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PHASE TRANSITIONS OF THE ALKALI-EARTH METAL FLUORIDES CaF_2 AND BaF_2 IN SHOCK WAVES*

Results are presented from a study of a compression wave front profile carried out by means of the manganin pressure sensor method, and also from X-ray structural and electron microscope investigations of specimens of CaF_2 and BaF_2 after they had been acted upon by shock waves of varying amplitude. It is shown that the alkali-earth metal fluorides CaF_2 and BaF_2 , under conditions of dynamic multistage compression, undergo phase transitions of the first kind from structures having coordination number 8 to a structure having coordination number 9, at comparatively low pressures. The orthorhombic lattice of the high pressure phase is isomorphic to the structure $\alpha\text{-PbCl}_2$ and has parameters $a = 3.56 \text{ \AA}$, $b = 5.94 \text{ \AA}$, and $c = 7.02 \text{ \AA}$ for CaF_2 , and $a = 4.03 \text{ \AA}$, $b = 6.72 \text{ \AA}$, and $c = 7.90 \text{ \AA}$ for BaF_2 . The density of the metastable phases is 9% greater than the density of the original substances.

INTRODUCTION

There are a number of reasons for the interest being shown in the study of possible phase reconstruction of crystal structures of compounds of the type AX_2 (A is a metal, X a metalloid). One reason is the broad potentiality (predicted by theory and repeatedly confirmed by experiment) for the formation of a continuous series of transitions of these compounds from structures having an anionic coordination number (c. n.) 4 of the type $\alpha\text{-SiO}_2$ to structures with c. n. = 9 of the type $\alpha\text{-PbCl}_2$ and possibly c. n. = 12 (MgCu_2). The determining factor for the occurrence of these transitions is the pressure: as a result of compression of matter and reduction of the cation-anion distances, crystal packing corresponding to structures having higher coordination numbers become energetically advantageous in accordance with the Goldschmidt law. This rule has been substantiated repeatedly both by experiments on static equipment [1-3] and by experiments with shock waves [4-7]. Under dynamic conditions, it has been possible in a number of studies to record the new phases directly, and by the use of radiographic methods to determine the parameters of their crystal lattices. In other cases, phase transitions were indicated by density jumps on the dynamic compression curves of substances or by a sharp change in the characteristics of the compression curves [5, 7]. Under dynamic conditions, the phase restructuring of the lattice is accompanied by disintegration of the shock wave front on several surfaces of discontinuity, registration of which is a good indication of the occurrence of this process.

In this study, an attempt has been made to obtain high-density phases of CaF_2 and BaF_2 , which initially have been crystallized in an extremely compact cubic structure having c. n. = 8.

EXPERIMENTAL RESULTS

The specimens for investigation were optically pure monocrystals of fluorides of calcium and barium. In all experiments, shock waves were introduced into the samples so that their direction coincided with the direction of the monocrystal [11]. In the first series of experiments, the shock wave profile was investigated using a manganin pressure sensor [7, 9-11]. Problems of measurement methodology were described in detail in [11]. Here we shall confine ourselves to presentation of the experimental layout (Fig. 1) and typical oscillograms of wave front recordings (Fig. 2a, 2b).

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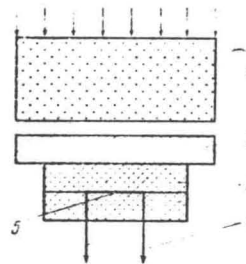


Fig. 1. Experimental arrangement for determining wave profiles in a sample by the manganin pressure sensor method:

- 1) charge BB; 2) aluminum or copper screen 10 mm thick; 3) investigated specimen of CaF_2 or BaF_2 ; 4) pressure sensor output; 5) manganin pressure sensor.

The fact of the registration of the multiwave structure of the shock wave undoubtedly demonstrates, especially for the CaF_2 specimens (Fig. 2a), the existence of phase transitions in these compounds. For BaF_2 this corroboration was not unambiguous, insofar as the first wave front therein (Fig. 2b) may be identified as an elastic compression wave. The possibility is not excluded that, under the conditions discussed, there occurs a phase transition of fluorides from the initial to a more compact structure.

