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## High-pressure phase transformation in cotunnite-type $\text{BaCl}_2$

J M Leger and A Atouf

CNRS, Laboratoire de Physico-Chimie des Matériaux, 1 Place A Briand, 92195 Meudon Cédex, France

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**Abstract.** A pressure-induced phase transformation in cotunnite-type structure compound has been observed for the first time *in situ*. Actually  $\text{BaCl}_2$  undergoes a reversible phase change at room temperature, which occurs at 21 GPa when increasing pressure and 15 GPa when decreasing. The high-pressure phase was indexed in a hexagonal cell. The volume change at the transition is 5% but the relative volume of the high-pressure phase in normal conditions is only 0.819. This could indicate a higher coordination number for the barium cation, still unknown in  $\text{AX}_2$  compounds. The behaviour of the low-pressure cotunnite phase appears anomalous as the bulk modulus is much higher than expected from bulk modulus-volume systematics.

### 1. Introduction

The  $\text{AX}_2$  compounds display a large number of crystal structures which can be distributed over four main groups: the quartz group with the tridymite, cristobalite,  $\alpha$  or  $\beta$  quartz and coesite structures; the rutile group; the fluorite group with the tetragonal or cubic fluorite and columbite structures; and, finally, the cotunnite structure. Numerous layered structures also exist; they can be related to one of the above groups. The coordination number increases from four in the quartz structure, to six in the rutile, eight in the fluorite and nine in the cotunnite structure, the latter being the highest coordination number found in the  $\text{AX}_2$  compounds.

Under pressure numerous phase transformations occur in these  $\text{AX}_2$  compounds [1]. The coordination number often increases with increasing pressure, although the exact transformation may vary with compound. For example, the increase of the silicon coordination number in  $\text{SiO}_2$  from four to six is well known when going from coesite to stishovite; in the same way the coordination number increases from six to eight when  $\text{PbO}_2$  transforms from rutile to fluorite structure.

Under high pressure, dioxides have been studied principally [2], and very few experiments have been devoted to halides. Only one investigation of a compound with cotunnite structure has been reported [3] by quenching experiments from moderate high pressures and temperatures, and the existence *in situ* of denser structures has not been considered.

The effect of pressure is generally to favour structures that are found at normal pressure with larger cations. Starting with the largest cation in the highest coordination number should lead to structures still unknown for the  $\text{AX}_2$  compounds under high pressure. In these compounds, the  $\text{BaX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) halides fulfil these conditions as they belong to the cotunnite structure.

At normal pressure  $\text{BaCl}_2$  exists only in the cotunnite structure ( $Pnam$ ), orthorhombic  $\text{PbCl}_2$  type. The cell parameters at normal pressure are  $a_0 = 7.872 \text{ \AA}$ ,  $b_0 = 9.425 \text{ \AA}$ ,  $c_0 = 4.732 \text{ \AA}$ , and there are four chemical formulae per molecule  $Z = 4$ . The cation has nine anion neighbours, six of which form a trigonal prism and three of which are located outside the trigonal faces coplanar with the cations. These prisms are stacked into rows of unlimited height along the  $c$  axis and they are connected by one edge to form arrays which alternate along the  $b$  axis, with identical rows shifted along  $c$  by half this cell parameter.

In this paper, we report the pressure–volume behaviour of cotunnite  $\text{BaCl}_2$  to 52 GPa at room temperature as observed by powder x-ray diffraction *in situ*.

