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High-pressure isosymmetric phase transition in orthorhombic lead fluoride

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Orthorhombic α-PbF_2 was investigated at high pressure by angle-dispersive, x-ray powder diffraction. A phase transition between the cotunnite-structured α phase (α-$PbCl_2$-type, space group $Pnam$, $Z=4$) and a second orthorhombic γ phase (Co_2Si-related, space group $Pnam$, $Z=4$) was observed beginning at close to 10 GPa. The experimental evidence is consistent with a first-order, isosymmetric transition with a volume change of 2%. There are only minor changes to the structural topology at the phase transition; however, the cation coordination number increases from nine to ten. This structure type represents a third possible high-pressure, postcotunnite structure in ionic AX_2 compounds, the choice of which is determined by the cation-anion radius ratio. [S0163-1829(98)00314-2]

I. INTRODUCTION

Under ambient conditions, PbF_2 crystallizes in the cotunnite-type structure[1] (α-$PbCl_2$-type, space group $Pnam$, $Z=4$), in which the cation coordination number (CN) is nine, which until recently was the highest CN known in ionic AX_2 compounds. At high-temperature, PbF_2 transforms to a fluorite-type phase[2] that has superionic properties.[3] Several metal dihalides, which adopt the cotunnite structure type, undergo phase transitions at high pressure. BaX_2 ($X=$Cl,Br,I), $SnCl_2$ and $PbCl_2$ (Refs. 4–6) transform to a monoclinic, postcotunnite structure, space group $P112_1/a$, $Z=8$, which is a derivative of the Co_2Si structure type, whereas BaF_2 (Ref. 7) transforms to a hexagonal, Ni_2In-type structure, space group $P6_3/mmc$, $Z=2$. The CN is ten in the monoclinic structure and eleven in the Ni_2In-type structure. The choice of the high-pressure structure is governed by the cation-anion radius ratio r_c/r_a, which ranges from 0.67 to 0.81 for the former series of dihalides and is 1.12 for BaF_2. The corresponding value for PbF_2 is 1.02, which lies between the above values, and thus it is of interest to determine the nature of the high-pressure phase of this compound. Recent high-pressure Raman experiments[8] on PbF_2 indicate a first-order phase transition at approximately 15 GPa. The number of observed Raman modes in the high-pressure phase rule out a Ni_2In-type structure; however, the exact nature of this phase remains to be determined. Present x-ray-diffraction results indicate that PbF_2 behaves differently from the metal dihalides investigated to date and are consistent with a first-order isosymmetric $Pnam \rightarrow Pnam$ phase transition at high pressure.

II. EXPERIMENTAL PROCEDURE

Powdered α-PbF_2 (Alfa Products, purity 99.99%) was mixed with silicone grease as a pressure-transmitting medium and placed in a stainless-steel gasket, preindented to a thickness of 120 μm with a 150 μm diameter hole along with a small amount of ruby powder between the anvils of a diamond-anvil cell (DAC). Pressures were measured based on the shifts of the ruby R_1 and R_2 fluorescence lines.[9,10] Silicone grease was chosen as a pressure-transmitting medium in order to avoid discontinuities in the data that are commonly observed at close to 10 GPa when using 4:1 methanol:ethanol. The ruby fluorescence lines broadened very slowly with pressure due to nonhydrostatic stress, but were always resolved. Their full widths at half maximum were essentially constant over the pressure range between 9 and 15 GPa, in which the phase transition in PbF_2 occurs.

Angle-dispersive, x-ray-diffraction patterns were obtained on an imaging plate placed between 81.07 and 147.90 mm from the sample using zirconium-filtered molybdenum radiation from a microfocus tube collimated to 130×130 μm. Exposure times were typically between 24–60 h. A DAC in which the rear diamond was mounted over a 16°-wide slit allowing access to an angular range $4\theta=80°$ was used for these experiments. An additional exposure was obtained using the same installation on the material recovered after the experiment in the gasket with a sample to plate distances of 143.37 mm.

The observed intensities on the imaging plates were integrated as a function of 2θ in order to give conventional, one-dimensional diffraction profiles. The individual diffraction peaks were fitted to pseudo-Voigt functions and the peak positions obtained were used for unit-cell refinements with the program U-FIT.[11] Profile fitting and simulations of powder diffraction patterns were performed using the program FULLPROF.[12] The cell constants of the starting powder were obtained from data acquired on a standard diffractometer using copper $K\alpha$ radiation. All figures in parentheses refer to estimated standard deviations.

