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A structural study on the PbFCl-type compounds MFCl (M = Ba, Sr and Ca) and BaFBr under high pressure

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Abstract. High-pressure x-ray diffraction studies on BaFCl and BaFBr up to 50 GPa, on SrFCl up to 42 GPa, and on CaFCl up to 27 GPa were performed at room temperature using a diamond anvil cell and synchrotron radiation. Data for the equations of state are given. The c/a ratios of the tetragonal structure of these compounds show different variations under pressure and structural phase transitions are observed for BaFCl and BaFBr at transition pressures of about 21 GPa and 27 GPa, respectively. A simple hard-sphere model is presented, which describes the observed structural variations almost quantitatively and accounts for the structural phase transition.

1. Introduction

Compounds of the PbFCl-type structure (space group $P4/nmm$, $Z = 2$) form a large family of interesting host materials for either divalent impurities in the case of divalent metal fluoride halides (MFX) or trivalent impurities in the case of trivalent oxide halides ($LnOX$) with rather high local symmetry at the impurity site (C_{4v}). Besides the well established application of Eu^{2+} :BaFBr in x-ray image plates, it was reported more recently [1] that Sm^{2+} :SrFCl could also find special applications as a more sensitive material than the ruby luminescence sensor [2] currently in use for pressure measurements in diamond anvil cells [3]. Furthermore, a basic understanding of the structural systematics at ambient conditions [4] as well as the crystal field variations in these materials under pressure [5, 6, 7] requires new structural studies in extended pressure regions in addition to the few previous studies on BaFCl [8, 9] and BaFBr [9] covering the pressure range only to 6.5 GPa, and the study on SmFCl [10] up to 22 GPa, which could have shown a special behaviour due to electronic changes expected for Sm in this extended pressure range.

2. Experimental details

Starting from high-purity materials (99.99%), single crystals of CaFCl, SrFCl, BaFCl and BaFBr were grown in the materials laboratory of the physics department, University GH Paderborn, by the standard Bridgman technique. Some of the samples were also doped with 0.1% Sm^{2+} for luminescence measurements. No differences between the doped and undoped samples were detected in the x-ray diffraction experiments. Fine powders suitable for powder x-ray diffraction were ground in a mortar, CaFCl in dry atmosphere because of its hygroscopic nature. The powdered samples were loaded into a gasketed diamond anvil

cell [11, 12] together with one or two ruby spheres of less than 10 μm diameter for pressure measurements using the non-linear pressure scale [13]. Different pressure media were used with the same results. The best diffraction spectra are obtained with ethanol:methanol:water (16:3:1) (see figure 1), whereas with mineral oil and boron powder some line broadening takes place at higher pressures. The x-ray diffraction measurements were performed at the energy dispersive station of HASYLAB/DESY (Hamburg) described elsewhere [14].

3. Experimental results

The measurements on CaFCl, on SrFCl, and on BaFCl, BaFBr were made in the pressure range of 27 GPa, 42 GPa and 50 GPa, respectively. Typical raw diffraction spectra of these compounds are shown in figure 1. Counting times of 30 min were used for SrFCl, BaFCl and BaFBr, while about 2 h was required for CaFCl due to its weak scattering power.

The lattice spacings d_{hkl} are determined by fitting Gaussian profiles to the diffraction lines and the results are shown in figure 2 as functions of pressure. Strongly overlapping diffraction lines with lower d values have not been indexed and only the d_{hkl} values marked with solid circles in figure 2 are used for the evaluations of the lattice parameters a and c . In the case of CaFCl, the lattice parameters are evaluated only up to 17 GPa due to the deterioration of the diffraction spectra. The lattice parameters a and c are used to calculate the solid lines for the d_{hkl} values in figure 2.

