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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 α-$PbCl_2$ and has parameters 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. 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 α-SiO_2 to structures with c. n. = 9 of the type α-$PbCl_2$ 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).

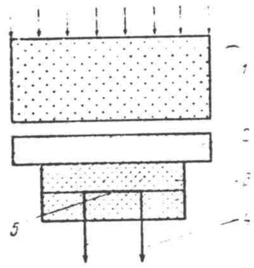

Fig. 1. Experimental arrangement for determining wave profiles in a sample by the manganin pressure sensor method:

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

*Izv., Earth Physics, No. 8, 1975, pp. 12-16, translated by John D. McIntosh.