low–energy phonons, high ionicity, electron-acceptor behavior, high resistivity, and anionic conductivity [1–3]. Barium fluoride is one of the alkaline earth fluorides that have a wide range of potential applications in microelectronic and optoelectronic devices, such as wide–gap insulating overlayers, gate dielectrics, insulators, and buffer layers in semiconductor-on-insulator structures and more advanced 3D devices [3]. Specifically, it is the fastest luminescent material that has been found to date, thereby making it an ideal high-density luminescent material for applications in gamma ray and elementary particle detectors [4].

At ambient conditions, BaF_2 crystallizes in the cubic fluorite structure with a space group of Fm3m, which consists of a cubic close-packed array of cations with anions occupying tetrahedral sites. Its excellent properties are related to its structural and electronic properties. At high pressure, the sequence of the phase transition follows the structural progression from cubic (Fm3m) fluorite structure to orthorhombic (Pnma) cotunnite-type structure to hexagonal ($P6_3/mmc$) Ni_2In-type structure, which in turn would be characterized by a progression in the cation coordination number from 8 to 9 to 11. Leger et al. [5] observed that the phase transition from the cubic to orthorhombic, to hexagonal phase occurred at 3 GPa and 12 GPa, respectively. Smith et al. [6] found that the two phase transitions occurred at 3 GPa and 14 GPa using in-situ X-ray diffraction and Raman techniques. Kanchana et al. [7] reported that the two calculated transition pressures are 2.84 and 12.8 GPa, respectively. There are many high–pressure studies on bulk BaF_2, however, to our knowledge, there has been no report of a phase transition study on nanoscale BaF_2. Previous studies on nanoscale materials under high pressures have revealed a series of interesting phenomena and novel properties, which may differ from those of their corresponding bulk counterparts. For instance, the size effects of nanoscale materials can enhance transition pressure [8–10], influence phase transition routines [11], and even lead to amorphization [12, 13]. With the rapid development of synthesis technology, the BaF_2 nanocrystals with controllable size and shape have been successfully prepared, providing access to systematically exploring high-pressure behaviors of BaF_2 nanomaterials.

In this work, we report an in situ high-pressure synchrotron radiation X-ray diffraction study of BaF_2

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nanocrystals with average grain sizes of 19 nm up to about 21.2 GPa at ambient temperature. The nanocrystal BaF_2 samples were prepared by the solvothermal synthesis method. The phase structures and average crystallite sizes of BaF_2 nanocrystals were determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). We found that the cubic fluorite phase of BaF_2 nanocrystals underwent two pressure-induced phase transformations, which were remarkably higher than the pressure occurring in the corresponding bulk BaF_2.

2 Experiments

The BaF_2 NCs were prepared by a liquid-solid-solution (LSS) solvothermal route [14, 15]. In a typical synthesis, oleic acid, ethanol, and sodium hydroxide were mixed together, the reactants of $Ba(NO_3)_2$ and NaF were added to the mixture under vigorous stirring for 1 h and then transferred into a autoclave, sealed and hydrothermally treated at the designed temperature of 180 ℃ for about 24 h. Then the system was cooled to room temperature naturally in air and the products were collected by centrifugation. The sample was characterized by TEM, Raman spectroscopy (532 nm excitation light), and XRD with Cu K_α radiation (λ=0.15418 nm). The sample powder was loaded into a gasketed high–pressure Mao-Bell-type diamond anvil cell (DAC) with 500 μm culet diamond anvils. A 120-μm-diameter hole was drilled through the center of a preindented 70-μm-thickness T-301 stainless steel gasket to form a sample chamber. A small amount of BaF_2 nanocrystals and a tiny ruby chip were placed inside the gasket hole and filled with silicone grease as the pressure medium. Pressure was determined from the frequency shift of the ruby R1 fluorescence line. High-pressure X-ray diffraction experiments were carried out up to 21.2 GPa using a synchrotron X-ray source (λ=0.6199 Å) of the 4W2 High-Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). The diffraction data were collected using a MAR165 CCD detector. The two-dimensional XRD images were analyzed using FIT2D software, yielding one-dimensional intensity versus diffraction angle 2θ patterns. High-pressure synchrotron XRD patterns were fitted by Rietveld profile matching using the MATERIAL STUDIO program. All measurements were performed at room temperature.

