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Effect of Ion Size on the Structure of Mixed Cation and Anion Fluoride Halides

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The systems SrFCl–SrFI, SrFBr–SrFI, SrFCl–BaFCl, SrFBr–BaFBr, and CaFCl–BaFCl were studied and characterized by the Guinier–Hägg X-ray powder diffraction technique. In the first two systems, PbFCl-type solid solutions were observed for $0.0 < x \leq 0.1$ in $SrFCl_xI_{1-x}$ and $0.0 < x \leq 0.4$ and $0.8 \leq x < 1.0$ in $SrFBr_xI_{1-x}$, with diphasic regions elsewhere. In the systems SrFCl–BaFCl and SrFBr–BaFBr, the phase relationships are similar with respect to PbFCl-type solid solutions in the regions $0.0 < x \leq 0.1$ and $0.6 \leq x < 1.0$ for $Sr_xBa_{1-x}FCl$ and $Sr_xBa_{1-x}FBr$. In addition, a previously unreported monoclinic phase exists in the intermediate composition range. In the system CaFCl–BaFCl neither a solid solution region nor an intermediate phase was observed. Lattice parameters are reported for all phases. In addition, an empirical correlation which relates the observed phase relationships to the cell volume parameter $\sigma = (V_2 - V_1)/V_1$, with $V_2 > V_1$, is presented.

Introduction

Lanthanide and alkaline earth fluoridehalides, *MFX*, with M = Ca, Sr, Ba, or a lanthanide and X = Cl, Br, I have been the subject of extensive physiochemical and crystallochemical studies, (e.g., (*1–15*) and references therein). Many additional studies relate to the phosphorescence properties of doped alkaline earth fluoridehalides. These phases all crystallize in the tetragonal (*P4/nmm*), PbFCl-type structure with a layer sequence of $(F\text{–}M\text{–}X\text{–}X\text{–}M\text{–})_n$ along the z axis. Atomic coordinates have been determined for SrFCl (*4, 5*), BaFCl (*3, 5*), CaFCl (*9*), BaFI (*9*), BaFBr (*8, 9, 13*), SmFCl (*8*), YbFCl (*8*), and SrFBr (*8*). The cations and nonfluoride anions are located in position 2*c*, ± $(\frac{1}{4},\frac{1}{4},z)$, and the fluoride anions in position 2*a*, ± $(\frac{3}{4},\frac{1}{4},0)$, corresponding to the setting of the space group *P*4/*nmm* with the origin at 2/*m* (*16*).

The alkaline earth *MFX* compounds were originally reported many years ago (*17*) and phase studies of the MF_2–MX_2 systems have been effected by cooling curve techniques (*18, 19*). Although such data provide evidence only for the *MFX*-type fluoridehalides and for solid solutions between MX_2, *MFX*, and MF_2, Fessenden and Lewin have reported preparation and characterization of rhombohedral (a = 11.4 Å, α = 107°20′) barium chloride trifluoride (Ba_2ClF_3), a phase that they indicated

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could not be prepared from the melt (*20*). In our studies of selected PbFCl-type fluoride halides which contain equimolar mixtures of either two cations or two nonfluoride anions, i.e., $SrFCl_{0.5}Br_{0.5}$ or $Ca_{0.5}Sr_{0.5}FCl$ (*21*), we found, as expected, that when the ionic sizes were similar the different cations randomly occupied the cation sites and the chlorine, bromine, and iodine atoms randomly occupied the nonfluoride anion sites. But when the size of the substituting ions differed significantly, our attempts to prepare $MFX_xX'_{1-x}$ and $M_xM'_{1-x}FX$ phases, i.e., $SrFCl_{0.5}I_{0.5}$ and $Ca_{0.5}Ba_{0.5}FCl$, were unsuccessful. These observations suggested that for these latter species solid solutions do not exist. There thus seemed to be a size limit beyond which PbFCl-type solid solutions do not form. In an attempt to determine this limit and to develop an empirical correlation scheme systematic studies of the systems SrFCl–SrFI, SrFBr–SrFI, SrFCl–BaFCl, SrFBr–BaFBr, and CaFCl–BaFCl were undertaken.

