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The Effect of Pressure and B-Cation Size on the Crystal Structure of $CsBF_3$ Compounds (B=Mn, Fe, Co, Ni, Zn, Mg)†

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The compounds $CsBF_3$, B = Mn, Fe, Co, Ni, Zn, Mg, occur with four related structures that are known, in other compounds, to transform into one another with increasing pressure. In this paper a phase diagram is presented showing the combined effect of pressure and B-cation size on the occurrence of these related structures. These structures have different proportions of cubic and hexagonal stacking of close-packed CsF_3 layers, and in all cases the proportion of cubic stacking increased with both pressure and B-cation size. This result is shown to be consistent with a stabilization mechanism for the intermediate structures involving displacement by electrostatic forces of the B cations from the centers of symmetry of their interstices. The high-pressure phases, identified by powder X-ray diffraction, were retained by quenching from 700C to room temperature before reducing the pressure. The transition pressures were relatively insensitive to preparation temperature. The retained phases required heating to 200–500C for a sluggish retransformation to their atmospheric-pressure form.

Introduction

Compounds with the chemical formula ABX_3 form an extensive class of structurally related compounds, provided the large A cation has a radius $1.0 < r_B < 1.9$ Å and the smaller B cation has a radius $0.5 < r_B < 1.2$ Å. In this formula X is an anion such as oxygen, sulfur, fluorine or chlorine. The related structures of this class can all be described by a stacking of ordered, close-packed AX_3 layers that everywhere avoids near-neighbor A cations, the B cations filling all-anion octahedral sites between these layers. Two types of stacking of the AX_3 layers fulfill these requirements: cubic and hexagonal. If there is only cubic stacking, the B-filled octahedra share only corners in three dimensions to form the cubic perovskite structure. Figure 1a shows a projection of the cubic network of B-filled octahedra within a hexagonal cell. This projection and the hexagonal basis are used for comparison with the other hexagonal structural members of this class of compounds, which are also shown in Fig. 1. Figure 1b, for example, shows one of the isolated linear chains of face-shared octahedra that form parallel to the *c*-axis if all of the stackings are hexagonal. Since this structure has a repeat distance of two AX_3 layers, it will be referred to as the 2L structure. Although an infinite number of ordered structures are theoretically possible, each having a different ratio of cubic to hexagonal stackings, only three intermediate structures have been identified in stoichiometric compounds: A two-to-one cubic to hexagonal stacking (cchcch) represented by Fig. 1c, a one-to-one stacking (hchc) shown in Fig. 1d, and the one-to-two cubic to hexagonal stacking (chhchhchh) of Fig. 1e. The repeat distances are six, four, and nine AX_3 layers, respectively, and the structures are therefore designated 6L, 4L, and 9L. More detailed discussions of these structures have been given by Katz and Ward (*1*) and by Wells (*2*).

It has already been shown that high pressure stabilizes cubic stacking relative to hexagonal stacking in this class of compounds. The 6L atmospheric-pressure form (APF) of $CsMnF_3$ and $TlNiF_3$ have been reported (*3*) to transform to the perovskite structure below 30 kbars, and the APF, 6L $RbNiF_3$ (*4*) shows the same transformation to perovskite at 20 kbars and 700C (*5*). The APF, 2L $CsNiF_3$ (*6*) transforms at 5 kbars to the 9L structure and again at 50 kbars to the 6L structure (*7*). Among oxides with 9L structures, the APF, 9L $BaRuO_3$ (*8*) transforms at 15 kbars to the 4L structure and again at 30 kbars to the 6L structure (*9*). The pressure required for these transformations in the system $Ba_{1-x}Sr_xRuO_3$ were systematically lowered