## 2. Experimental procedure

The powder x-ray diffraction experiments under pressure were performed in a diamond anvil cell. The anvil flats were  $500 \mu\text{m}$  and the sample filled the cavity  $150 \mu\text{m}$  in diameter drilled in a T301 gasket (thickness  $250 \mu\text{m}$ ) which was preindented to  $100 \mu\text{m}$ . No liquid pressure-transmitting medium such as the usual 4:1 methanol–ethanol mixture could be used as the sample was very hygroscopic and, no solid pressure-transmitting medium was added as the bulk modulus of  $\text{BaCl}_2$  was expected to be rather low. Powdered silver metal acting as a pressure marker was mixed with the sample. Powder x-ray diffraction experiments were performed using the angular dispersive method ( $2\theta_{\text{max}} = 40^\circ$ ) with the zirconium-filtered radiation from a molybdenum fine-focus tube. The sample-to-film distance was  $24.73 \text{ mm}$  and the exposures lasted for about 24 h. The diameters of the Debye rings were read with a low-magnification microscope. The pressure was determined from the lattice parameter of silver calculated from the (220) and (311) lines, and using the Birch equation of state with  $B_0 = 106.1 \text{ GPa}$  and  $B'_0 = 4.7$  [4]. The uncertainties are estimated to be  $\pm 0.08 \%$  in volume and  $\pm 0.7 \text{ GPa}$  in pressure.

## 3. Results

Below 21 GPa, the seven strongest diffraction lines from the orthorhombic normal-pressure cotunnite phase were observed (see figure 1). Above 21 GPa, the strongest line (211) disappeared together with the (120), (121) and (322) lines, while two other lines appeared. This clearly indicated a phase transition. When decreasing pressure, the lines of the new phase remained visible down to 15 GPa where the lines of the low-pressure phase began to reappear. The large-pressure hysteresis showed that the transition is of first-order. It seems that the volume change at the transition might be large as shown by the broadening of the diffraction lines, which indicates that the crystallites are then broken.

An experimental run was performed without any pressure marker in order to reduce the accidental overlap of the diffraction lines from the high-pressure phase with those from silver and to determine the lattice cell in the best conditions. In this experiment the pressure was directly increased to a pressure well in excess of the transition pressure (later calculations indicated a pressure of 52 GPa). In these conditions seven diffraction lines of the high-pressure phase were observed and an additional one became visible when decreasing pressure. Two diffraction patterns of the high-pressure phase are indicated in table 1.

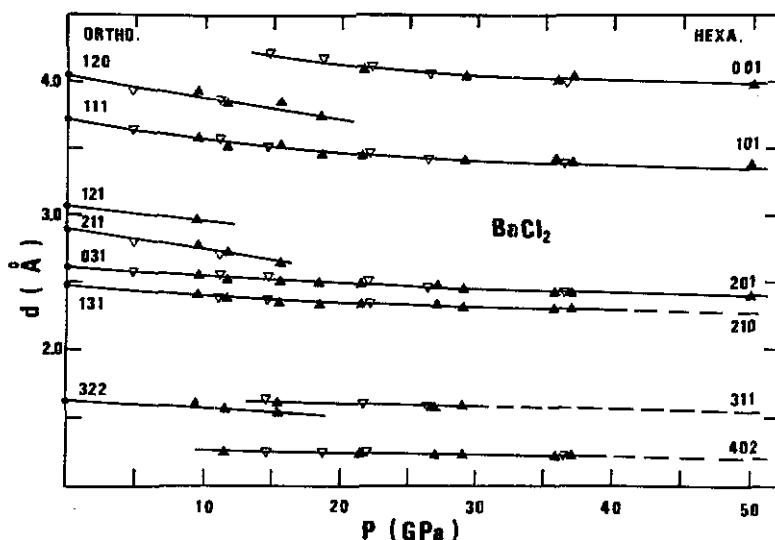


Figure 1. Interplanar distances of  $BaCl_2$  as a function of pressure. ▲: increasing pressure; ▽: decreasing pressure; ●: values at normal pressure.

Table 1. X-ray powder diffraction patterns of the high-pressure phase of  $BaCl_2$ . vw: very weak; w: weak; m: medium; s: strong.