III. RESULTS

The following cell constants were obtained for the starting material: $a=6.4436(9)$, $b=7.6479(9)$, and $c=3.8999(7)$ Å. All reflections observed could be attributed to cotunnite-type PbF_2. No significant changes to the diffraction pattern were observed between ambient pressure and 6.6 GPa. At 9.8 GPa, the linewidth of the 200 reflection increased by 35% relative to those of the other lines and the observed position of the 011 reflection was no longer in

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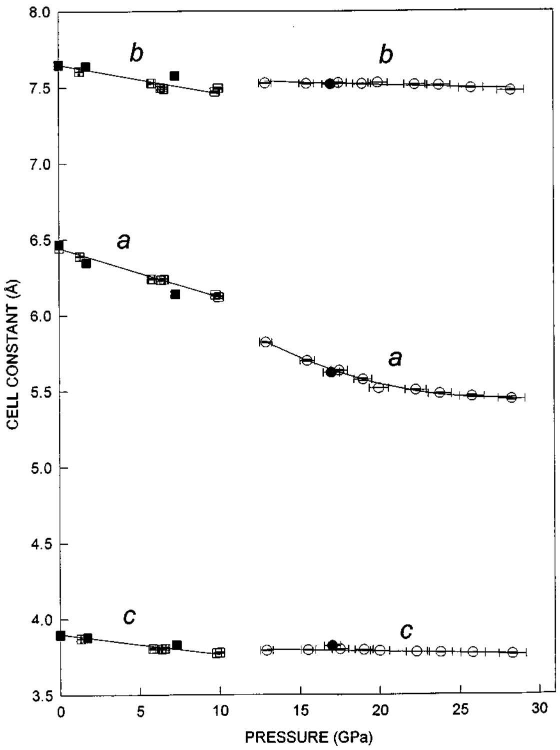

FIG. 1. Cell constants of PbF_2 as a function of pressure. Open symbols refer to points obtained upon compression and solid symbols to those obtained on decompression. Symbols □ and ○ correspond to α- and γ-PbF_2, respectively. Solid lines represent least squares fits to the data.

agreement with the position calculated using the other observed reflections. These changes indicate the beginning of a phase transition. In addition, important changes in the intensity of certain diffraction lines were observed between 9.8 and 12.9 GPa. In particular the previously intense 200 reflection was no longer visible and the 020 reflection increased in intensity. These changes are similar to those observed in other cotunnite-type metal dihalides[4–7] and are consistent with the appearance of preferred orientation at the phase transition. The 011 and 031 interplanar distances were found to increase abruptly; however, all lines could still be indexed based on an orthorhombic unit cell with *Pnam* reflection conditions. In fact, the standard deviations of the cell constants were lower at 12.9 than at 9.8 GPa and the difference between observed and calculated d_{hkl} values was typically less than 0.001 Å. This indicates a better fit to the orthorhombic cell at 12.9 GPa, which results from the completion of the phase transition. The a cell constant decreased significantly at the transition, whereas b and c increase, Fig. 1. The decrease in a and the increase in c were also observed at the transitions between cotunnite-type and either monoclinic, post-cotunnite-type or hexagonal, Ni_2In-type (orthorhombic setting) phases in other metal dihalides.[4–7] In the present case, however, there is no indication of a change in crystal system, nor in unit-cell content and the magnitude of the changes in cell constants, and consequently the volume change, Fig. 2, is greatly reduced. No deviation from orthorhombic symmetry was observed between 12.9 and 28 GPa and the diffraction patterns could always be indexed in accordance with *Pnam* reflection conditions, Table I.