3 Results and discussion

Figure 1(a) exhibits the TEM image of a typical BaF_2 nanocrystal sample. We can observe that the as-synthesized nanocrystals with a square shaped. It is noted that there are some rod-like stripes in the image, which should be the side view of the square, and their width indicates the thickness of the squares. This interesting result demonstrates that most of the as-prepared BaF_2 nanosquares are plate-like with a mean size of length around 19±3 nm in a narrow distribution (Fig. 1(b)). The inset of Fig. 1(a) is the SAED pattern of the as-prepared BaF_2 nanocrytals, in which all of the reflections have been indexed and are consistent with the XRD result. The XRD patterns of the BaF_2 nanocrystals under ambient conditions are shown in Fig. 2. The sample can be indexed to a fluorite-type phase of BaF_2 with no impurity phase. The lattice constant of BaF_2 nanocrystals, a_0, has been determined to be 6.204 Å. It is consistent with the value of a_0=6.200 Å (PDF Card No. 04-0452). As we know, BaF_2 crystallized in the cubic fluorite-type lattice belongs to the space group Fm3m based on the group theory analysis. The first–order Raman spectrum of BaF_2 contains only one Raman line at 240 cm^{-1} [6]. Fig. 3 shows the Raman spectrum of BaF_2 nanocrystals in ambient conditions. The first-order Raman peak at 243 cm^{-1} is observed, which is characteristic of a pure cubic phase of BaF_2.

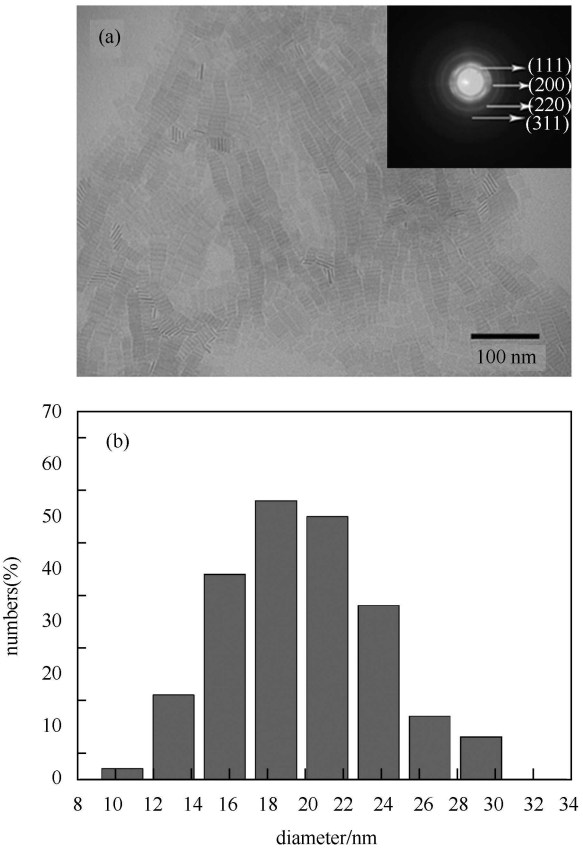

Fig. 1. (a) TEM images of the as-synthesized BaF_2 nanocrystals; (b) Particle size distribution histograms of the BaF_2 nanocrystals.

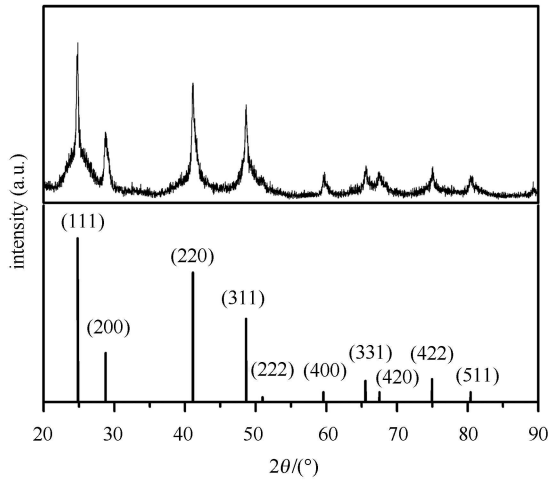

Fig. 2. XRD pattern of the as-prepared BaF_2 nanocrystals.