Experimental

All of the systems listed above were investigated over the full composition range. Samples were prepared on the basis of the following three hypothetical equations:

$$SrF_2 + xSrX_2 + (1 - x)SrI_2 = 2SrFX_xI_{1-x}\ (0 < x < 1.0) \quad (1)$$

$$0.5\ MX_2 + (0.5 - x)MF_2 + xBaF_2 = M_{1-x}Ba_xFX\ (0 < x < 0.5) \quad (2)$$

$$xMX_2 + (0.5 - x)BaX_2 + 0.5\ BaF_2 = M_xBa_{1-x}FX\ (0 < x < 0.5). \quad (3)$$

In all the equations, X = Cl or Br; in Eqs. (2) and (3), M = Ca or Sr. All reactants except $CaCl_2$ and CaF_2 were obtained from Cerac, Inc., Milwaukee, Wisconsin. CaF_2 was obtained from Matheson, Coleman and Bell, Norwood, Ohio, and $CaCl_2$ from Mallinckrodt, St. Louis, Missouri. After being heated under vacuum at 400°C, the reactants were found pure by X-ray powder diffraction analysis. All subsequent reactant and product manipulations were effected in an argon-filled glove box. Reactants were weighted according to requisite stoichiometric ratios to yield composition variations of $x = 0.1$. The samples, all of which had a total weight of 1g, were ground together in an agate mortar, confined in recrystallized Al_2O_3 boats, and heated in an atmosphere of dried argon in a tube furnace. The heating cycle consisted of (a) annealing at 750° for 4 hr, (b) heating to 1100°C (above the melting points of MFX compounds), and (c) cooling to room temperature at a constant rate of 60°C/hr.

Pulverized portions of the products were examined by X-ray diffraction techniques. Interplanar *d* spacings were determined from Guinier–Hägg photographs. Platinum powder (a = 3.9237(1) Å, at 24 ± 2°C) was used as an internal calibrant. The lattice parameters were determined by a linear regression procedure (*22*). For selected samples diffractograms were also obtained with a Siemens X-ray powder diffractometer with Ni-filtered copper $K\alpha$ radiation at a scan rate of 0.5°/min. Reflection intensity data were obtained by averaging the three data sets collected from each sample by the height-half-width procedure.

Theoretical powder diffraction intensities were calculated to determine if chlorine, bromine, or iodine substitution occurred at the fluorine site. Calculations were effected on a CDC CYBER 750 computer with the program ANIFAC (*23*) for selected $SrFX_xX'_{1-x}$ phases by using z atomic parameter values of 0.20 and 0.64, respectively, for M and X, based upon data reported for SrFCl and BaFCl (*5*). Scattering factors with appropriate dispersion correction terms were taken from the *International Tables* (*24*). Absorption effects were not considered in the calculations.

Selected specimens were examined in a

Phillips EM300 electron microscope operated at 100 kV. The specimens were ground thoroughly in the glove box with a mortar and pestle, mixed with EM grade acetone, and sonicated for 3 min. A holey carbon grid was swept through the acetone solution, transferred in the laboratory atmosphere to the goniometer, and inserted quickly into the microscope.

Results and Discussion

SrFCl–SrFI and SrFBr–SrFI System

The results obtained for these systems are summarized in Table I and Fig. 1. The major portion of the SrFCl–SrFI system is diphasic, consisting of SrFCl and $SrFCl_{0.1}I_{0.9}$. Solid solubility occurs only near the SrFI end member over the limited composition range $0.0 < x < 0.1$ in $SrFCl_xI_{1-x}$. The SrFBr–SrFI system is similar, but solid solution occurs at both ends of the system. The two phase region extends only over the range $0.4 < x < 0.8$. Comparison of the experimental and theoretical X-ray powder diffraction intensities for the $SrFCl_{0.1}I_{0.9}$, $SrFBr_{0.8}I_{0.2}$, and $SrFBr_{0.4}I_{0.6}$ phases indicates clearly both that the individual X atoms (X = Cl, Br, or I) substitute randomly into the specific X sites for these layers and that the fluorine layer sites are not occupied by the other halide ions.