The variations of the lattice parameters a and c under pressure are shown in figures 3 and 4, respectively, and the corresponding variations in the unit cell volumes are given in figure 5. The volume compressibility moduli K_0 and the linear compressibility moduli K_{a0} and K_{c0} and their pressure derivatives K'_0 , K'_{a0} and K'_{c0} are determined with the Murnaghan equation of state. The results are given in table 1 with 'restricted' error estimates in brackets [15, 16]. The corresponding curves are shown as solid lines in figures 3–5. In this limited pressure range the Birch [17], Murnaghan [18] and other [19] equations of state give within the stated restricted errors the same values of K_0 and K'_0 . For BaFCl and SrFCl K_0 values determined by ultrasonics and Brillouin scattering are available. The present results for SrFCl are in reasonable agreement with the values $K_{a0} = 169$ GPa, $K_{c0} = 149$ GPa and $K_0 = 54$ GPa determined by Brillouin scattering [20]. However, for BaFCl there is some discrepancy with the data $K_{a0} = 139$ GPa, $K_{c0} = 122$ GPa and $K_0 = 44$ GPa from Brillouin scattering [21] we cannot account for. K_{c0} from the present study is about twice that from Brillouin scattering. In consequence the values determined for K_0 do not agree. However, for high-pressure experiments K_0 and K'_0 mainly play the role of fit parameters and may not have the meaning of the thermodynamical $K_0 = -VdP/dV|_{P \rightarrow 0}$ determined by Brillouin scattering experiments.

Table 1. Values of K_0 and K'_0 for CaFCl, SrFCl, BaFCl and BaFBr in the PbFCl-type structure obtained by least-squares fitting of the Murnaghan equation of state to the experimental data.

	K_{a0} (GPa)	K'_{a0}	K_{c0} (GPa)	K'_{c0}	K_0 (GPa)	K'_0
CaFCl	365(35)	9(10)	213(12)	2(4)	97(17)	2(1)
SrFCl	191(10)	16(7)	163(14)	12(3)	61(4)	5(1)
BaFCl	155(10)	17(4)	237(12)	0(1)	62(6)	4(1)
BaFBr	156(14)	15(4)	121(28)	9(2)	44(7)	5(1)

Figure 6 gives the variation of c/a under pressure for the four compounds investigated as a function of the directly measured unit cell volume V . Clearly, CaFCl shows a very strong decrease in c/a under compression. For SrFCl, the variation is moderate. For BaFBr