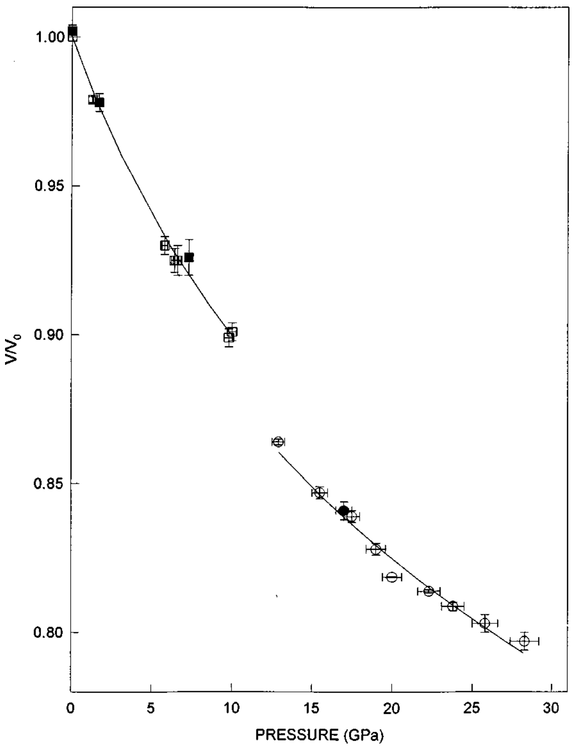

FIG. 2. Relative volume of PbF_2 as a function of pressure. Legend as for Fig. 1. Solid lines represent Birch-Murnaghan equations of state using the parameters obtained in this study.

Upon decompression, Figs. 1 and 2, the reverse transition was observed; however, it can be noted that the changes in relative intensity of the diffraction lines at the transition were not reversible and that, while there were only slight differences in position of the diffraction lines between the starting material and the recovered sample, there were very significant differences in relative intensity. In particular the 200 reflection, which had a relative intensity of 40% in the starting material, was absent in the diffraction pattern of the recovered sample as it was absent in the pattern of the high-pressure phase. This indicates that the preferred orientation

TABLE I. High-pressure diffraction data for PbF_2, *Pnam*, $Z=4$, at 22 GPa: $a=5.506(1)$, $b=7.518(2)$, $c=3.778(1)$ Å.

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}[a]	*hkl*
3.759	3.759	7	12	020
3.377	3.376	61	63	011
3.105	3.105	72	84	120
2.877	2.878	100	100	111
2.133	2.133	20	23	211
2.088	2.088	65	71	031
1.664	1.664	18	23	231
1.614	1.614	28	31	122
1.558	1.558	12	10	202
1.552	1.552	10	8	240

[a] Intensities calculated using the theoretical positions from Ref. 8 given in Table II with a preferred orientation along [100] as was found in the recovered, cotunnite-type phase.

induced at high pressure was retained in the recovered sample. This very strong preferred orientation is characteristic of cotunnite-type compounds at high pressure[4–7] and is a result of the anisotropy of the cotunnite structure, which is built up of columns of capped trigonal prisms. The cell constants of the recovered sample were $a=6.465(5)$, $b=7.650(6)$, and $c=3.894(3)$ Å.

IV. DISCUSSION

The present results indicate that the high-pressure phase of PbF_2 is different from those of other metal dihalides investigated up to now,[4–7] which adopt either a monoclinic structure with $Z=8$ or a hexagonal structure with $Z=2$. The unit cell of the high-pressure phase remains orthorhombic and there is no evidence for cell doubling. At 12.9 GPa, the b/c cell constant ratio is 1.985, which is very different from the 1.732 corresponding to a hexagonal lattice.