In Table I the lattice parameters and the cell volumes are compiled for various compositions of $SrFBr_xI_{1-x}$. The effect of the anion size differences is apparent in the cell volume data. The cell volume increases by 34% from the smaller anion terminus to the iodide rich terminus of the two phase region

TABLE I

LATTICE PARAMETERS AND CELL VOLUMES FOR THE TETRAGONAL $SrFCl_xI_{1-x}$ AND $SrFBr_xI_{1-x}$ PHASES

Composition	a(Å)	c(Å)	V(Å^3)	Comment	Reference[a]
SrFCl	4.124(9)	6.959(3)	118.4		(*4*)
	4.125(8)	6.957(9)	118.4	single phase	(*5*)
	4.129(2)	6.966(4)	118.8		(*6*)
	4.126(4)	6.959(4)	118.5		
$SrFCl_xI_{1-x}$ for $0.1 < x < 1$				two phases	
$SrFCl_{0.1}I_{0.9}$	4.233(2)	8.826(8)	158.2	single phase	
$SrFCl_{0.05}I_{0.95}$	4.243(6)	8.830(1)	159.0	single phase	
SrFI	4.254(2)	8.849(4)	160.2	single phase	
	4.253(2)	8.833(7)	159.8		(*6*)
SrFBr	4.218(6)	7.342(5)	130.7		(*34*)
	4.218(2)	7.337(5)	130.5	single phase	(*6*)
	4.220(6)	7.336(5)	130.7		(*7*)
	4.217(8)	7.337(0)	130.5		
$SrFBr_{0.9}I_{0.1}$	4.221(0)	7.367(9)	131.3	single phase	
$SrFBr_{0.8}I_{0.2}$	4.223(4)	7.399(4)	132.0	single phase	
$SrFBr_xI_{1-x}$ for $0.4 < x < 0.8$				two phases	
$SrFBr_{0.4}I_{0.6}$	4.232(3)	8.292(8)	148.5	single phase	
$SrFBr_{0.2}I_{0.8}$	4.241(6)	8.562(4)	154.0	single phase	
SrFI	4.254(2)	8.849(4)	160.2	single phase	

[a] This work, except as noted.

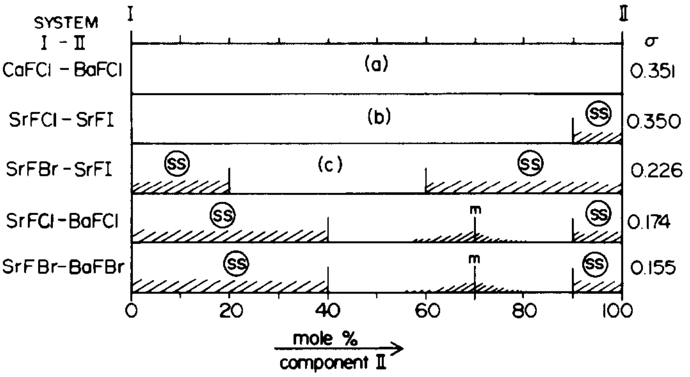

FIG. 1. Phase relationships in some (MFX)–$(MFX)'$ systems. In this figure ss represents a region of solid solution, m represents a monoclinic distortion of the PbFCl-type structure, a represents a polyphasic system with no solid solution, and b and c represent diphasic regions.

for the SrFCl–SrFI system, but only 12.5% for the SrFBr–SrFI system. The reduced solid solution solubility limits in the SrFCl–SrFI system no doubt result from the great size disparity between the ions (1.67 and 2.06 Å, respectively, for chloride and iodide ions (*25*)). The fact that solubility occurs only on the SrFI side is indicative of the ability of the structure to accomodate a limited number of smaller ions in the iodide sites. The interatomic Sr–Cl distance, 3.10 Å (*5*), is close to the sum of the Sr^{2+} and Br^- radii (3.14 Å). Hence preparation of $SrFCl_xBr_{1-x}$ phases (*21*) with a random distribution of chlorine and bromine atoms is possible, but preparation of similar $SrFCl_xI_{1-x}$ phases at normal temperature and pressure conditions is impossible. Similar difficulties were observed for the $PbCl_2$–PbI_2 system (*26*).

SrFCl–BaFCl and SrFBr–BaFBr Systems

As might be expected, the $SrFX$–$BaFX$ systems (X = Cl, Br) are also similar. The X-ray powder diffraction patterns of the products show solid solution regions for both systems in the composition ranges near the termini with $0.6 \leq x < 1.0$ and $0 < x \leq 0.1$ for $Sr_xBa_{1-x}FX$. Lattice parameters of selected phases are compiled in Table II. In the composition region between the solid solution limits, selected X-ray diffraction reflections are split into multiplets. This splitting, which varies as a function of composition, produces the sharpest reflections near $x = 0.3$ for $Sr_xBa_{1-x}FX$, and its character at this composition is presented graphically in Fig. 2. From an analysis of the diffraction patterns for samples of this composition it was concluded that the phase is identical in both systems, and that it exhibits monoclinic symmetry. Lattice parameters calculated by linear regression analysis (*22*) of 16 coincidence-free reflections are presented in Table II (in the first monoclinic setting to illustrate the distortion in the *ab* plane). In Table III the observed reflection intensities and the experimental and calculated interplanar *d* spacings are listed.