$P = 52 \text{ GPa}$			$P = 30 \text{ GPa}$		
$a = 6.942 \text{ \AA}$			$a = 7.083 \text{ \AA}$		
$c = 3.956 \text{ \AA}$			$c = 4.058 \text{ \AA}$		
$d_{\text{obs}}$ ( $\text{\AA}$ )	$d_{\text{calc}}$ ( $\text{\AA}$ )	$hkl$	$d_{\text{obs}}$ ( $\text{\AA}$ )	$d_{\text{calc}}$ ( $\text{\AA}$ )	$I_{\text{obs}}$
3.972	3.956	001	4.024	4.058	w
—	—	110	3.555	3.541	vw
3.320	3.305	101	3.340	3.384	w
2.405	2.393	201	2.428	2.447	s
2.265	2.272	210	2.298	2.318	m
1.548	1.537	311	1.569	1.569	m
1.384	1.379	320	1.412	1.407	w
1.186	1.197	402	1.230	1.224	w

The best indexation in the tetragonal, hexagonal or orthorhombic systems was obtained for a hexagonal cell. Only one solution was then allowed:  $a = 7.088 \text{ \AA}$  and  $c = 4.080 \text{ \AA}$  at a pressure of about 30 GPa. Assuming that the number of formulae per lattice cell was three, then the volume jump at the transition is 5%.

The variations of the cell parameters in both phases are shown in figure 2. The main compression of the cotunnite orthorhombic structure is along the  $a$  axis which shows an anomalous pressure dependence while the  $b$  and  $c$  axes are nearly three times less compressible than the  $a$  axis.

The variations of the relative volume are shown in figure 3. The Birch equation of state was fitted to the data in both phases:

$$P = \frac{3}{2} B_0 x (1 + x)^{5/2} (1 + \alpha x) \quad \text{where } x = (V/V_0)^{-2/3} - 1, \alpha = \frac{3}{4} (B'_0 - 4)$$

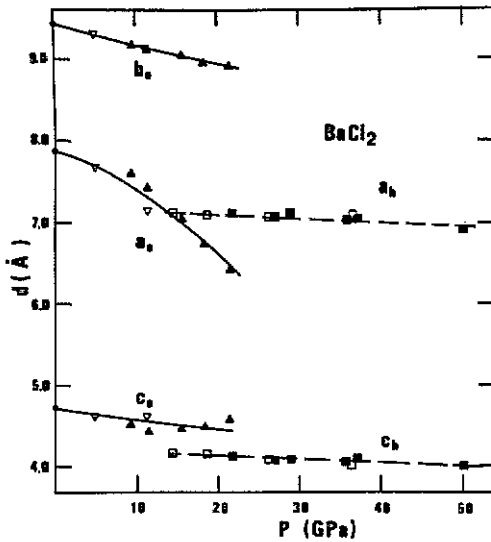


Figure 2. Cell parameters of  $\text{BaCl}_2$  as a function of pressure. The low-pressure phase is of the cotunnite structure (orthorhombic,  $Pnam$ ,  $\text{PbCl}_2$ -type); the high-pressure phase was indexed in a hexagonal cell with  $Z = 3$ . Filled symbols: increasing pressure; open symbols: decreasing pressure; triangles: orthorhombic cell; squares: hexagonal cell.