The cotunnite ($Pnam$, $Z=4$), monoclinic postcotunnite ($P112_1/a$, $Z=8$) and Co_2Si ($Pnam$, $Z=4$) structures are distortions of the Ni_2In structure ($P6_3/mmc$, $Z=2$).[13] The Ni_2In structure is built up of columns of pentacapped trigonal prisms (CN$=11$), which are aligned along **a** if one adopts an orthorhombic $Pnam$ setting for this structure. The above, lower-symmetry structures are obtained by rotating these columns which removes one cap in the case of the Co_2Si and postcotunnite structures (both CN$=10$) and two caps in the case of the cotunnite structure (CN$=9$). Cotunnite-type, Co_2Si-type and Ni_2In-type (orthorhombic $Pnam$ setting) structures have been shown to exhibit characteristic values for the cell constant ratios a/b and $(a+b)/c$,[7,14] which are, respectively, 0.80–0.90, 3.3–4.0, 0.66–0.74, 3.1–3.3, and 0.70–0.78, 2.9–3.2. The ratios for the $a/2$, subcell of the monoclinic, post-cotunnite structure lie within the range of characteristic values for the Co_2Si-type structures as this structure is only a slight distortion of the Co_2Si type.[5,6] The representative points for cotunnite ($PbCl_2$), Co_2Si, and Ni_2In are shown in the plot in Fig. 3 along with the changes in axial ratios observed at high-pressure for $PbCl_2$, which undergoes a cotunnite→postcotunnite transition, BaF_2, which undergoes a cotunnite→Ni_2In transition, and PbF_2. It can be seen that, while the values for all three cotunnite-type metal dihalides shift towards those of the high-pressure phases, the magnitude of the shift is significantly smaller for PbF_2. In addition, whereas above the transition the axial ratios observed for $PbCl_2$ and BaF_2 are within the usual ranges for Co_2Si-type and Ni_2In-type structures, respectively, the values for PbF_2 just above the transition (0.773, 3.521) are well outside the ranges of all three structure types. In the high-pressure phase, these values decrease significantly to (0.729, 3.431) at 28 GPa, but still lie outside the range of values for Co_2Si-type structures. In contrast, the values for the other dihalides only shift slightly in the high-pressure phases. It can also be noted that at the transition, the changes in axial ratios are much less for PbF_2 than for the other compounds. This is also true for the volume change which is 2% for PbF_2 as compared to approximately 5% for the other two compounds. The present observations indicate that the behavior of PbF_2 is distinct from other metal dihalides investigated to date and secondly that the structure of the high-pressure phase is likely to be related to, but slightly different from, that of Co_2Si.

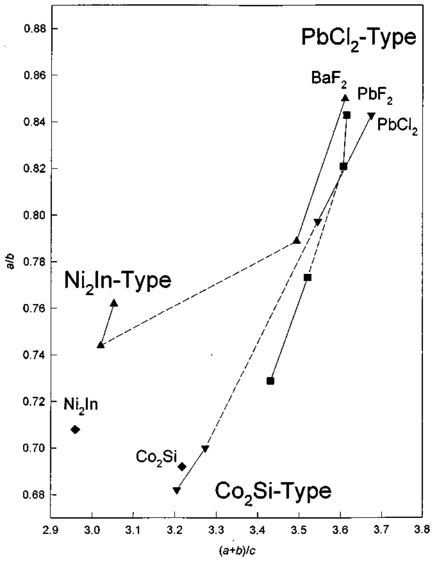

FIG. 3. Plot of the cell constant ratio a/b vs $(a+b)/c$ for selected cotunnite-type and related compounds. Symbols △, □, ▽, and ◇, correspond to BaF_2, PbF_2, $PbCl_2$, and A_2B alloys, respectively. Continuous changes within a phase and discontinuous changes at the phase transition are represented by solid and dashed lines, respectively.

The present results concur with recent Raman-scattering measurements,[8] which indicated the presence of a first-order transition at 14.7 GPa on compression and 13 GPa on decompression. Some band broadening was observed just above 10 GPa, which is likely to be due to the structural changes found to begin at this pressure. Seven Raman modes were observed in the spectrum of the high-pressure phase, termed γ-PbF_2. The authors were thus able to rule out a Ni_2In-type structure for which only 2 Raman modes are predicted from group theory. They also commented that the high-pressure spectrum is much simpler than what would be expected for a monoclinic, postcotunnite structure, which would have 36 Raman-active modes. Both the cotunnite structure and an orthorhombic, Co_2Si-related structure ($Pnam$, $Z=4$) would be expected to have 18 Raman-active modes. Six of the possible 18 bands were observed in the spectrum of the cotunnite-type phase under pressure and the increase in the number of bands to 7 is consistent with a transition to a second $Pnam$ phase.

In the same paper,[8] the results of first-principles calculations on PbF_2 as a function of pressure are presented. In particular, the structural parameters and axial ratios for the α phase were calculated for several pressures (Note: the $Pbnm$ setting was used for these calculations rather than the $Pnam$ setting used here). Calculations indicate significant increases in the rate of change of cell constant ratios and structural parameters beginning at a volume of about 14 Å^3/atom, which from the present P-V data corresponds to 14 GPa. In particular, the cell constant ratio a/b decreases significantly and the pressure dependence of cell constant b, K_b, decreases dramatically in agreement with the present results, Figs. 1 and 3, and certain atomic positional param-

TABLE II. Atomic positions of PbF_2, at ambient pressure and 22 GPa and those of Co_2Si. All atoms are on $4c$ sites (x, y, $\frac{1}{4}$) in the space group $Pnam$, $Z=4$.