The nature of the symmetry change is such that the axis perpendicular the layers, the tetragonal *c* axis, must possess as a maximum C_2 symmetry. A plot of the $Sr_xBa_{1-x}FCl$ *c* parameter against composition, x, fits the linear equation, $c = 7.222 - 0.263x$, with an r^2 value of 1.000. A plot of cell volume against composition fits the linear equation, $V = 139.47 - 20.898x$, with an r^2 value of 0.999. These relationships are

TABLE II

LATTICE PARAMETERS AND CELL VOLUMES FOR THE TETRAGONAL AND MONOCLINIC $Sr_xBa_{1-x}FCl$ AND $Sr_xBa_{1-x}FBr$ PHASES

Composition	a(Å)	b(Å)	c(Å)	γ (deg.)	V(Å^3)	Reference[a]
SrFCl	4.126(4)		6.959(4)		118.5	
$Sr_{0.9}Ba_{0.1}FCl$	4.151(9)		6.986(3)		120.4	
$Sr_{0.8}Ba_{0.2}FCl$	4.189(8)		7.011(6)		123.1	
$Sr_{0.7}Ba_{0.3}FCl$	4.211(9)		7.037(4)		124.8	
$Sr_{0.6}Ba_{0.4}FCl$	4.238(1)		7.064(8)		126.9	
$Sr_{0.3}Ba_{0.7}FCl$	4.344(6)	4.300(7)	7.143(6)	91.43(7)[b]	133.4	
$Sr_{0.1}Ba_{0.9}FCl$	4.370(4)		7.197(7)		137.5	
BaFCl	4.390(9)		7.220(1)		139.2	
	4.393(9)		7.224(8)		139.5	(*5*)
	4.391(3)		7.226(4)		139.4	(*6*)
SrFBr	4.217(8)		7.337(0)		130.5	
$Sr_{0.9}Ba_{0.1}FBr$	4.241(7)		7.350(5)		132.2	
$Sr_{0.8}Ba_{0.2}FBr$	4.273(6)		7.361(4)		134.4	
$Sr_{0.7}Ba_{0.3}FBr$	4.310(8)		7.370(0)		137.0	
$Sr_{0.6}Ba_{0.4}FBr$	4.340(5)		7.379(8)		139.0	
$Sr_{0.3}Ba_{0.7}FBr$	4.448(7)	4.423(7)	7.408(2)	90.40(6)[b]	145.7	
$Sr_{0.1}Ba_{0.9}FBr$	4.482(1)		7.434(9)		149.4	
BaFBr	4.502(8)		7.436(1)		150.8	
	4.503(2)		7.435(4)		150.8	(*8*)
	4.508(4)		7.441(15)		151.2	(*9*)

[a] This work, except as noted.

[b] First monoclinic setting (*16*).

considered as evidence that the stacking present in the basic structure persists in the monoclinic-distorted structure. The absence of an identifiable two phase region and the observation that the distortion increases gradually, reaches a maximum near the middle of the monoclinic composition region, and then slowly recedes, are taken

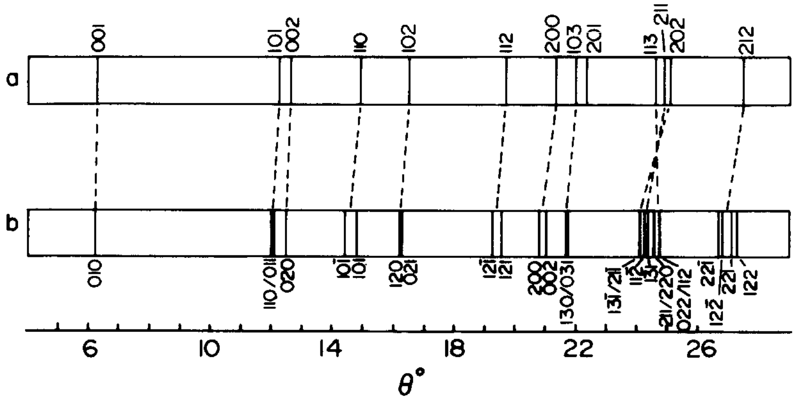

FIG. 2. Changes that occur in the X-ray diffraction pattern of an $Sr_xBa_{1-x}FX$ phase upon transformation from tetragonal (a) to monoclinic (b) symmetry. (Indices are expressed in the second setting.)