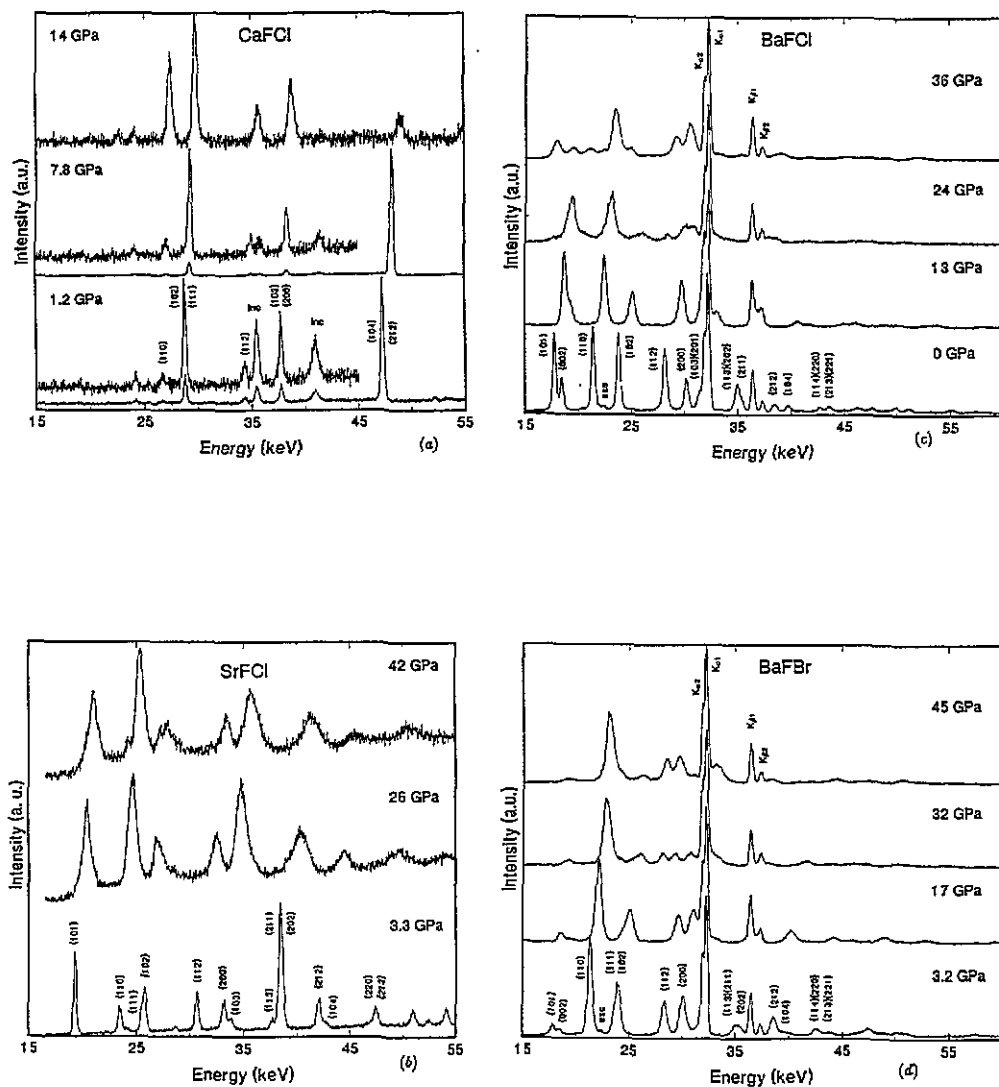


Figure 1. Typical raw diffraction spectra of (a) CaFCl, (b) SrFCl, (c) BaFCl and (d) BaFBr at different pressures with indexing given for the most prominent lines at the lower pressure only. The lines labelled with In c, esc, $K\alpha$ and $K\beta$ refer to diffraction peaks from the inconel gasket, escape peak and fluorescence lines of Ba, respectively. The pressure transmitting medium was ethanol:methanol:water (16:3:1) and mineral oil for CaFCl only.

and BaFCl the variation of c/a is marginal at low pressure but c/a decreases strongly at high compression. These findings on BaFCl and BaFBr do not agree with earlier results

