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A Structure Refinement of the High Pressure Modification BaI_2-II

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A high pressure phase BaI_2-II, which can be quenched and retained as a metastable form at ambient conditions, is reported. The structure has been determined by X-ray investigations using single crystals. BaI_2-II crystallizes in an anti-Fe_2P-type arrangement, space group $P\bar{6}2m$, a = 9.142(6) Å, c = 5.173(3) Å, which is slightly denser than the $PbCl_2$-type structure found at normal pressure. Structural features of the two phases are discussed in comparison.

Introduction

General principles, governing phase transitions under pressure, have often been formulated. The high pressure chemistry of the halides of alkaline earths and of divalent rare earths furnishes another good example illustrating the validity of such rules. Most of the transitions observed in this field of AB_2 compounds can be interpreted in purely geometric terms by discussing ion compression, radius ratios, and increase in coordination and packing efficiency (*1*). In all cases where such geometric effects are believed to dominate, the $PbCl_2$-type arrangement seems to be the last link in the chain of transitions in the pressure ranges so far investigated. However, in some compounds these parameters are overruled by electronic effects, and the high pressure phase has a distorted $PbCl_2$-type structure (e.g., SrI_2-II (*2*)), or a structure which is normally encountered in intermetallics (e.g., NdI_2-II (*3*)), or in compounds with mainly covalent interactions. The high pressure transition of BaI_2 is another example of such changes in bonding type under pressure.

Previous Work

Earlier investigations on BaI_2 have proved the existence of a new high pressure phase (BaI_2-II) which can be quenched and retained as a metastable form at ambient conditions. However, the $PbCl_2$-type structure is easily restored by tempering at temperatures above 470 K (*4*). Estimates of the thermodynamic data of the transition ($\Delta H_{575\,\mathrm{K}}$ = 3.1 kJ/mole, ΔS = 5.5 J/mole × K, $\Delta V_{295\,\mathrm{K}}$ = 0.58 cm^3/mole) taken from the p,T diagram indicate that the phase transition must be of a reconstructive type. X-ray powder diagrams could be indexed on the basis of a primitive hexagonal cell (a = 9.147(6) Å, c = 5.173(3) Å, refined from Guinier powder data). The intensities agree well with those calculated for an anti-Fe_2P-type arrangement, which was therefore accepted as a model structure. However, a detailed comparison of this arrangement with the $PbCl_2$-type structure found at am-

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bient pressure is only possible on the basis of accurate positional parameters.

BaI_2-II is presumably not the first example for a more ionic antitype structure. Haase and Brauer have claimed that an isotypic phase $BaCl_2$(hex.) is formed during the thermal decomposition of $BaCl_2 \cdot 2H_2O$ in the temperature range between 310 and 540 K (*5*). Surprisingly, we have not been able to prepare this modification starting from anhydrous $BaCl_2$ in the pressure range up to 3.0 GPa with temperatures varying between 440 and 770 K. (Similarly, our experiments with $BaBr_2$ at 3.0 to 4.0 GPa and 770–870 K gave no quenchable high pressure phase.) We therefore assume that the formation of anti-Fe_2P-type $BaCl_2$ is kinetically controlled in a topotactic reaction and/or probably enhanced by partial substitution of chloride ions by OH^- on the smaller anion site.

The same seems to be true for BaI_2 itself. Our high temperature Guinier investigations tracing the thermal decomposition of the hydrate under vacuum have shown anti-Fe_2P-type diagrams in a small temperature range overlapping with those of a hydrate and of the anhydrous phase.