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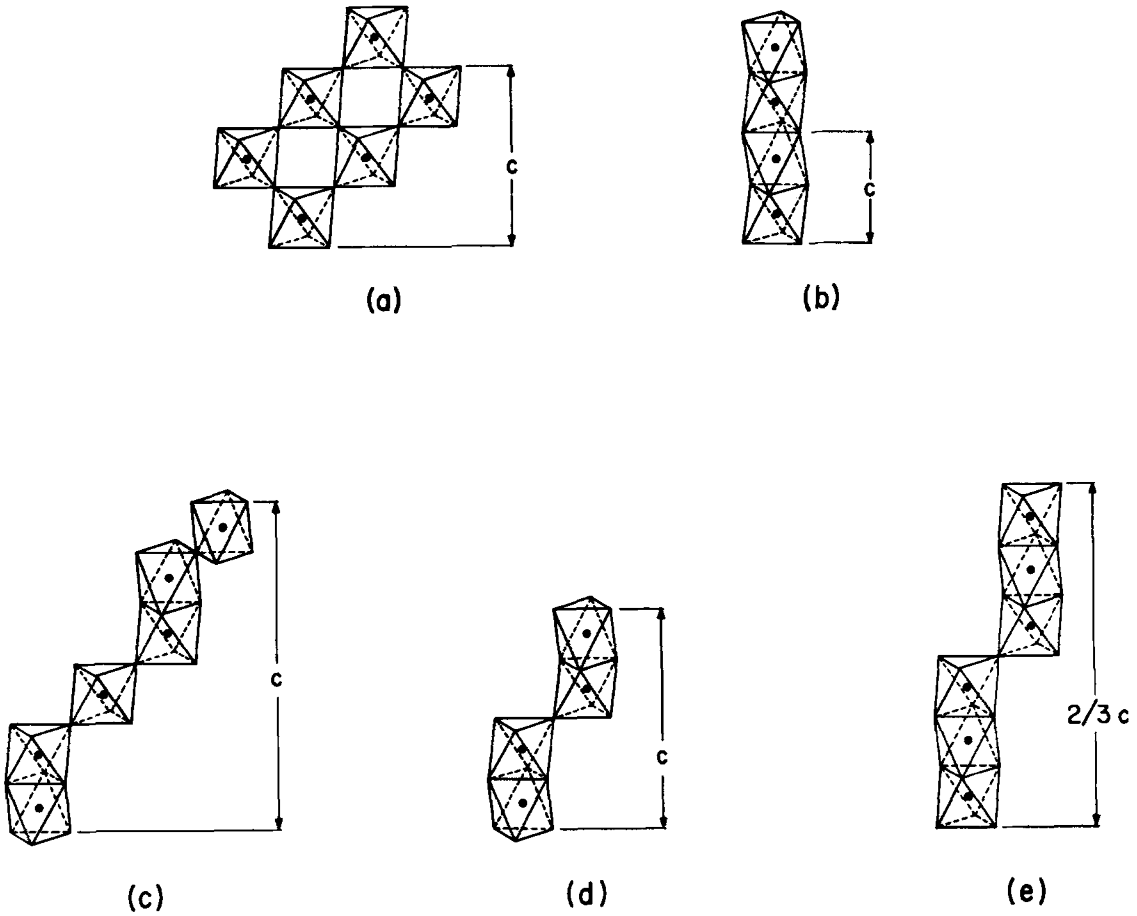

FIG. 1. Projection of octahedra network of (110) plane ofhexagonal unit cell.

by the addition of the perovskite $SrRuO_3$ (*9*). The APF, 2L $BaMnO_3$ (*10*) transforms at 30 kbars to the 9L structure (*3*, *11*) and at 90 kbars to the 4L structure (*3*), while the APF, 4L $SrMnO_3$ transforms at 50 kbars to the 6L structure (*3*, *11*).

In this paper we report a study of the simultaneous effect of pressure and B-cation size on the structural sequences occurring in the general class of compounds $CsBF_3$.

Experimental

The high pressure forms of $CsBF_3$ compounds were prepared by the reaction of stoichiometric mixtures of CsF and the appropriate BF_2 at elevated pressures (up to 80 kbars) and temperature. The dried reagent grade fluorides were weighed, ground with an agate mortar and pestle, and loaded into cylindrical gold capsules within a glove bag filled with dry nitrogen. Multi-phased products were obtained when these precautions were not taken.

These syntheses were performed in a high-pressure belt apparatus (*12*) capable of developing pressures to 90 kbars. Pressure calibration of the apparatus was accomplished by observing the resistance discontinuities at the transition points of Bi, Tl, and Ba reported by Kennedy and LaMori (*13*). A tubular graphite heater was used in the pressure cell. The specimen capsules were made of gold tubing (0.01 in. thick × 0.6 in. long × 0.15 in. dia.) fitted with 0.1 in. thick gold end plugs. In a typical run, the specimen was subjected to the desired pressure, and then the temperature was raised rapidly and held for $\frac{1}{2}$ hr. The specimen was quenched to room temperature before the pressure was released.

Structural analysis on the products thus obtained were carried out with a Norelco verticle X-ray powder diffractometer using monochromatic (LiF crystal) CuK_α radiation.