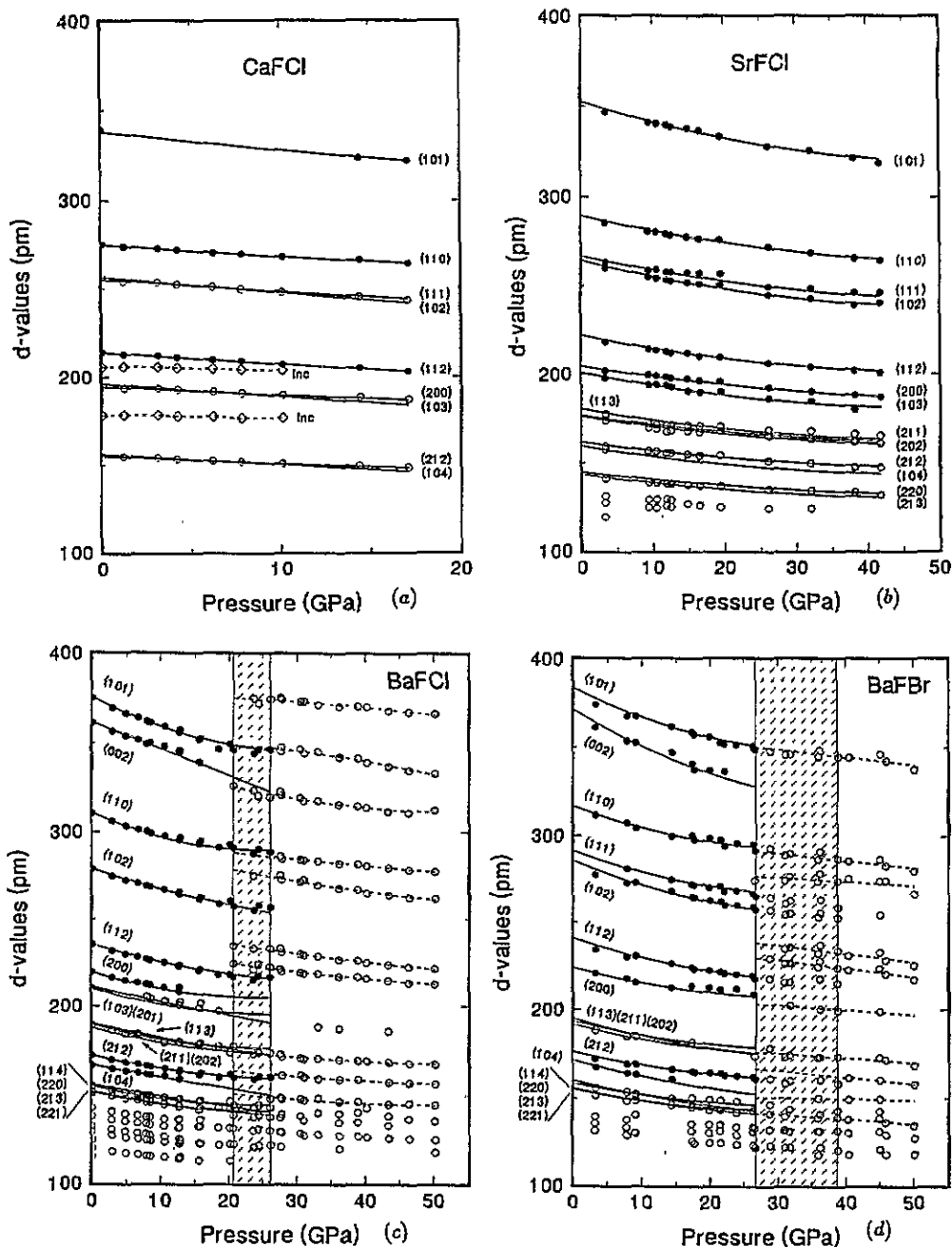


Figure 2. Effect of pressure on the lattice spacings d_{hkl} of (a) CaFCl, (b) SrFCl, (c) BaFCl and (d) BaFBr with indexing for the PbFCl structure. Full circles represent the data used in the evaluation of the lattice parameters and for the comparison of the calculated d_{hkl} values (solid lines) with the other line positions (open circles). The mixture region of two phases is shadowed and dashed lines are guides to the eye only.

[9], which show a strong decrease of c/a up to 5 GPa. On the other hand, single-crystal measurements on BaFCl [8] show also only a slight variation of c/a up to 6.5 GPa, in

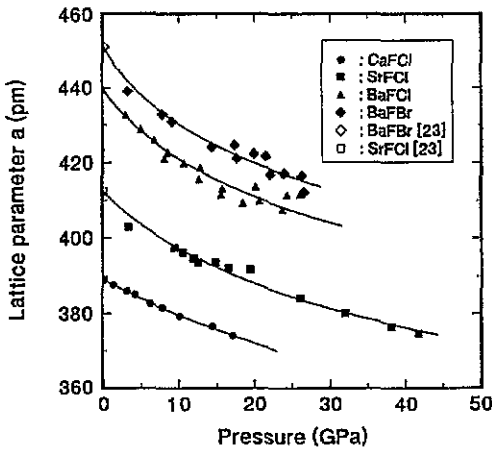


Figure 3. Effect of pressure on the lattice parameter a for CaFCl, SrFCl, BaFCl and BaFBr with least-squares fitting curves.

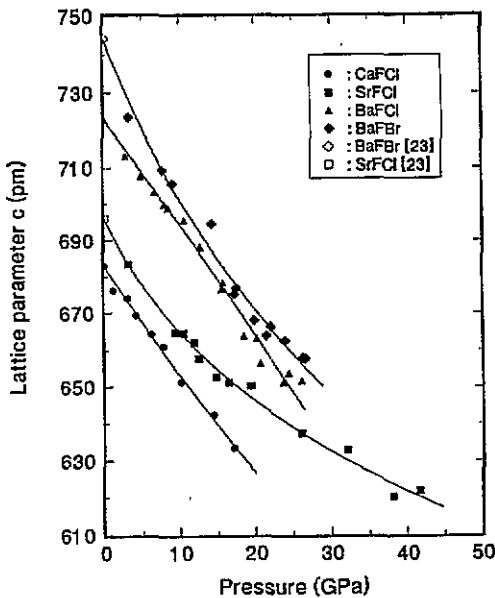


Figure 4. Effect of pressure on the lattice parameter c for CaFCl, SrFCl, BaFCl and BaFBr with least-squares fitting curves.

agreement with the present measurements. Possibly, different preparation methods for the sample material may cause this deviation at low pressure.