Experimental

Details of all our high pressure experiments on BaI_2 have been published elsewhere (*4*). BaI_2 was prepared by thermal decomposition of the hydrate in a dynamic vacuum with temperatures increasing very slowly to 673 K. All subsequent handling of the hygroscopic product proceeded under argon atmosphere. Guinier photographs showed $PbCl_2$-type BaI_2 to be the only phase present. Single crystals of the high pressure phase were grown in a belt-type apparatus at 3.0 GPa in boron nitride containers. Initially, the temperature was raised to 1273 K for $\frac{1}{2}$ hr to enhance crystallization and then slowly reduced to 874 K where it was kept for 72 hr. The pressure was then released after quenching the specimen to ambient temperatures. The white transparent product was inspected for single crystals and a platelike specimen 0.05 mm thick with polygonial outlines and about 0.07 mm in diameter was chosen and sealed under argon in a glass capillary. The spacegroup $P\bar{6}2m$ was inferred from Weissenberg films showing hexagonal symmetry and no systematic extinctions. Intensities were collected in ω-scan mode on a Phillips PW 1100 four circle diffractometer using Ag$K\alpha$ radiation (graphite monochromator). To ensure a good absorption correction, the crystal was carefully measured and data were taken in the hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, and $h\bar{k}\bar{l}$ sections of reciprocal space in the range $3° \leqq \Theta \leqq 20°$. The intensities of three standard reflections were measured at fixed intervals throughout the data collection. The time used for background measurements at the beginning and end of the scan was half the time used for the scan itself. Each reflection was corrected for background and for Lorentz and polarization effects. The absorption correction ($\mu = 106.5$ cm^{-1}) and later least squares refinements were computed using the program SHELX76 (*6*) (scattering factors were taken from (*7*)). Data reduction gave 299 unique reflections with an internal consistency of $R_{\text{int}} = 4.5\%$ based on the merging of equivalent reflections. The positional parameters of Fe_2P were used as a model for least squares refinements which converged within a few cycles to $R = 2.7\%$ ($R = \Sigma||F_o| - F_c||/\Sigma|F_o|$) using unit weights for all reflections and anisotropic thermal parameters.

Results and Discussion

The positional parameters for BaI_2-II are given in Table I, together with the anisotropic thermal parameters which merit attention, because they offer an insight into

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR BaI_2-II

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	B
Ba(1)	1b	0	0	$\frac{1}{2}$	0.0263(7)	U_{11}	0.0153(10)	$U_{11}/2$	1.78
Ba(2)	2c	$\frac{1}{3}$	$\frac{2}{3}$	0	0.0211(5)	U_{11}	0.0353(9)	$U_{11}/2$	2.04
I(1)	3f	0.2563(2)	0	0	0.0171(5)	0.0215(7)	0.0291(8)	$U_{22}/2$	1.74
I(2)	3g	0.5918(2)	0	$\frac{1}{2}$	0.0242(6)	0.0390(9)	0.0287(8)	$U_{22}/2$	2.29

Note. Thermal parameters are given in Å². B equivalent isotropic factor (Hamilton (*11*)).

special features of the structural geometry (Fig. 1). In a tricapped trigonal prismatic coordination (Fig. 2a), Ba(1) has six apical iodine neighbors at 3.491(1) Å and three in the equatorial position at a longer distance (3.734(2) Å), giving an average distance of 3.573 Å. In a similar geometry (Fig. 2b), however, Ba(2) has the six apical anions farther away (3.791(1) Å) and three closer equatorial contacts (3.456(1) Å) (average cation–anion distance 3.679 Å). The trigonal prism around Ba(1) is more contracted in the a,b plane. This explains the differences in the thermal anisotropy of Ba(1) ($U_{11} \geqq U_{33}$) and Ba(2) ($U_{11} \leqq U_{33}$). The smaller void in the Ba(1) position favors an ordered substitution by atoms of different size. Ordering is encountered in isotypic intermetallics (e.g., GdAuIn) and also in compounds related to β-K_2ThF_6 (*8*). Our high pressure experiments with SrI_2/BaI_2 mixtures have shown that Sr can substitute Ba up to 40 mole% in this high pressure phase.