The retransformation of the quenched products was studied by heating the specimens in recrystallized alumina boats in a flowing stream of scrubbed

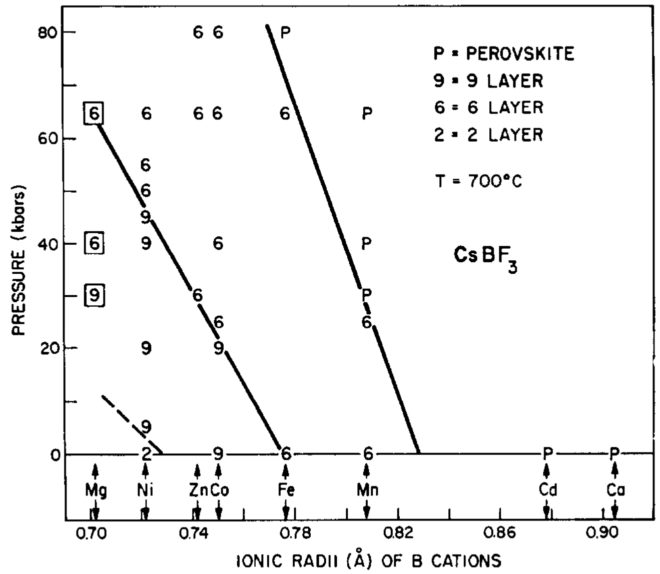

FIG. 2. Structural phase diagram of $CsBF_3$ compounds.

nitrogen. The temperature was increased in 100C increments and held for a few hours. After each of these heat treatments, the samples were X-rayed to determine the onset and completion of retransformation which was too slow for DTA.

Results and Discussion

Figure 2 summarizes the effect of pressure and B-cation size on the structures of the $CsBF_3$ compounds with B = Mn, Fe, Co, Ni, Zn, and Mg. The cell dimensions and volumes per formula unit are given in Table I. As anticipated, the pressure-sensitive structures of these compounds form the series of polytypes illustrated in Fig. 1. In all cases pressure increases the proportion of cubic to hexagonal stacking of the close-packed CsF_3 layers. The observed transformation pressures were rather insensitive to preparation temperature (400–900C), but all specimens reported in Fig. 2 and Table I

TABLE I

UNIT CELL DIMENSIONS (Å) AND VOLUME/$CsBF_3$ (Å^3) FOR $CsBF_3$ COMPOUNDS

	Structure type			
Compound	2L (hex.)	9L (hex.)	6L (hex.)	Perovskite (cubic)
$CsMgF_3$		6.16 × 22.13 80.8 Å^3	6.04 × 14.45 76.1 Å^3	
$CsNiF_3$	6.24 × 5.22 88.0 Å^3	6.15 × 22.32 81.2 Å^3	6.05 × 14.55 76.9 Å^3	
$CsZnF_3$			6.09 × 14.67 78.5 Å^3	
$CsCoF_3$		6.20 × 22.36 82.7 Å^3	6.09 × 14.67 78.5 Å^3	
$CsFeF_3$			6.16 × 14.86 81.3 Å^3	4.283 78.6 Å^3
$CsMnF_3$			6.21 × 15.07 84.0 Å^3	4.328 81.1 Å^3

were uniformly quenched from 700C. The temperature insensitivity of the transformation pressures for this class of polytypes has been similarly noted in earlier studies of the effect of pressure on the structures of $RbNiF_3$ (*5*), $CsNiF_3$ (*7*), and the system $Ba_{1-x}Sr_xRuO_3$ (*9*).

This particular group of compounds was chosen for study because their structures at atmospheric pressure form a series of polytypes that exhibit an increased proportion of cubic stacking of the CsF_3 layers as the size of the B-cation increases. Within this one series of compounds, the structures range from complete hexagonal stacking in 2L $CsNiF_3$ through the 9L $CsCoF_3$, and the 6L $CsFeF_3$, $CsMnF_3$ sequence to the complete cubic stacking found in the perovskite (P) $CsCdF_3$ (*14*). Only the 4L sequence of alternating cubic and hexagonal stacking is missing. The ionic radii used in Fig. 2 were calculated from the related series of KBF_3 compounds, all of which have the perovskite structure. The values were obtained by subtracting the ionic radius of the F^- ion in twofold coordination (*15*) from one-half of the cubic unit-cell dimension (*16*). This set of radii is consistent both with the volumes of the $CsBF_3$ compounds reported here and with the BF_2 rutile compounds. This consistency is particularly evident for the series of compounds having a 6L structure, which includes all of the B cations of this study.