Of special interest is the observation of a structural phase transition in BaFCl at about 21 GPa and in BaFBr at about 27 GPa as indicated by the corresponding changes in the spectra in figures 1(c) and 1(d). The d spacings of the new structure are given in figures 2(c) and 2(d). Apparently, the (110) line of the PbFCl structure shows a smooth transition into the high-pressure phase (figures 2(c) and 2(d)) and remains the strongest line of the high-pressure phase (figures 1(c) and 1(d)). The transition region of the two-phase mixture in BaFBr on increasing pressure is somewhat wider than in BaFCl; however, in both cases a

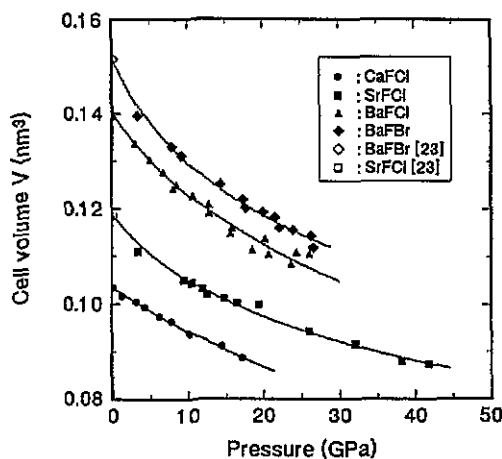


Figure 5. Effect of pressure on the cell volume V of CaFCl, SrFCl, BaFCl and BaFBr with least-squares fitting curves.

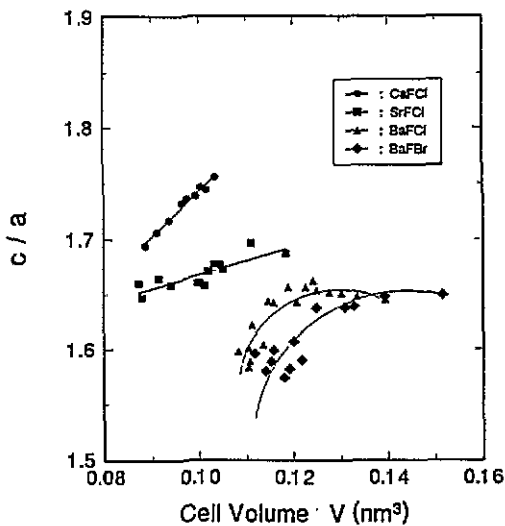


Figure 6. Variation of the c/a ratios for CaFCl, SrFCl, BaFCl and BaFBr versus cell volume V .

hysteresis of about 10 GPa is observed for this transition when the pressure is decreased. The unusual behaviour of the c/a ratio of BaFCl and BaFBr may reflect the instability of the tetragonal structure at high pressure. In the cases of SrFCl and CaFCl, no structural phase transition is observed up to 41 GPa and 27 GPa, respectively.

4. Discussion

4.1. Structural systematics of PbFCl-type compounds

Beside the fluoride halides MF_X there are two other families of compounds which crystallize in the PbFCl-type structure. These are the oxide halides MO_X and the hydride halides MH_X.

The structural systematics of the oxide halides of the lanthanides has been discussed by Bärninghausen *et al* [22]. The structure is formed by layers parallel to (001) each occupied by a single kind of ion. The sequence of the layers is X–M–2O–M–X, where the O layer is doubly occupied with respect to the M and X layers. The lattice parameter a is given by the basal size of the relatively rigid MO coordination polyhedron and is almost independent of the size of the X ions. Only for very large X ions is the lattice parameter a affected by the size of these ions. On the other hand, the lattice parameter c is mainly determined by the size of the X ions. For small ions the XX' double layers partially interpenetrate and the cations are coordinated by five X ions at almost the same distance (cf. figure 7(a)) and four O ions on the other side. For large X (cf. figure 7(b)) the X layers are more closely packed and therefore their interpenetration is reduced. Thereby the M–X' distance increases and the coordination number at the M site is decreased. With increasing X size the structure changes from a coordination lattice to a layered structure with only van der Waals interaction between the XX' double layers [22].