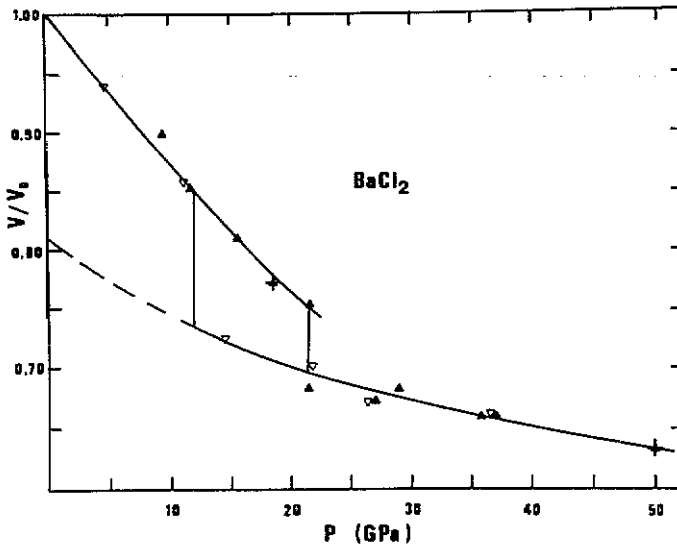


Figure 3. Relative volume of  $\text{BaCl}_2$  as a function of pressure.  $\blacktriangle$ : increasing pressure;  $\nabla$ : decreasing pressure; + indicate standard deviations. The low-pressure phase is of the cotunnite structure (orthorhombic,  $Pnam$ ,  $\text{PbCl}_2$ -type); the high pressure phase was indexed by a hexagonal cell with  $Z = 3$ .

$B$  is the bulk modulus and  $B'$  its first pressure derivative. The subscript zero refers to values at normal pressure. In both phases the bulk modulus and its first pressure derivative were determined from a least-squares fit. The initial relative volume of the high-pressure phase was calculated in the same way. The following results were

obtained:

- (i) Low-pressure phase (orthorhombic cotunnite structure):  $B_0 = 69.8 \pm 0.5$  GPa,  $B'_0 = 1.40 \pm 0.05$
- (ii) High-pressure phase (hexagonal):  $B_0 = 69.3 \pm 2$  GPa,  $B'_0 = 8.6 \pm 0.1$ ,  $(V_{\text{hex}}/V_{\text{ortho}})_{P=0} = 0.819 \pm 0.01$ .

The value for the relative volume of the high-pressure phase at normal pressure is in excellent agreement with the value determined from a direct extrapolation of the cell parameters.

The behaviour of  $BaCl_2$  under pressure shows very peculiar characteristics. Firstly, the bulk modulus of the low-pressure phase is much larger than the values deduced from the bulk modulus–volume systematics [5] or from the polyhedral bulk modulus as a function of the cation–anion distance [6] (see below). Furthermore, the pressure derivative of the bulk modulus is lower than the values generally expected which are in the range of 4 to 7. This enhanced bulk modulus together with a lowered pressure derivative could be an indication of the presence of anisotropic stress components which give rise to lower volume variations [7] and actually yield an apparent higher bulk modulus and lower pressure derivative. This is noticeable when powder x-ray diffraction experiments under pressure are performed in diamond anvil cells without a gasket. These effects have been pointed out in some compounds [8]. In the present experiments a gasketed configuration was used with no pressure-transmitting medium, as the sample is very hygroscopic. However, even in a solid environment such a gasketed configuration strongly reduces the anisotropic stress components and only minor variations of the bulk modulus are then observed [8]. In addition, no effect of such stresses could be detected on the silver marker mixed with the sample in the present experiments: in cubic lattices, their presence is indicated by an  $hkl$  dependence of the lattice parameter [7] which was not observed here. Another way of checking the possible existence of anisotropic stress components is to use the Vinet equation of state [9]:

$$P = 3B_0(1 - y)/y^2 \exp \delta(1 - y)$$

where

$$y = (V/V_0)^{1/3}$$

and

$$\delta = \frac{3}{2}(B'_0 - 1).$$

The meanings of the pressure derivatives deduced from the different equations of state are not exactly the same and the values cannot easily be compared. This last equation yields a linear function when it is written in a logarithmic form:  $\ln Py^2/3(1 - y) = \ln B_0 + \delta(1 - y)$  and this makes the analysis of the data easier. The correlation coefficient of the higher pressure data is better than 0.90 and indeed, the two lower pressure data could be slightly in error, especially the point at 9.4 GPa which should be at 7.7 GPa. However, the results at low pressure are very sensitive to any volume error ( $y \simeq 0$ ). A lower volume variation such as this could be an indication of the presence of some anisotropic components in this pressure range. Nonetheless, the bulk modulus deduced from the higher pressure experimental data ( $P > 14$  GPa) only is 71.8 GPa and is in excellent agreement with the previous one: 69.8 GPa. This confirms the high value of the bulk modulus.