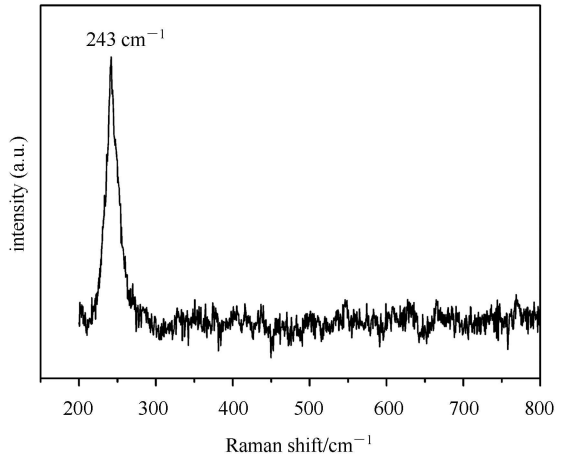

Fig. 3. Raman spectrum of the BaF_2 nanocrystals in ambient conditions.

Some selected high-pressure synchrotron radiation X-ray diffraction patterns for BaF_2 nanocrystals are shown in Fig. 4. With increasing pressure, the diffraction lines shift toward higher 2θ angles accompanied by a change of the relative intensities At 5.8 GPa, new diffraction peaks start to appear in the XRD patterns, indicating an occurrence of the phase transition. With increasing pressure to 10.8 GPa, additional diffraction peaks assigned to the high-pressure phase arise, and in the meantime all diffraction peaks from the cubic phase disappear, which means the cubic phase completely transformed into a high-pressure phase. Our Rietveld refinement for this new high-pressure phase using an orthorhombic structural model (space group Pnma) at 10.8 GPa yields a very good fit with residuals R_{wp}=0.7% (Fig. 5(a)) At 14.4 GPa, a new diffraction peak begins to emerge. At the same time, some peaks from the orthorhombic phase turn to be fairly weak and finally vanish at 21.2 GPa. The variation of the ADXD pattern indicates a second

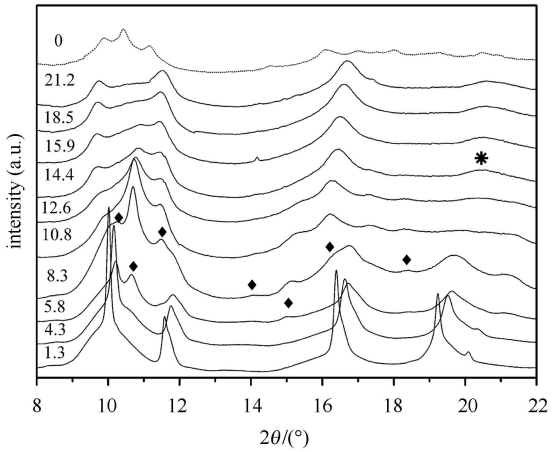

Fig. 4. X-ray diffraction patterns of BaF_2 nanocrystals at selected pressures at room temperature. Diamonds indicate the orthorhombic phase diffraction peaks. The asterisk indicates the hexagonal phase diffraction peak.