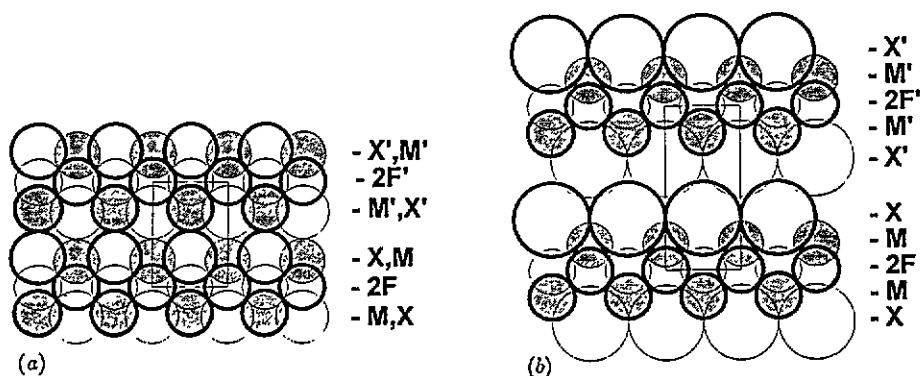


Figure 7. Projection of the PbFCl-type structure in [100] for (a) $r_X/r_M = 1.2$ and (b) $r_X/r_M = 1.66$. With increasing size of the X anion the PbFCl-type structure changes from a coordination variant to a layer variant.

The structural systematics of the fluoride halides MFX and hydride halides MHX is very similar to that of the oxide halides [9, 23, 24]; however, the MF and especially MH coordination polyhedra are less rigid than the MO coordination polyhedra with their partially covalent M–O bonding. Hence, the influence of the X ions on the lattice parameter a is stronger for the fluoride halides and the hydride halides.

A qualitative model for the structural behaviour of the fluoride halides was given in an early work [9]. This is a hard-sphere model with the following additional assumptions: (i) the M–F distance is given by the sum of the corresponding ion radii, (ii) the M tetrahedron around the F ions is undistorted and determines the lattice parameter a as long as the diameter of the X ion is smaller than a , (iii) when the X diameter exceeds the size of the basal plane of the MF coordination tetrahedron, the X diameter determines the lattice parameter a and the MF coordination polyhedron is flattened in order to match the larger lattice parameter a at constant M–F distance. In this model the strength of ‘bondings’ is implicitly given by the manner of construction. Figure 8(a) gives the variation of the c/a ratio with the X size calculated within this model. One can distinguish five regions where the slope $d(c/a)/d(r_X)$ is different due to the changes in the inter-ionic contacts [9]. In regions I–III the lattice parameter a is determined by the MF coordination polyhedron and therefore fixed for a given M. But the lattice parameter c and hence c/a decreases with decreasing size of X. In

region III the gap between the X ions opens and X' moves in the direction of M: hence the strong variation of c/a in region III. In regions I and II the variation of c/a is only due to the opening of the X-M-X coordination angle with decreasing size of X. But in region I this opening is further limited by the X-F contact. In region IV the diameter of X exceeds the size of the basal plane of the MF coordination polyhedron and a is determined by the diameter of X whereas c is almost constant. Therefore c/a decreases with increasing size of X. The value of c/a is also affected by the size of M with respect to the size of Y (O, F, H). For very small cations M a new region II' appears in the structure field diagram (figure 9) in place of region II. The situation in this region is similar to that in region III, but the opening of the X-M-X angle is already limited by the X-F contact.