TABLE III

OBSERVED AND CALCULATED INTERPLANAR *d* SPACINGS (Å) AND OBSERVED INTENSITIES FOR MONOCLINIC $Sr_{0.3}Ba_{0.7}FX$ (X = Cl, Br)

$Sr_{0.3}Ba_{0.7}FCl$				$Sr_{0.3}Ba_{0.7}FBr$		
$d_{exp.}$	$d_{calc.}$	I/I^0	hkl^a	$d_{exp.}$	$d_{calc.}$	I/I^0
7.09	7.143	6	010	7.405	7.408	5
3.706	3.711	10	110	3.812	3.813	10
3.676	3.683	8	011	3.796	3.798	5
3.565	3.571	12	020	3.704	3.704	10
3.093	3.094	25	$10\bar{1}$	3.149	3.148	30
3.016	3.017	30	101	3.129	3.126	40
2.759	2.759	100	120	2.847	2.846	100
2.749	2.747		021	2.839	2.840	
2.337	2.338	25	$12\bar{1}$	2.400	2.399	15
2.303	2.305	20	121	2.390	2.389	18
2.170	2.171	25	200	2.224	2.224	25
2.149	2.149	30	002	2.212	2.212	35
2.089	2.088	17	130	2.159	2.159	15
2.083	2.083		031	2.157	2.156	
1.8880	1.8886	12	$21\bar{1},13\bar{1}$	1.9430	1.9429	10
	1.8872		$13\bar{1},131$	1.9371	1.9377	
1.8768	1.8777	6	$11\bar{2},21\bar{1}$	1.9252	1.9244	5
1.8691	1.8694		$131,11\bar{2}$	1.9189	1.9184	5
1.8542	1.8556	6	220,211	1.9140	1.9143	
	1.8534		211,112	1.9073	1.9084	15
1.8426	1.8431	20	112,220		1.9069	
	1.8418		022	1.8989	1.8991	

[a] Expressed in second monoclinic setting (*16*).

as indications of the absence of a discrete phase change associated with the transition. Thermochemical measurements will clearly be necessary to verify this hypothesis.

It is appealing to explain the nonorthogonal angle and the differing *a* and *b* parameters on the basis of cation ordering. The monoclinic distortion begins when $\frac{1}{2}$ the cation sites are filled with the larger cation, reaches a maximum when $\frac{3}{4}$ of the sites are so filled, and then decreases. A comparison of interatomic distances in SrFCl (*5*) with crystal radii (*25*) indicates that the ions are in direct contact. Thus, since the radius of Ba^{2+} is 0.16 Å greater than that of Sr^{2+} (*25*), substitution of Ba^{2+} for Sr^{2+} should create some internal pressure as has been observed in other systems (*27*). One can envision a process in which barium atoms replace strontium atoms in the lattice. When about half the cation sites have been filled with the larger atom, the layer rearranges into an ordered array to facilitate packing and to relieve internal strain. Such an arrangement might have Ba atoms situated along the face diagonal of the square array. Further substitution increases the distortion until $\frac{3}{4}$ of the sites are filled with the larger cation. Beyond that composition some regions of the structure must approximate the normal PbFCl-type structure, and the distortion must decrease, ultimately yielding a PbFCl-type solid solution region. If the domain size is very small, superstructure reflections would not be expected in the X-ray diffraction pattern; indeed, the Guiner–Hägg patterns in the composition region $0.3 < x < 0.6$ were more diffuse than normal.

Six different electron diffraction zones were examined in the microscope. (The tendency of the crystallites to exhibit preferred orientation limited the number of zones that could be aligned.) Evidence for superstructure reflections was not apparent in any of the zones examined.

CaFCl–BaFCl System

Only mixtures were observed in this system: CaFCl, CaF_2, and $BaCl_2$ form on the calcium rich side and CaF_2, $BaCl_2$, and BaFCl form on the Ba rich side. For $x = 0.5$ a mixture of fluorite-type CaF_2 and the orthorhombic α phase of $BaCl_2$ was obtained. The lattice parameters of all compounds are constant over the entire composition region, indicative of the absence of solid solution between the individual compounds. The melting of a 1 : 2 stoichiometric mixture of $CaCl_2$ and BaFCl also yielded a mixture of CaF_2 and $BaCl_2$. From both of these procedures products with lattice parameters very close to those reported in the literature (Table IV) were obtained.