As in the previous examples studied, all members of this class of compounds transform with pressure to a series of polytypes having a higher proportion of cubic stacking. The APF, 2L $CsNiF_3$ transforms at 5 kbars to the 9L form, and then to the 6L form at 47 kbars. The APF, 9L $CsCoF_3$ transforms to the 6L form at 22 kbars. For $CsFeF_3$, the APF, 6L structure transforms at about 70 kbars to the perovskite structure while the APF, 6L $CsMnF_3$ requires only 26 kbars for the same transformation. Since the 4L polytype was found for $BaMnO_3$, $SrMnO_3$ and the $Ba_{1-x}Sr_xRuO_3$ system, we expected to find a 4L region between the 9L and 6L polytypes. However, careful examination of the 9L to 6L phase boundary for the $CsBF_3$ compounds yielded no evidence for the 4L polytype.

The percentage of decrease in volume resulting from each of the high pressure transformations is shown in Table II. These volume changes (3.3–7.7 %) were calculated from the lattice constants determined at atmospheric pressure as given in Table I. It should be noted that each type of transformation falls within a narrow range of volume change and that this amount of change decreases as the amount of hexagonal stacking decreases.

TABLE II

VOLUME DECREASE (%) DUE TO PRESSURE-INDUCED TRANSFORMATIONS OF $CsBF_3$ COMPOUNDS

	B-cation				
Transformation	Mg	Ni	Co	Fe	Mn
2L → 9L		7.7			
9L → 6L	5.8	5.3	5.1		
6L → Perov				3.3	3.4

The two dominant factors determining the phase type in this class of compounds are the electrostatic, or Madelung energies and the relative ionic sizes. The electrostatic repulsion between B cations of face-shared octahedra may be reduced by displacements of the cations from the centers of symmetry of their interstices parallel to the *c*-axis so as to increase the B–B separation and allow for greater screening by the common near-neighbor anions. Such displacements give maximum stabilization if only pairs share common octahedral-site faces. However, every B–B interaction is still reduced if triples share common faces as in the 9L structure. For larger strings of face-shared octahedra, only the end members can be thus stabilized, and the electrostatic energy gained by terminating the string apparently becomes smaller than the loss in energy associated with the introduction of a layer of alternate-type stacking. The possibility of such a displacement is presumably responsible for stabilization of the three intermediate phases, since the narrowness of the phase field of the 4L structure, where it appears, suggests that considerable energy is required to alternate the stacking sequence. Such a stabilization mechanism is consistent with Fig. 2, since larger B-cation displacements are possible for the smaller ions and are inhibited by the application of pressure, which reduces the size of the interstice. Interestingly, the smallest ions with closed-shell cores, Mg and Zn, do not form any compound with composition $CsBF_3$ at atmospheric pressure (*17*). Rather than form either the 2L or 9L structures, they crystallize with chemical formula $Cs_4B_3F_{10}$ (*6*). The structure (*18*) can be derived from the tetragonal $A_4B_3F_{10}$ structure, which consists of the following stacking sequence along the tetragonal *c*-axis: $[(AX\text{–}BX_2)_3\text{–}AX]_n$. This is to be contrasted with the cubic perovskite stacking along a (001) axis: $(AX\text{–}BX_2)_n$. The close-packed AX_3 layers make an angle with the tetragonal *c*-axis and are confined to the $(AX{-}BX_2)_3{-}AX$ segments. If, now, these close-packed AX_3 layer segments have hexagonal rather than cubic stacking, face-shared triplets occur within the segments, and these triplets are terminated by the AX–AX layers making an angle with the axis of the triplets. Thus the characteristic triplets of the 9L structure are present, but the chain of face-shared octahedra are broken by the introduction of additional AX rather than by the formation of a cubic stacking. Since relatively large displacements of small cations would create considerable elastic strain across the cubic-stacked AX_3 plane of the 9L structure, the relative stability of this $A_4B_3F_{10}$ alternative becomes plausible where the B cations are small. In the case of Ni, both the 2L $CsNiF_3$ and $Cs_4Ni_3F_{10}$ structures are formed at atmospheric pressure. Apparently the strong octahedral-site preference energy of a Ni^{2+} ion, which has a partially filled outer *d* shell, inhibits the magnitude of the displacements from the center of its interstice relative to the slightly larger Zn^{2+} cation.