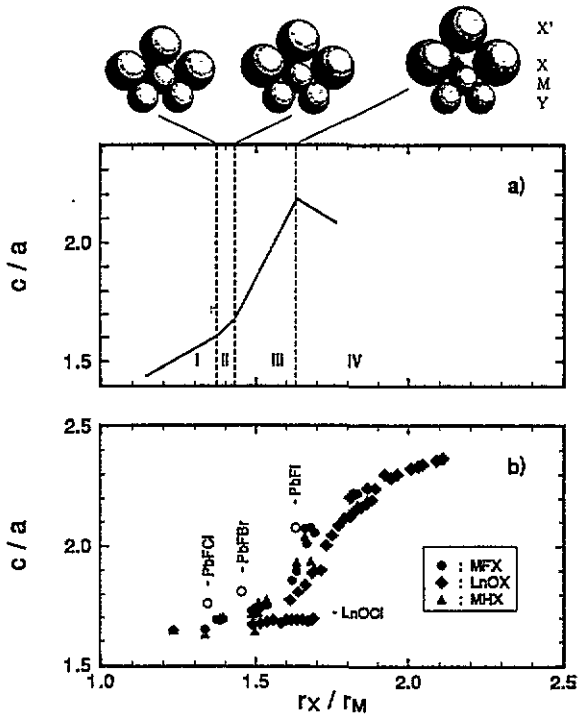


Figure 8. Variation of the c/a ratios of PbFCl-type compounds (PA/nmm) with the relative size (r_X/r_M) of the X anion (a) calculated with a modified hard-sphere model [9] and (b) observed for compounds MFX, MHX and MOX. Top line: M coordination polyhedra for different r_X/r_M ratios; front X anion omitted for clarity.

This geometrical model can be applied in an almost quantitative way and also to the oxide halides and the hydride halides, when one uses a slightly different representation. In order to compare different cations M the relative size of the anions (r_X/r_M) is used instead of the absolute size r_X (figure 8(b)). Most of the compounds with PbFCl-type structure fall close to a line which resembles the calculated curve from the model described above. For such a simple model the agreement is remarkably good, though the great variations in electrostatics, polarizability and softness of the ions are not considered. Only the compounds PbFX show some distinct deviations. Thus purely geometrical aspects are the dominating factors for the structural parameters, with a small systematic shift, however, between the calculated and the observed values. On the other hand, both calculated and observed slopes

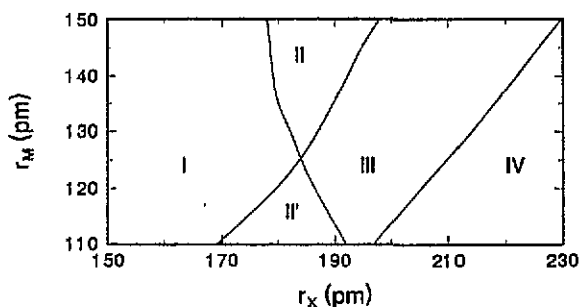


Figure 9. Structure field diagram from the geometrical model for the PbFCl-type compounds.

$d(c/a)/d(r_X/r_M)$ are in good agreement in regions I–III. A decrease of the c/a ratio as predicted by the model for very large X ions is not observed. For very large anions the hard-sphere model fails. This can already be seen from the fact that for example the lattice parameter a of CaFI is smaller than the usually accepted diameter for I ions.

4.2. Structural systematics of PbFCl-type compounds under pressure

At ambient conditions only discrete points in the c/a versus r_X/r_M diagram are given by the various compounds. However, under pressure the r_X/r_M ratio can be varied continuously because the halide anions are approximately ten times more compressible than the di- and trivalent cations under consideration [25]. Figure 10 gives the observed variation of the c/a ratio of some fluoride halides with respect to the relative anion size r_X/r_M under pressure. The ion radii under pressure are calculated from the ion radii [26] and their compressibilities [25]. Despite the fact that the volume compressibilities of these compounds show large differences ($K_0 = 44\text{--}100$ GPa) the variation of the aspect ratio c/a with pressure is given by the same curve in figure 8(b). For large X ions the variation of the c/a ratio with pressure is strong (i) because the r_X/r_M ratio decreases rapidly with increasing pressure owing to the high compressibility of large anions and (ii) because of the rapid drop of the c/a ratio with decreasing r_X/r_M ratio in region III (cf. figure 8(a)). Correspondingly, for compounds with small anions the aspect ratio is almost independent of pressure. However, for the compounds with the smallest r_X/r_M ratio (BaFCl and BaFBr) this observation holds only at low pressure. At higher pressure (decreasing r_X/r_M) the c/a ratio decreases drastically which may be considered as a precursor of the structural instability observed in these compounds at slightly higher pressures.

