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The Alkali-Poor Part of the Pseudoternary Triangle $AX/BX_2/MX_3$: Crystal Structures, Properties, and Potentials of (Alkali)/Alkaline-Earth/Rare-Earth Chloride Materials

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Halides of mono-, di-, and trivalent metals of the general formulas AX, BX_2, and MX_3 may react with each other, forming a large variety of ternary and even quaternary phases in the solid state. Aside from the alkali-poor quaternary chlorides of the $ABMX_6$ type, which are derivatives of the UCl_3 type of structure, the alkali cation free pseudoternary chlorides that form in the systems BCl_2/MCl_3, especially with B = Ba, are reviewed. Examples of ternary chlorides are Ba_2EuCl_7, with isolated $[EuCl_7]$ monocapped trigonal prisms; $Ba_2Cl[ScCl_6]$, with isolated octahedra $[ScCl_6]$ and lonesome Cl^-; $Ba_8[\{(Sm_6)Z\}Cl_{32}]$, and $Ba_9[\{(Sm_6)Z\}Cl_{34}]$, with Z being presumably an oxide ion residing in the large hole of the $[Sm_6Cl_{36}]$ polyhedral clusters that occur in these fluorite type superstructures; and, finally, $BaGdCl_5$, with corrugated layers of edge-connected $[GdCl_8]$ square antiprisms. These halides may be cationic conductors ($AgSrSmCl_6$), insulating mixed-valence halides such as $NaNd_2Cl_6$, or semiconductors such as Pr_2Br_5 with interesting magnetic ordering at lower temperatures, or they may serve as hosts for luminescent ions. Ba_2ErCl_7, for example, is an efficient near-infrared to near-ultraviolet upconversion material.

Contents

Introduction

At ambient conditions, all of the rare-earth elements M (Sc, Y, La, Ce−Lu) form trihalides, MX_3 (X = F, Cl, Br, I), with the exception of EuI_3, where EuI_2 is more stable. They adopt a small number of crystal structure types with coordination numbers between 11 and 6, where the ratio of the ionic radii of M^{3+} and X^- plays an important role. Considering chlorides alone, the problem may be reduced to the lanthanide contraction, and the coordination numbers and structure types are as follows: 9-coordination and UCl_3 type structure for $LaCl_3$ through $GdCl_3$, 8-coordination and $PuBr_3$ type structure for $TbCl_3$, and 6-coordination for M = Dy−Lu, including Y ($AlCl_3/YCl_3$ type), as well as for M = Sc ($FeCl_3/BiI_3$ type).[1]

The binary rare-earth chlorides, MCl_3, may react with other binary chlorides, ACl, with A being in principle any monovalent cation, especially Li−Cs, Ag, In, Tl, NH_4, or BCl_2, with B being any divalent cation, particularly from alkaline-earth elements (Ca, Sr, Ba,) or (potentially truly divalent) rare-earth elements (Eu, Yb, Sm, Tm, Nd, Dy), to form ternary chlorides. The edges of the triangle of the pseudoternary system $AX/BX_2/MX_3$ in Figure 1 exhibit the compound types that have been found in the ternary systems AX/MX_3, BX_2/MX_3, and AX/BX_2 and for which at least for one example of a crystal structure determination has been reported.

Much work has been done during the last 2 decades to explore the AX/BX_2 and AX/MX_3 type systems.[2,3] Composition/temperature phase diagrams were determined, (in most cases small) crystals grown, and crystal structures solved. Physical properties were investigated to a lesser extent, although in some sample cases magnetic properties were followed, as were spectroscopic properties that hint at potential uses in laser or upconversion materials.