	PbF_2 (ambient)[a]	PbF_2 (22 GPa)[b]	Co_2Si[c]
Pb	(0.2657, 0.1042, $\frac{1}{4}$)	(0.28, 0.10, $\frac{1}{4}$)	(0.298, 0.111, $\frac{1}{4}$)
F1	(0.362, 0.437, $\frac{1}{4}$)	(0.33, 0.44, $\frac{1}{4}$)	(0.326, 0.438, $\frac{1}{4}$)
F2	(0.034, 0.346, $\frac{3}{4}$)	(0.05, 0.29, $\frac{3}{4}$)	(0.038, 0.282, $\frac{3}{4}$)

[a] Reference 1.
[b] Reference 8.
[c] Reference 15.

TABLE III. Selected Pb-F distances and minimum F-F distance (Å) in PbF_2 at ambient pressure and 22 GPa using the atomic positions from Refs. 1 and 8 given in Table II.

	Ambient	22 GPa
$(Pb\text{-}F)_1$	2.41	2.52
$(Pb\text{-}F)_2 \times 2$	2.45	2.33
$(Pb\text{-}F)_3$	2.54	2.50
$(Pb\text{-}F)_4 \times 2$	3.03	2.68
$(Pb\text{-}F)_5$	2.64	2.56
$(Pb\text{-}F)_6 \times 2$	2.69	2.54
$(Pb\text{-}F)_7$	3.94[a]	3.04
$(F\text{-}F)_{min}$	2.81	2.69

[a] Lies outside lead coordination polyhedron.

eters, such as x_{Pb} and y_{F_2}, exhibit large shifts. No calculations were performed for the γ phase, but we now show that the changes obtained from the calculations for the α phase in fact reproduce the behavior observed at the $\alpha \rightarrow \gamma$ transition. The atomic positional parameters shift towards those of a Co_2Si-type structure, Table II. The calculated positions corresponding to the pressure range investigated for the γ phase are not constant, which concurs with the important changes in cell constant ratios observed in the present study. It was not possible to refine the structure of the γ-PbF_2 due to the very low x-ray scattering factor of F^- as compared to Pb^{+2}; however, the intensities calculated using the positions from the theoretical study[8] are in agreement with those observed experimentally, Table I. It can be noted that the relative intensities calculated using Co_2Si positions[15] are not in such good agreement, principally due to the difference in x_{Pb}. This result was checked by full profile fitting using the theoretical PbF_2 positions and those of Co_2Si. A Bragg R factor of 9% was obtained using the theoretical positions as compared to 13% using Co_2Si positions. In both cases a preferred orientation along [100] was included. As discussed above, the cell constant ratios observed experimentally for γ-PbF_2, Fig. 3, are different from those observed typically for Co_2Si-type structures and are displaced slightly towards those of cotunnite-type structures, it can be seen from Table II that the same is true for the atomic positions. The theoretical calculations for the α phase successfully reproduce the $\alpha \rightarrow \gamma$ phase transition, while retaining a $Pnam$ space group, and there is no experimental evidence for a symmetry change. Both theory and experiment thus concur that PbF_2 undergoes a isosymmetric phase transition from a cotunnite-type structure to a Co_2Si-related structure, which is required by Landau theory to be first order.[16] The 2% volume change obtained in this study and the hysteresis observed in the Raman experiment[8] confirm the first-order nature of the transition. The present observation of an isosymmetric phase transition in PbF_2 adds a new example to the relatively short list of materials[16] that undergo such transitions. It can be noted that a recent theoretical study predicts an isosymmetric phase transition in α-quartz, at which the silicon coordination number would increase from four to five.[17]

Principal interatomic distances in γ-PbF_2 at 22 GPa calculated using the experimental cell constants and theoretical atomic positions are listed in Table III along with the corresponding distances in the cotunnite-type structure at ambient pressure. The lead ion is surrounded at ambient pressure by nine fluoride ions at distances between 2.41 and 3.03 Å. In γ-PbF_2 at 22 GPa, the corresponding nine distances range between 2.33 and 2.68 Å; however, an additional anion, which was at 3.94 Å at ambient pressure, has entered the polyhedron and lies at a distance of 3.04 Å, and thus CN has increased to 10. These changes to the coordination polyhedron are responsible for the shifts in frequency of several Raman modes at the phase transition.[8]