4.3. Structural transitions under pressure

In BaFCl and BaFBr structural transitions are observed at 21 GPa and 27 GPa, respectively. The stability region of the PbFCl-type structure is thus limited under pressure. Estimates of the ion radii at the transition pressures yield for both compounds a critical ratio of $r_X/r_M \simeq 1$, i.e. the X anion is compressed to the size of the cation. Because the Cl ion is smaller than the Br ion the transition pressure for BaFCl is lower than that for BaFBr. There is no compound MFX which could show this critical value at ambient conditions, because Ba is already the last (stable) element with the largest divalent cation.

The structure of the high-pressure phase could not be identified. Attempts to index the diffraction spectra do not yield satisfactory results.

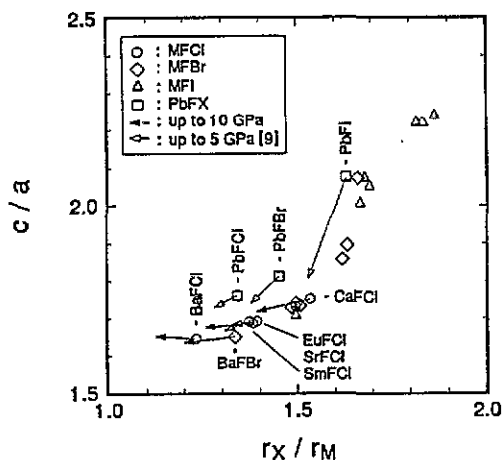


Figure 10. Variation of the c/a ratio versus the r_X/r_M ratio of some MFX compounds under pressure.

Acknowledgments

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References

- [1] Shen Y R, Gregorian T and Holzapfel W B 1991 *High Pressure Res.* 7 73
- [2] Piermarini G J, Block S and Barnett J D 1973 *J. Appl. Phys.* 44 5377
- [3] Jayaraman A 1983 *Rev. Mod. Phys.* 55 65
- [4] Flahaut J 1974 *J. Solid State Chem.* 9 124
- [5] Shen Y R, Gregorian T, Tröster Th, Schulte O and Holzapfel W B 1990 *High Pressure Res.* 3 144
- [6] Gregorian T, Shen Y R, Tröster Th and Holzapfel W B 1991 *Eur. J. Solid State Inorg. Chem.* 28 117
- [7] Shen Y R and Holzapfel W B 1993 *J. Alloys Compounds* 192 53
- [8] Beck H P, Limmer A, Denner W and Schulz H 1983 *Acta Crystallogr.* B 39 401
- [9] Haberkorn R 1988 *Thesis* Friedrich-Alexander-Universität Erlangen-Nürnberg
- [10] Bolduan F, Hochheimer H D and Beck H P 1985 *Phys. Status Solidi b* 127 673
- [11] Syassen K and Holzapfel W B 1975 *Europhys. Conf. Abstr.* A 1 75
- [12] Huber G, Syassen K and Holzapfel W B 1977 *Phys. Rev. B* 15 5123
- [13] Mao H K, Bell P M, Shaner J M and Steinberg D J 1978 *J. Appl. Phys.* 49 3276
- [14] Großhans W A, Düsing E F and Holzapfel W B 1984 *High Temp.-High Pressures* 16 539
- [15] Schulte O and Holzapfel W B 1993 *Phys. Rev. B* at press
- [16] Vohra Y K and Holzapfel W B 1993 *High Pressure Res.* 11 223
- [17] Birch F 1947 *Phys. Rev.* 71 809
- [18] Murnaghan F D 1967 *Finite Deformation of an Elastic Solid* (New York: Dover)
- [19] Holzapfel W B 1991 *Molecular Systems under High Pressure* ed R Pucci and G Piccitto (Amsterdam: Elsevier) p 61; 1991 *Europhys. Lett.* 16 67
- [20] Polian A private communication
- [21] Fischer M, Sieskind M, Polian A and Lahmar A 1993 *J. Phys.: Condens. Matter* 5 2749
- [22] Bärninghausen H, Brauer G and Schultz N 1965 *Z. Anorg. (Allg.) Chem.* 338 250
- [23] Beck H P 1976 *J. Solid State Chem.* 17 275
- [24] Beck H P and Limmer A 1983 *Z. Anorg. (Allg.) Chem.* 502 185
- [25] Narayan R 1979 *Pramāna* 13 559
- [26] Shanon R D 1976 *Acta Crystallogr.* A 32 751