In order to identify this structure, a series of X-ray structural analysis experiments were carried out on the specimens that were preserved after shock compression. The equipment described in [12], which provides for final pressure amplitudes of 120, 200, 350, and 500 kbar in the specimens, was used. In this apparatus, multiple shock compression (3-4 fundamental wave circulations) is achieved with the maximal pressure parameters cited. Here the total time the specimen is acted upon by the shock wave was ~5-7 sec, and the circulation time of shock waves in a specimen before the final pressure is established was ~0.5 μsec (the specimens used were all disks 16 mm in diameter and 1 mm thick).

The experiments were carried out for two different initial specimen temperatures: +20 and -150°C. In a number of other cases, porous samples of CaF_2 having

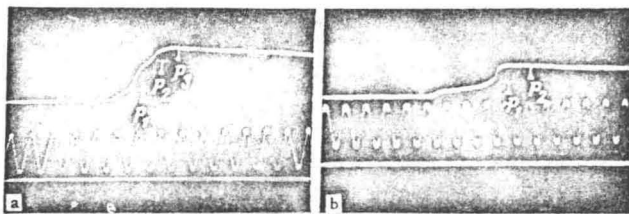


Fig. 2. Shock wave front profiles in CaF_2 and BaF_2 :

- a) CaF_2 : $P_1 = 64$ kbar, $P_2 = 200$ kbar, $P_3 = 280$ kbar;
 b) BaF_2 : $P_1 = 85$ kbar, $P_2 = 178$ kbar. The frequency of the sinusoidal scale mark is 5 MHz.

initial density $\rho_0 = 2.3 \text{ g/cm}^3$ were used to obtain a substantial increase in the temperature of the compressed specimens [13].

Structural analysis of the preserved specimens was carried out on a unit of the URS-55 type by two methods. In the first, monocrystal samples preserved after shock compression were subjected to X-ray diffraction analysis by the Laue method in an RKSO-2 chamber [14]. An X-ray tube with a molybdenum anode was used as the radiation source. The operating regime of the tube (voltage 45 kv, anode current 10 ma) made it possible to obtain a combined spectrum of bremsstrahlung and characteristic X-rays. Such a spectrum makes it possible to record on the diffraction patterns, along with the Laue reflections, reflections from the preserved monocrystal and the Debye rings from the polycrystalline phase during its formation in shock-compressed specimens. The appearance of Debye rings on the X-ray diffraction patterns of shock-compressed monocrystals is a result of the diffraction of the characteristic radiation either on the polycrystals of the initial phase formed as a result of the inverse transition of the high-pressure phase in rarefaction waves [14] or due to high residual temperatures, or directly on the polycrystals of the metastable high-pressure phase.

Figure 3 shows a typical X-ray diffraction pattern from this series of experiments, on which both kinds of reflection — highly altered as a result of asterism (stretched out radially), Laue spots, and Debye rings — are clearly visible. The latter were registered in all series of experiments with specimens of CaF_2 and BaF_2 except for fluorite, which is compressed at $t = +20^\circ\text{C}$ by shock waves with maximal pressures of 120 and 200 kbar, and in the majority of cases corresponded to reflections from the polycrystalline fractions of the original structure. Note also that asterism of the Laue spots was recorded in all experiments including those with maximal loads of 500 kbar. This is an indication of incomplete phase transition of the matter in the shock wave (part of it remains in the initial fluorite structure).