Given octahedral-site B cations and formal ionic charges, the phase type in this class of compounds might thus be expected to be determined by geometrical factors alone. Were this the case, then all of the phases of a given type should fall between straight lines in Fig. 2, and there should be a regular progression from the 2L to the 9L, 4L, 6L, and P structures on passing from the lower left-hand corner to the upper right-hand corner of the diagram. The fact that, with only one exception, this condition is fulfilled indicates the dominating influence of the geometrical factor. Significantly, the exception occurs in $CsMgF_3$, which contains the most basic and ionic of the B cations. A larger effective charge on the Mg^{2+} ions increases the electrostatic repulsive energy between Mg^{2+}-ion pairs sharing a common octahedral-site face, so that cubic stacking must be favored. This reasoning is consistent with the direction of the observed discrepancy in the 9L–6L boundary of $CsMgF_3$. The regularity of the boundary obtained for all the other members of the $CsBF_3$ compounds shown in Fig. 2 may be attributed to the fact that all the B cations come from the first transition series and that there is a regular change in basicity with ionic size for all members (except on passing from Ni to Zn).

The stability of the high pressure phases at atmospheric pressure was studied by determining the temperature required for retransformation to the atmospheric pressure form. These retransformations were very sluggish, requiring several hours at temperatures ranging from 200–500C. It was found that the higher the pressure required to effect a transformation, the lower was the temperature for retransformation. The $CsFeF_3$, which required 70 kbars for transformation to the perovskite, retransformed at 200C while the 9L $CsNiF_3$, formed at 5 kbars, required 500C for retransformation to the 2L form. These retransformation temperatures were considerably lower than those found for the high-pressure phases in the $Ba_{1-x}Sr_xRuO_3$ system, where treatment at 1200C for 3 hr resulted in only partial retransformation (*9*).

Some of the high-pressure phases examined showed interesting magnetic and optical properties. The 6L forms of yellow $CsNiF_3$ and lavender $CsCoF_3$ both exhibited ferrimagnetic properties similar to the 6L forms of $RbNiF_3$ (*4*, *19*, *20*) and $CsFeF_3$ (*21*, *22*). Results of more detailed investigation of the properties of the high-pressure forms of the $CsBF_3$ compounds will be reported later.

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References

1. L. Katz and R. Ward, *Inorg. Chem.* **3**, 205 (1964).
2. A. F. Wells, "Structural Inorganic Chemistry," 3rd ed. Clarendon Press, Oxford (1962).
3. Y. Syono, S. Akimoto, and K. Kohn, Technical Report of Institute for Solid State Physics, Ser. A, No. 337, Nov. 1968, University of Tokyo.
4. W. Rudorff, J. Kandler and D. Babel, *Z. anorg. allgem. Chem.* **317**, 261 (1962).
5. J. A. Kafalas and J. M. Longo, *Mat. Res. Bull.* **3**, 501 (1968).
6. D. Babel, *Z. Naturforsch.* **20a**, 165 (1965).
7. J. M. Longo and J. A. Kafalas, *J. Appl. Phys.* (to be published March 1969).
8. P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.* **4**, 306 (1965).
9. J. M. Longo and J. A. Kafalas, *Mat. Res. Bull.* **3**, 687 (1968).
10. A. Hardy, *Acta Cryst.* **15**, 179 (1962).
11. A. W. Sleight and B. Chamberland (to be published).
12. H. T. Hall, *Rev. Sci. Instr.* **31**, 125 (1960).
13. G. C. Kennedy and P. N. LaMori, "Progress in Very High Pressure Research," pp. 304–314 (F. Bundy, W. Hibbard, and H. Strong, eds.). Wiley, New York (1961).
14. H. A. Klasens, P. Zalm, and F. O. Huysman, *Philips Res. Rept.* **8**, 441 (1953).

15. R. D. Shannon and C. T. Prewitt, *Acta Cryst.* (to be published 1969).
16. J. B. Goodenough and J. M. Longo, "Crystallographic and Magnetic Properties of Perovskite and Perovskite-related Compounds," Landolt–Bornstein Tabellen (to be published 1969).
17. D. Babel, *Structure and Bonding* **3**, 1 (1967).
18. D. Babel (to be published).
19. G. A. Smolenskii, V. M. Yudin, P. P. Syrnikov, and A. B. Sherman, *Fiz. Tverd. Tela* **8**, 2965 (1966); *Engl. Trans. Soviet Phys.—Solid State* **8**, 2368 (1967).
20. M. W. Shafer, T. R. McGuire, B. E. Argyle, and G. J. Fan, *Appl. Phys. Letters* **10**, 202 (1967).
21. M. Eibschutz, L. Holmes, H. J. Guggenheim, and H. J. Levinstein, *J. Appl. Phys.* (to be published March 1969).
22. J. Portier, A. Tressaud, R. Pauthenet, and P. Hagenmuller, *Compt. Rend. Acad. Sci., Paris* **267**, 1329 (1968).