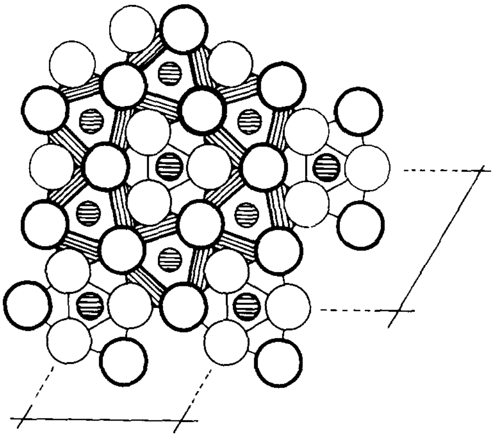

FIG. 1. The structure of BaI_2-II as viewed along [001]. Small circles indicate Ba, larger circles I; atoms in $z = 0$ are graphed with light lines, those in $z = \frac{1}{2}$ in bold lines.

I(1) has two Ba(1) and two Ba(2) as closest neighbors in a tetrahedral arrangement (Fig. 2c). I(2) is surrounded by five cations (four Ba(2) and one Ba(1)) in a pyramidal configuration (Fig. 2d). The mean cation–anion distances are 3.47 Å and 3.77 Å, respectively, and we expect that I(1) can be substituted by smaller anions (cf. the arguments given for the existence of $BaCl_2$(hex) in the section entitled Previous Work).

In the $PbCl_2$-type structure found at ambient pressures we have virtually the same coordination polyhedra, except that they are less symmetric. This is equivalent with a slight increase in effective coordination numbers in the high pressure modification, in accordance with the pressure-coordination rule. The secondary coordination, however, is completely different. In BaI_2-II the coordination polyhedra of the same kind share faces in a columnar arrangement along [001]. Additional face sharing connects the columns formed by the polyhedra around Ba(2) to a honeycomblike structure leaving channels into which the Ba(1) ions are inserted. Ba(1) and Ba(2) are displaced