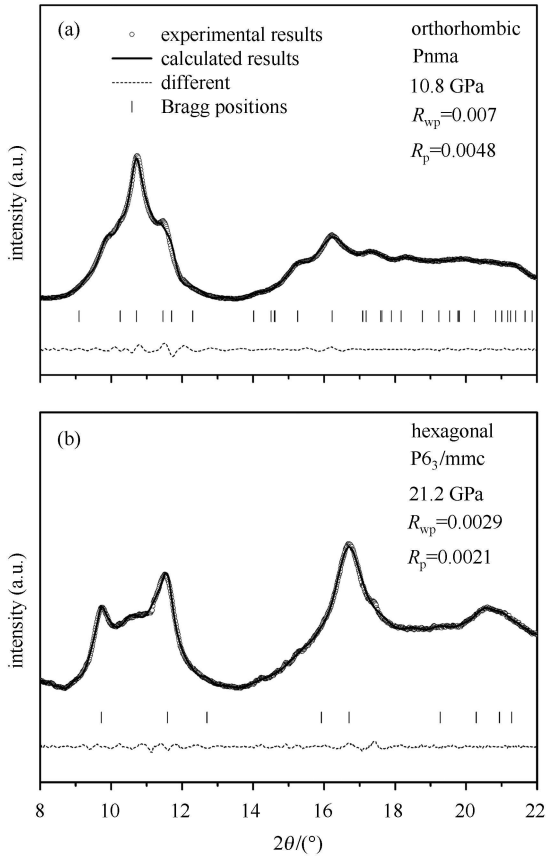

Fig. 5. Rietveld full-profile refinements of the diffraction patterns collected on compression at (a) 10.8 GPa and (b) at 21.2 GPa.

phase transition of BaF_2 nanocrystals begins at 14.4 GPa and completes at 21.2 GPa. Fig. 5(b) presents the Rietveld refinement of BaF_2 nanocrystals performed at 21.2 GPa showing good agreement with a hexagonal cell with space group $P6_3/mmc$ with residuals R_{wp}=0.29%. In our work, the sequence of the pressure-induced phase transitions of BaF_2 nanocrystals follows the structural progression from cubic fluorite structure to orthorhombic α-$PbCl_2$ type structure to hexagonal Ni_2In-type structure Upon decompression, the pure α-$PbCl_2$-type metastable phase is retained when the pressure is released. Fig. 6 presents the Rietveld refinement of BaF_2 nanocrystals released from 21.2 GPa to ambient conditions, showing good agreement with orthorhombic structure with residuals R_{wp}=0.64%. The result indicates that the phase transformation is irreversible, which is consistent with the observation of bulk BaF_2 [5].

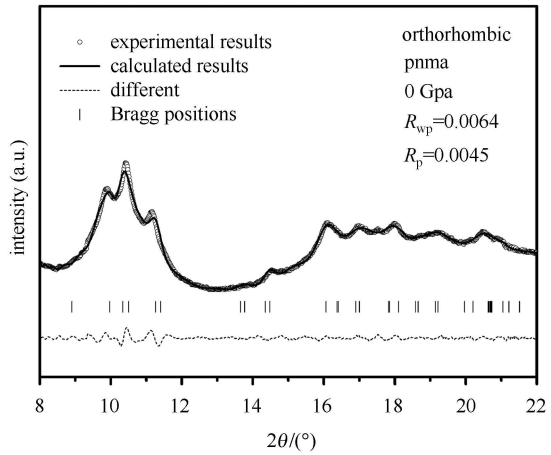

Fig. 6. Full profile rietveld refinement of the diffraction pattern for BaF_2 nanocrystals released from 21.2 GPa to ambient conditions.

From the above analysis, we can clearly see that two phase transformations of the BaF_2 nanocrystals occur at 5.8 and 14.4 GPa, which are higher than those in bulk BaF_2 [5–7]. This result is consistent with our previous observation of nanocrystalline CaF_2 [16]. In finite size, where the surface energy terms become an important part of the total free energy, these effects need to be considered. The surface energy appears to be the dominant factor in determining the stable states in finite sized systems. When the sample size is decreased to one certain value, the surface energy begins directing the enhancement of structural stability and BaF_2 nanocrystals are expected to exhibit special behaviors in phase transition pressures. It can be indicated that the grain size effect plays a significant role in the high–pressure behaviors of BaF_2 nanocrystals

4 Conclusion

We synthesized BaF_2 nanocrystals with an average size of 19 nm in a fluorite-type structure. The high-pressure behaviors of the nanocrystalline BaF_2 sample have been investigated by angle-dispersive synchrotron X-ray powder diffraction measurement up to 21.2 GPa at ambient temperature. Two phase transitions from fluorite-type to α-$PbCl_2$-type and Ni_2In-type phases of the BaF_2 nanocrystals occur at 5.8 and 14.4 GPa, which are higher than those in bulk BaF_2. The two high-pressure stable structures are confirmed by Rietveld refinements of the X-ray diffraction data. Upon decompression, the α-$PbCl_2$-type metastable phase is retained when the pressure is released. It suggests that the size effects are found to influence the BaF_2 nanocrystals' high-pressure behaviors and the surface energy plays a significant role in the structural stability.

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