#### 4. Discussion

It is the first time that a phase transition of the cotunnite structure is observed *in situ* under the effect of pressure. This phase transformation takes place at room temperature and is reversible when pressure decreases. This means that it cannot be observed from quenching experiments under high pressure.

The hexagonal cell with  $Z = 3$  that we propose for the high-pressure phase indicates that the volume change at the transition is 5%, a typical value for first-order transitions.

The structure of the high-pressure phase does not correspond to any previously known structure. However, a hexagonal phase with the same number of formulae by unit cell as we found under high-pressure has been reported [10] at normal pressure for  $\text{BaCl}_2$ . This was observed during the dehydrating process of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; the following compounds appeared with increasing temperature:  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{BaCl}_2 \cdot 1\text{H}_2\text{O}$ ;  $\text{BaCl}_2(\text{cubT}) + \text{BaCl}_2(\text{hex})$ ;  $\text{BaCl}_2(\text{ortho})$ ;  $\text{BaCl}_2(\text{cubH})$ . The hexagonal phase of anti- $\text{Fe}_2\text{P}$  type, was always mixed with the cubic low-temperature form (cub T) and appeared or disappeared at the same time. The volume difference between the orthorhombic  $\text{PbCl}_2$ -type and the hexagonal anti- $\text{Fe}_2\text{P}$  phases is very small, of the order of 1%, the former being denser. It appears that hexagonal phases with parameters in agreement with this anti- $\text{Fe}_2\text{P}$  structure have already been reported in some  $\text{AX}_2$  compounds such as  $\text{US}_2$  or  $\text{USe}_2$  [11] also of cotunnite structure in normal conditions. The high-pressure phase of  $\text{BaCl}_2$  we observed at room temperature cannot be this anti- $\text{Fe}_2\text{P}$  phase: neither the lattice parameters nor the relative intensities of the diffracted lines are in agreement with such a structure. In the anti- $\text{Fe}_2\text{P}$  structure, the cell parameters are  $a = 8.103 \text{ \AA}$  and  $c = 4.651 \text{ \AA}$  and the strongest lines are (111), (110), (101) and (211). In normal conditions, the cell parameters of the high-pressure hexagonal phase would be markedly smaller:  $a = 7.50 \text{ \AA}$  and  $c = 4.50 \text{ \AA}$ ; in addition the strongest lines are not ones mentioned above but are (201), (210) and (311).

A hexagonal anti- $\text{Fe}_2\text{P}$  structure was also observed at normal pressure in  $\text{BaI}_2$  after thermal quenching under pressures of 1–3.5 GPa between 200 and 550 °C [3]. This hexagonal phase is slightly denser than the cotunnite phase, in contrast to the results concerning  $\text{BaCl}_2$  at normal pressure.

Among the  $\text{AX}_2$  compounds, only dioxides have been thoroughly studied but no oxide with the cotunnite structure exists at ambient pressure. Phase transformations of dioxides in the fluorite structure, which is about 7% less dense than the cotunnite structure at normal pressure, have been observed under pressure.  $\text{UO}_2$  was examined by x-ray diffraction under high pressure and was found to transform into an orthorhombic structure, most probably of the cotunnite type as the cell parameters are in agreement with such a structure [12].  $\text{CeO}_2$  undergoes a phase change at 31 GPa; the high-pressure phase observed by Raman spectroscopy is in agreement with a cotunnite structure [13]. In  $\text{TbO}_{1.75}$ , a transformation to an enlarged cotunnite-type cell was proposed [2]. In  $\text{PrO}_{1.83-1.95}$  and  $\text{ThO}_2$  a transformation to an orthorhombic phase with  $Z = 4$  was observed [2]; the structure was proposed to be related to the  $\text{Ni}_2\text{Si}$ -type structure and was described as a post-cotunnite phase. The terbium, praeodymium and thorium dioxides were only examined at normal pressure after pressurization to 10–30 GPa, heating with a laser to 600–800 °C and quenching. It seems difficult to draw definite conclusions from these quenching experiments under high pressure as it is impossible to assess that no phase transformation occurred at

room temperature during the release of pressure. Our results definitely show that phase transformation in the cotunnite structure does happen at room temperature and is reversible.