The experimental P-V data for the α and γ phases were fitted using a Birch-Murnaghan equation of state:[18]

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 + 0.75(B_0' - 4) \times [(V/V_0)^{-2/3} - 1]\},$$

where B_0 and B_0' are the bulk modulus and its first derivative at ambient pressure. The fit for the α phase, Fig. 2, yielded a bulk modulus of 66(7) GPa with a B_0' of 7(3). This B_0 is only slightly higher than that of fluorite-type β-PbF_2 61 GPa (Ref. 19). The data for γ-PbF_2 were fitted assuming that $B_0' = 7$ as in α-PbF_2; a B_0 value of 69(10) GPa was thus obtained. The initial relative volume of this phase could not be measured experimentally and was added as an additional parameter in the fit and a value of 0.973(15) was obtained.

The bulk modulus scales with $1/V_0$. If one takes the bulk modulus of β-PbF_2, 61 GPa and multiplies the ratio of initial volumes 209.58 $Å^3$/192.18 $Å^3$, a value of 66.5 GPa is obtained for α-PbF_2. Similarly for γ-PbF_2, one obtains 68.4 GPa, which is in very good agreement with the value obtained experimentally. This indicates that there are no significant changes in bonding nature nor a significant increase in anion-anion repulsive interactions, unlike other cotunnite-type compounds studied in which very large increases in bulk modulus were observed at the phase transition.[4–7]

The compressibility of both α-PbF_2 and γ-PbF_2 is anisotropic. In α-PbF_2, compression along **a** is twice that along **b** and 43% greater than that along **c**. At the phase transition, compressibility along **a** increases while compression along **b** and **c** decreases by almost an order of magnitude; thus compression in γ-PbF_2 occurs almost exclusively along the **a** direction. This is significantly different from the behavior of other cotunnite-type metal dihalides,[4–7] for which compression in the high-pressure phase is much less anisotropic.

The present results indicate that the choice of high-pressure structure in cotunnite-type compounds depends on the radius ratio, r_c/r_a. The monoclinic, postcotunnite structure (CN=10), space group $P112_1/a$, $Z=8$, is obtained for the metal dihalides with large anions, BaX_2 ($X=$Cl,Br,I) and $SnCl_2$ and $PbCl_2$ (Refs. 4–6), for which r_c/r_a, ranges from 0.67 to 0.81. An orthorhombic, Co_2Si-related structure (CN =10), space group $Pnam$, $Z=4$, is observed for PbF_2, for which $r_c/r_a=1.02$, whereas a hexagonal Ni_2In-type structure (CN=11), space group $P6_3/mmc$, $Z=2$, is obtained for BaF_2 (Ref. 7) for which r_c/r_a is 1.12. The high value of r_c/r_a in the latter compound favors the higher coordination number of eleven in the Ni_2In-type structure. The low-symmetry structure observed for the metal dihalides with large anions is stabilized by the greater polarizability of Cl^-, Br^-, and I^-. It can be noted that the r_c/r_a values above give an indication of which structure will be adopted; the actual critical values for the transition to one of these three structures will be higher as they correspond to the r_c/r_a ratios at high pressure immediately prior to the phase transition.

V. SUMMARY

Cotunnite-type α-PbF_2 undergoes a first-order, isosymmetric phase transition above 10 GPa to a second orthorhombic phase with a Co_2Si-related structure. A volume change of 2% is observed at the transition and the cation coordination number increases from 9 to 10. The experimentally-observed, high-pressure behavior of PbF_2 is in good agreement with the changes predicted by theoretical calculations for the α phase and we can now show that these changes correspond to the isosymmetric phase transition. The behavior of PbF_2 is distinct from that of other cotunnite-type metal dihalides, which adopt either a hexagonal, Ni_2In-type structure or a monoclinic, postcotunnite structure at high pressure. The present results indicate that there is now a third possible high-pressure structure for these compounds, the choice of which is determined by the cation-anion radius ratio.

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