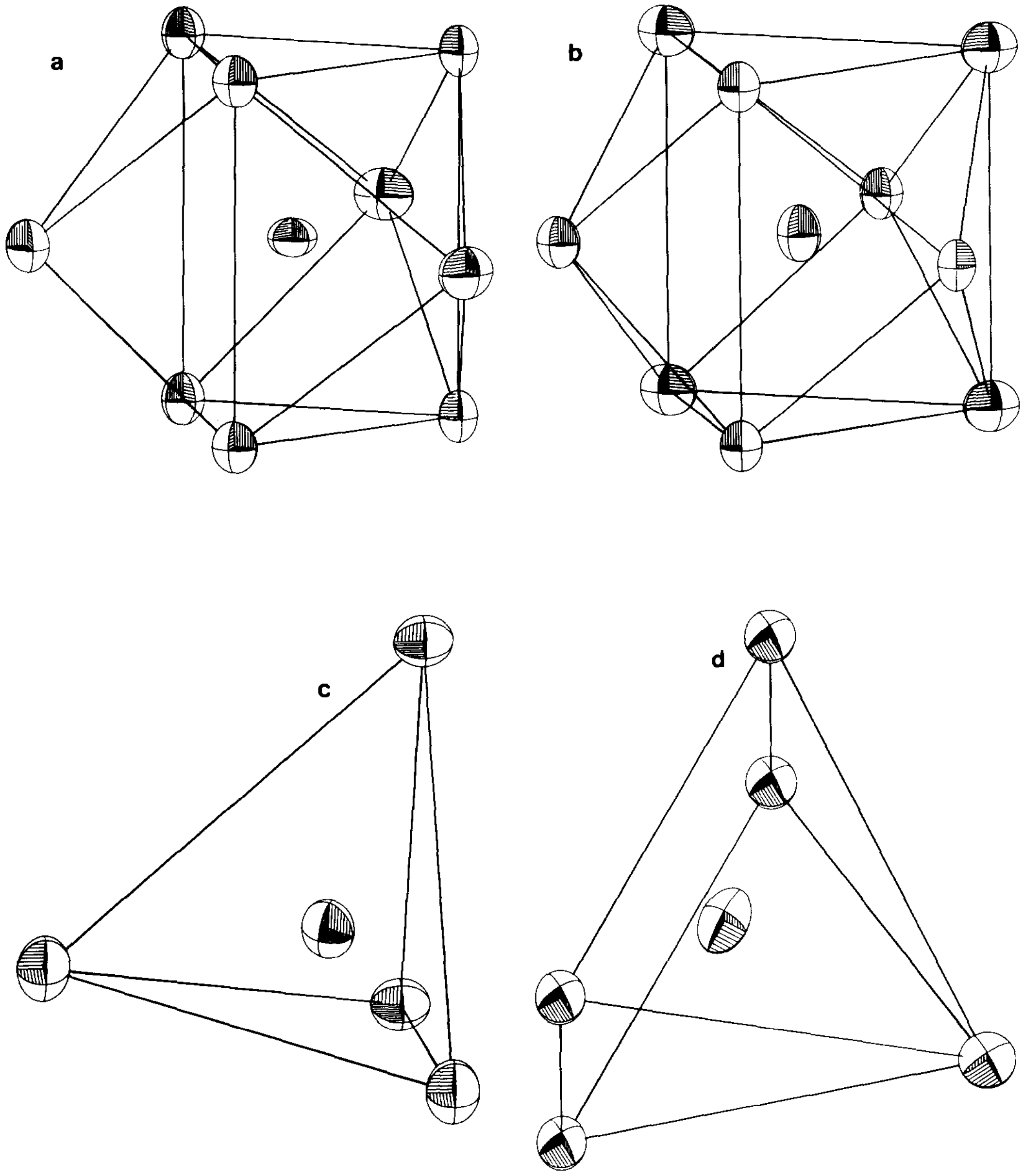

FIG. 2. Coordination polyhedron around (a) Ba(1), (b) Ba(2), (c) I(1), and (d) I(2); *c* axis vertical, ORTEP II plot (*10*).

by $c/2$; the anions apical to Ba(1) are therefore equatorial to Ba(2) and vice versa.[1]

This high pressure transition shows some unusual features. The reconstructive transformation seems to offer little advantage when looking at the packing efficiency, which is only 0.8% better in BaI_2-II. Moreover, though effective coordination numbers increase slightly, the mean cation–anion distance decreases to 3.626 Å compared with 3.663 Å in the $PbCl_2$-type structure, and this is certainly not in line with the pressure–distance paradox (*9*) which usually holds for such transformations. Arguments, which may be offered as an explanation, are contradictory. Since the two modifications have not been investigated at equilibrium pressures and temperatures, these findings may reflect a marked difference in compressibility and thermal expansion of the two phases. At the conditions for the transition, the distances in the $PbCl_2$-type phase might have decreased well below those in the anti-Fe_2P-type phase. But this would also mean that the packing efficiency in the former structure is better under such conditions. Our high pressure experiments with divalent halides have shown that most of the observed transitions can be interpreted on a purely geometric reasoning in comparing packing efficiency, coordination numbers, and radius ratios. The high pressure polymorphism of iodides, however, seems different. Typical coordination structures where ionic interactions play a major role are changed into structural arrangements which are usually only encountered in compounds where covalent or even metallic bonding prevails. Perhaps the structural geometry of BaI_2-II—so far unusual for salt-like compounds—is an indicative for such changes in the nature of bonding type under high pressure conditions.

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[1] The structure has only two free positional parameters. A decrease in $x_{I(1)}$ reduces the cross section of the trigonal prism around Ba(1), whereas a variation in $x_{I(2)}$ will mainly rotate the columns of the I(2) polyhedra around the Ba(2) ions. With this in mind, it becomes evident that these parameters can vary only slightly in the chemically so different compounds crystallizing with this (or the antitype) arrangement. They could be determined fairly well by purely geometric calculations maximizing anion–anion distances.

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