The structure of the high-pressure phase of  $BaCl_2$  remains to be exactly established. In the dioxides, the previously proposed  $Ni_2Si$ -type structure does not appear to be likely, as it is simply the anti-type of the cotunnite  $PbCl_2$  structure [14], and no increase of the coordination number takes place. In the case of  $BaCl_2$ , the observed diffraction lines are not in agreement with an orthorhombic lattice, but with a hexagonal one, and the structure is then different from the anti- $Fe_2P$  structure. No hexagonal structure with three formulae by unit cell and a coordination number higher than nine is known in the  $AX_2$  compounds. Among the  $AB_2$  alloys, a hexagonal cell with three molecules is known to exist for  $Ni_2P$  and  $Cr_2Si$ , in addition to  $Fe_2P$ , but no agreement with the line intensities has been obtained.

The normal-pressure relative volume of the high-pressure phase, 0.819, is surprisingly small, although in excellent agreement with the direct extrapolations of the lattice parameters of the hexagonal cell. Such a large volume difference would imply a definitely higher coordination of the barium atom, at least 10 but more likely 11 or 12, which is still unknown in the  $AX_2$  compounds.

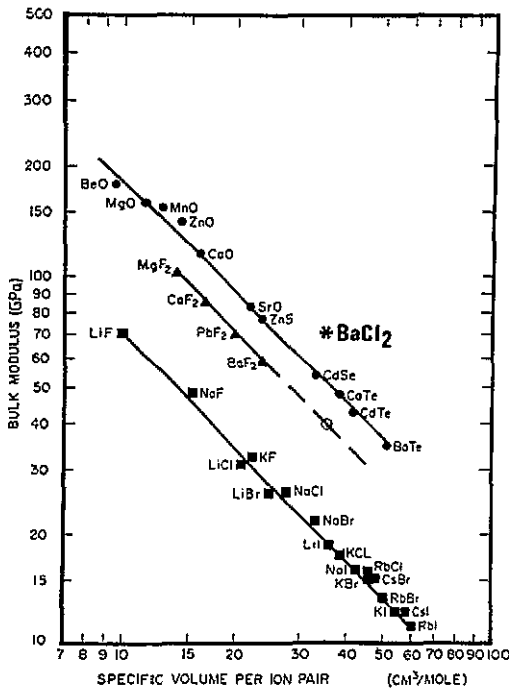


Figure 4. Bulk modulus of diatomic ionic compounds as a function of the specific volume. Data from [5]; O: expected value for  $BaCl_2$ ; \*: experimental value.

Anderson [5] pointed out that:  $B_0 V_0 / S^2 Z_a Z_c = \text{constant}$ . From published data, this constant is equal to  $700 \text{ GPa cm}^3$ ; in this expression  $S$  is the ionicity, close to one for halides,  $Z_a$  and  $Z_c$  are the formal charges of the cation and anion,  $V_0$  is the mean molar volume of an atomic pair and is defined as  $V_0 = 2M/nd_0$ , where  $M$  is the molar mass,  $n$  the number of atoms per formula and  $d_0$  the density in normal



conditions. Application to  $\text{BaCl}_2$  yields  $B_0 = 39.8$  GPa (see figure 4) as compared to the experimental value of 69.8 GPa. The difference between these two values is very large, well outside the error uncertainties, and the macroscopic bulk modulus of  $\text{BaCl}_2$  is anomalously high, being greater than in covalent compounds of the same specific volume per ion pair. No bulk modulus of a compound with cotunnite structure has ever been determined. It is possible that high coordination number found in the  $\text{PbCl}_2$  structure leads to an enhanced bulk modulus, although the previous data were in agreement for compounds with different coordination numbers, ranging from six ( $\text{NaCl}$  structure) to eight (fluorite and cubic  $\text{CsCl}$ -type structures).