From these experiments it must be concluded that CaFCl does not react with BaFCl to form homotypic mixed crystals even though the compounds are isostructural.

Summary

It is apparent from the experiments reported herein that the behavior of mixed PbFCl-type fluoride halides varies from complete miscibility to complete immiscibility. Havighurst *et al.* (*28*) examined a series of cubic pseudobinary halides having a common ion and developed a correlation which relates solid solution or mixed crystal formation from aqueous solution to lattice parameter differences. A related relationship based upon the volume difference of the fluoride halide parent cells is presented in Table V. In this relationship the parameter, σ, is computed as $(V_2 - V_1)/V_1$,

TABLE IV

LATTICE PARAMETERS AND VOLUMES PER CATION OF PHASES OBSERVED IN THE CaFCl–BaFCl SYSTEM WITH APPROPRIATE LITERATURE VALUES

x (mole fract. Ca)	Phase(s)	a(Å)	b(Å)	c(Å)	V/z(Å^3)	Comments	Reference[a]
1.0	CaFCl	3.889(4)		6.823(1)	51.60	single phase	
		3.894(3)		6.818(20)			(*9*)
		3.894(3)		6.809(6)			(*6*)
$0.5 < x < 1$		CaFCl + CaF_2 + $BaCl_2$				mixture	
0.5	$BaCl_2$	7.875(2)	4.736(0)	9.422(9)	43.92	two phases	
	and	7.865(8)	4.731(4)	9.421(8)			(*30*)
	CaF_2	5.462(4)			40.75		
		5.462(6)					(*33*)
$0.0 < x < 0.5$		CaF_2 + $BaCl_2$ + BaFCl				mixture	
0.0	BaFCl	4.392(0)		7.225(0)	69.70	single phase	
		4.391(3)		7.226(4)			(*6*)
		4.393(9)		7.224(8)			(*5*)

[a] This work, except as noted.

TABLE V

Correlation between Anion or Cation Substituted Fluoride Halide Systems and Volume Difference of Parent Species

System	σ[a]	Comment[b]	References[c]
SrFBr–EuFBr	0.004	Complete ss	(*21*)
CaFCl–YbFCl	0.026	Complete ss	(*21*)
SrFCl–SrFBr	0.104	Complete ss	(*21*)
CaFCl–SrFCl	0.146	Complete ss	(*21*)
SrFBr–BaFBr	0.155	ss + monoclinic distortion	
SrFCl–BaFCl	0.174	ss + monoclinic distortion	
SrFBr–SrFI	0.226	ss for $0.2 \leq [I] \leq 0.6$	
SrFCl–SrFI	0.350	ss for $[I] < 0.9$	
CaFCl–BaFCl	0.351	no solubility	

[a] $\sigma = (V_2 - V_1)/V_1$ with $V_2 > V_1$.

[b] ss = solid solution.

[c] This work, except as noted.

with $V_2 > V_1$. In this equation V_2 and V_1 represent the volumes of the unit cells of the parent structure. It is seen from these data that as the quantity "σ" increases the systems change from solid solution, first, to the monoclinic distortion, subsequently, to a progressively smaller solid solution region, and ultimately, to insolubility. Although data are not available to substantiate that a monoclinic distortion will result from the presence of different sized anions, such behavior is to be expected on the basis of the layered nature of the parent structures.

Brauer and Müller (*29*) studied the $SrCl_2$–$BaCl_2$ system and obtained a cubic symmetry solid solution for up to ~23 mole% $BaCl_2$, followed by a narrow two phase region, and finally, at 30 mole% $BaCl_2$, the orthorhombic symmetry of the $BaCl_2$ structure type. That the volume difference relationship developed for the PbFCl-type structure is specifically applicable only to a common structure type is demonstrated by applying it to this system. The parameter σ, derived from the volume of $BaCl_2$ (*30*) and $SrCl_2$ (*31*), is 0.023. As such, complete solid solution would be expected. However, if the volume of $PbCl_2$-type (high pressure (*32*) form, stable at atmospheric pressure once formed) $SrCl_2$ is used, $\sigma = 0.145$, a value very close to the region of the monoclinic distortion observed for the PbFCl-type structure.

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