In addition to studies using the Laue method, specimens were subjected to X-ray diffraction in an RKD diffraction chamber of diameter 57.3 mm. The characteristic radiation of a copper anode ($\lambda K\alpha = 1.5405 \text{ \AA}$) was used as the radiation source. The specimens were prepared in the form of columns of diameter 0.5 and height 5 mm made out of crushed monocrystals preserved after explosive compression. Figure 4 shows diffraction patterns of the original CaF_2 specimen and the same specimen compressed under pressures of 200 kbar at an initial temperature of -150°C . Alongside the lines of the initial phase on the diffraction pattern of the compressed specimen, there is a series of lines that differ in phase from the original. Analogous X-ray diffraction patterns were also obtained for specimens of BaF_2 given the same conditions. At pressures of 120 kbar, the initial temperature is -150°C ; in both investigated fluorides, the lines of the new phase are

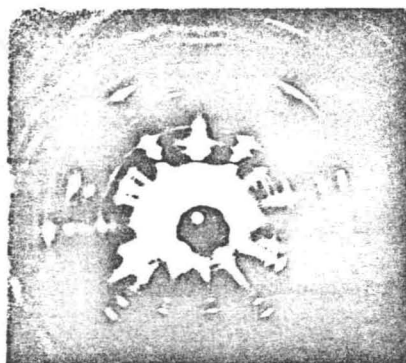


Fig. 3. Laue diffraction pattern of CaF_2 specimen after shock compression: $P = 200$ kbar, $t = -150^\circ\text{C}$.

also recorded, although their number and intensity were considerably lower.

In all other cases ($P > 200$ kbar, $t = -150^\circ\text{C}$; all pressures at specimen temperatures of $+20^\circ$, porous specimens of fluorides of Ca), practically no lines of the new phase were detected. This indicates that at an initial temperature of -150°C and pressure of 200 kbar, nearly optimal conditions are realized for preserving the metastable phase of fluorides of calcium and barium after removal of pressures. It is interesting to note that the number of lines of this phase and their intensity varied greatly in separate experiments carried out using a rigorously identical setup. Apparently the size of the crystallites of this phase is at the limit of sensitivity of X-ray structural analysis methods, $L \approx 10^{-4} \text{ cm}$. According to [15], the reflection of X-rays from the crystallite takes place when its dimensions exceed the wavelength of the radiation by a factor of 1000. To substantiate this hypothesis, some of the specimens (those which had exhibited the greatest contrast to one another) were subjected to analysis by a UEMB-100 electron microscope. The use of electron diffraction on a crystal lattice having a wavelength 10 times less than that of the characteristic radiation of copper made it possible in both cases to record on the electron-diffraction patterns new lines of identical number and intensity, in order to study the structure of specimens. These results enable us to evaluate the maximum dimensions of crystallites of the high pressure phase formed in shock waves: $L \sim 10^{-3} - 10^{-4} \text{ cm}$.

Our count of lines in the Debye powder diagrams and electron diffraction patterns containing lines of the new phase led us to identify it as an orthorhombic phase, isostructural to $\alpha\text{-PbCl}_2$ (spatial group Pmnb , coordination number 9), with lattice parameters close to those

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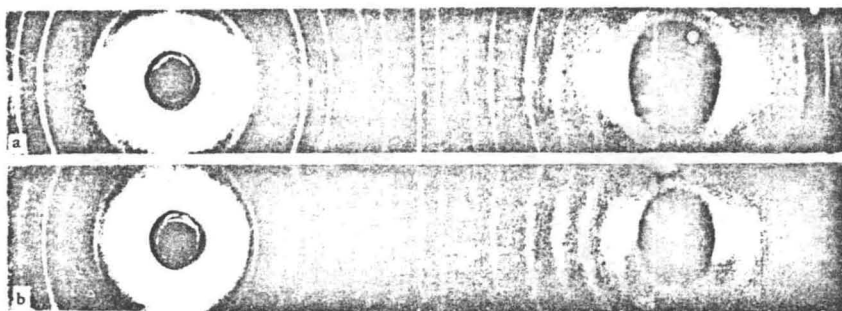


Fig. 4. Debye powder diagrams of CaF_2 before (a) and after (b) shock compression: $P = 200$ kbar, $t = -150^\circ\text{C}$.