A generalized relationship has been derived from oxides and silicates by Hazen and Finger [6] which they also applied to halides, sulphides, selenides tellurides, phosphides, arsenides, antimonides and carbides:

$$(B_p d^3)/(S^2 Z_a Z_c) = 750 \pm 20 \text{ GPa } \text{\AA}^3.$$

In this expression  $B_p$  is the polyhedral bulk modulus,  $d$  is the mean cation-anion distance,  $Z_a$  and  $Z_c$  are the formal anion and cation charges, and  $S^2$  is an empirical term for the relative ionicity of the bond, defined as 0.5 for  $\text{R}^{2+}-\text{O}$  bonds in oxides and 0.75 for halides. This relationship yields the bulk modulus of the various cation polyhedra. In the case of  $\text{BaCl}_2$ , the mean cation-anion distance  $d_{\text{Ba}-\text{Cl}}$  is equal to 3.255  $\text{\AA}$  at normal pressure. The above relation then leads to a polyhedral bulk modulus  $B_p = 32.6$  GPa that is much lower than the experimentally measured macroscopic bulk modulus, 69.8 GPa. A macroscopic bulk modulus lower than the polyhedral bulk modulus would be easy to account for as tilting of the cation coordination polyhedra may induce a lowering of the total volume without compression of the polyhedra. Here, we are in the opposite situation. Again, the difference between theoretical and experimental values is very large.

In addition to this anomalous bulk modulus of cotunnite  $\text{BaCl}_2$ , its first pressure derivative is also anomalous; being too low when comparing cotunnite  $\text{BaCl}_2$  with many compounds where values of  $B'_0$  ranging from four to six are frequently encountered. From the form of the equation of state a pressure derivative of the bulk modulus lower than four indicates an instability. This is indeed what is observed: the variation with pressure of the  $a$  parameter is anomalous even at low pressures and a phase transformation actually takes place at 21 GPa.

The value of the bulk modulus of the high-pressure phase is nearly the same as that of the low-pressure phase and is in better agreement with the bulk modulus-volume systematics as the volume is now reduced. The first pressure derivative is now much higher than four as sometimes encountered.

## 5. Conclusion

The cotunnite  $\text{BaCl}_2$  compound has been studied by angular-dispersive powder x-ray diffraction as a function of pressure to 52 GPa at room temperature. A first-order phase transformation occurs as 21 GPa with a large field of hysteresis. A phase transformation from the most dense structure known up to now for  $\text{AX}_2$  compounds to a still denser form does therefore take place under pressure at room temperature; it is reversible and therefore, not quenchable. The conclusions drawn from quenching experiments under high pressure should be carefully considered for

establishing phase diagrams. The x-ray diffraction patterns of the high-pressure phase have been indexed in a hexagonal cell. It does not bear any analogy with any previously proposed post-cotunnite structure, orthorhombic  $Ni_2Si$ -type or hexagonal anti- $Fe_2P$ . The determination of the high-pressure structure is difficult as few lines were observed. It seems that the decrease of the volume as calculated at normal pressure is very large. The volume behaviour of  $BaCl_2$  is very anomalous: the bulk modulus and the polyhedral bulk modulus of the cotunnite phase are much larger than expected from the relations between the bulk modulus and the specific volume or the polyhedral bulk modulus and the cation-anion distance; in addition, the first pressure derivative of the bulk modulus is also anomalously low. The origin for the high polyhedral or macroscopic bulk modulus of the low-pressure phase is very puzzling and experiments on similar compounds are underway.

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