



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 \AA . 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: $a = 3.56 \text{ \AA}$, $b = 5.94 \text{ \AA}$, 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 , 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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