	Paper [3]		This paper	
	CaF_2	BaF_2	CaF_2	BaF_2
a , [Å]	3.581	4.035	3.56	4.03
b , [Å]	5.959	6.705	5.94	6.72
c , [Å]	7.009	7.911	7.02	7.90
ρ , g/cm ³	3.465*	5.441	3.49	5.44
$\frac{\Delta V}{V} \cdot 100\%$	-9.1*	-9.8	-9.9	98

*Values of the crystal density ρ and the relative change in specific volume $\Delta V/V$ of the high pressure phase of CaF_2 in paper [3] are calculated from the lattice parameters shown in the same column.

given in [3]. These parameters, together with ρ , the density of the new phase, and $\Delta V/V$, the relative jump in specific volume, are shown in the table.

Note that the accuracy of determination of the lattice parameters of the high pressure phase synthesized in the described experiments was 0.02 Å. Such a relatively large error is due to the great broadening of the lines of the new phase, especially in the region of large angles 2θ . This broadening is apparently due to strong internal stresses in the specimen, and also the small size of the crystallites of the new phase.

DISCUSSION OF EXPERIMENTAL RESULTS

The results obtained show with certainty that fluorides of the alkali-earth metals CaF_2 and BaF_2 , under conditions of dynamic multistage compression, undergo phase transitions of the first kind from a structure having coordination number 8 to a structure having coordination number 9, at comparatively low pressures. These results show that during dynamic loading of specimens, the same dense fluoride phases are formed, under certain conditions, as in the static case. The new phases are metastable under normal conditions, and their recrystallization temperature is near-normal. The following facts bear this out.

1. The absence of high pressure phases in experiments where the initial temperatures are $+20^\circ\text{C}$ and specimens are porous, and also when they are precooled at pressures greater than >300 kbar. The reason for this is the high residual temperature of the specimens. Apparently this is why the orthorhombic phase of CaF_2 and BaF_2 was not detected in [16].

2. Prolonged holding of specimens of the new phase at room temperature (~ 30 days) or roasting specimens for 15 min at $t = 200^\circ\text{C}$ lead to the reverse transition from the $\alpha\text{-PbCl}_2$ structure to the original structure.

From the correlation of intensities of the lines of the fluorite and orthorhombic phases it follows that the number of the latter in specimens tested under optimal conditions ($P = 20$ kbar, $t = -150^\circ\text{C}$) does not exceed

50% of lines of the initial phase. Because the new phase is obtained under approximately the same conditions in both substances investigated, it may be assumed that other fluorides of alkali-earth metals also possess similar properties.

Analyzing the conditions of the appearance of orthorhombic phases in this study, we note also the following situation. In [5], where there was a dynamic adiabatic curve for fluorite at 1 Mbar pressure, an extremely sharp drop in its compressibility was recorded. Extrapolation of the little-compressed branch of the adiabatic curve toward zero pressures corresponded to the density of the metastable phase, which exceeds that of the initial phase by a factor of 1.73. Clearly the nature of the overdense phase from [5] is not in any way related to the orthorhombic phase obtained in the present study, which apparently is only an intermediate stage on the way to the appearance of still denser packings with a possible limiting value of 12 for the coordination number. Unfortunately this last link in the chain of transitions of compounds of the type AX_2 has not yet been confirmed directly by experiment, although there are indirectly related facts that are difficult to explain on any other basis [5]. From this point of view the results of this study, which provide a confirmation for the idea of the appearance, under the influence of pressure, of a continuous series of more and more dense packings in AX_2 compounds, and which also indicate the relative ease of the transition from dense cubic packing with coordination number 8 to a lattice having coordination number 9, are also an indirect indication of the possibility of the existence of further structural modifications.

MAIN RESULTS

This article has presented the conditions and results of experiments in the explosive synthesis of a high-density phase of fluorides of calcium and barium, which is an orthorhombic modification of the type $\alpha\text{-PbCl}_2$ having coordination number 9 and belonging to the spatial group Pmnb . The parameters of the lattice of the new phase have been determined: $a = 3.56$ Å, $b = 5.94$ Å, and $c = 7.02$ Å for CaF_2 , and $a = 4.03$ Å, $b = 6.72$ Å, and $c = 7.90$ Å for BaF_2 , and the upper limits of the dimensions of its crystallites have been evaluated. It has been shown that complete transition of the fluorite phase to the orthorhombic phase does not take place in dynamic experiments.

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