At the MCl_3-rich side of especially the $NaCl/MCl_3$ systems with M = La−Sm, a curious phase width was found that could be rationalized as substitution of M^{3+} by Na^+ and, for electroneutrality, addition of further Na^+ into interstices that are empty in the parent UCl_3 type structure in the [00.1] direction, according to the general formula $A_{2x}(A_xM_{2-x})X_6$. M^{3+} may also be substituted by B^{2+}, as the example of $Na(BaLa)Cl_6$ may show. In other words, the pseudoternary system $AX/BX_2/MX_3$ also contains the quaternary halides $ABMX_6$. Attempts to sort out the boundaries of the existence of the $ABMX_6$ type derivatives of the UCl_3 type of structure

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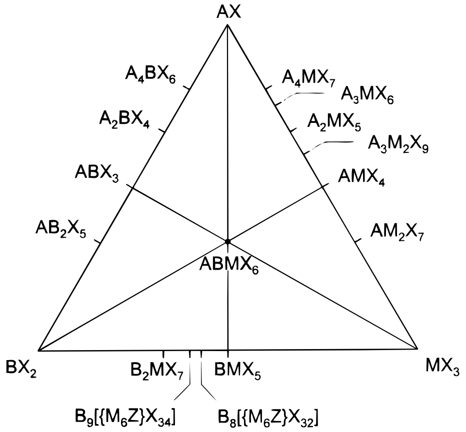
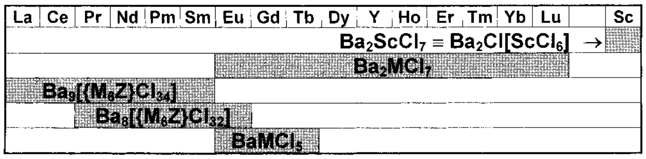


Figure 1. The pseudoternary system $AX/BX_2/MX_3$.



La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu		Sc
																$Ba_2ScCl_7 \equiv Ba_2Cl[ScCl_6]$ →	▨
						▨ Ba_2MCl_7	▨	▨	▨	▨	▨	▨	▨	▨	▨		
▨ $Ba_9[\{M_6Z\}Cl_{34}]$	▨	▨	▨	▨	▨												
		▨ $Ba_8[\{M_6Z\}Cl_{32}]$	▨	▨	▨	▨											
						▨ $BaMCl_5$	▨	▨									

Figure 2. Compound formation in the $BaCl_2/MCl_3$ type systems.

led us to a closer inspection of the BX_2/MX_3 type systems.[4] For the $BaCl_2/MCl_3$ type systems, we were successful in the determination of crystal structures of four types of compounds, i.e., B_2MX_7, $B_9[\{M_6Z\}X_{34}]$, $B_8[\{M_6Z\}X_{32}]$ (for Z, see below), and BMX_5 (Figures 1 and 2).

The UCl_3 Type of Structure and Its Chloride Derivatives

The UCl_3 type of structure may be considered as a distorted variant of a hexagonal closest packing of spheres of the general composition MX_3. The distortion originates from the different sizes of M^{3+} and X^- and yields a reduction of the coordination number of M^{3+} from 12 (anticuboctahedron) to 9 (tricapped trigonal prism; see Figure 3). In the UCl_3 type of structure, the $[MX_9]$ polyhedra share common faces in the [00.1] direction of the hexagonal unit cell (space group *P*6$_3$/*m*). The columns thereby formed are shifted against each other parallel to [00.1] by $^1/_2c$, so the caps of each column are also corners of the trigonal prisms of the three surrounding columns. Each X^- ligand then has three M^{3+} as nearest neighbors, in accord with the formulation $MX_{9/3}$.

The unit cell contains two formula units of MX_3. The cell content is therefore M_2X_6. As Figure 4 shows, there are empty channels parallel to [00.1]. In principle, one has four positions for additional cations, crystallographically the positions (2a) 0,0,$^1/_4$ and (2b) 0,0,0 in space group *P*6$_3$/*m* (No. 176). These positions represent a heavily compressed octahedron (2b) and an equatorially heavily compressed tricapped trigonal prism (Figure 5). The distances between the centers of the channels are $^1/_4c$ (2a−2b) and $^1/_2c$ (2a−2a or 2b−2b), respectively. With the lattice constant *c* between 415 and 450 pm in these chlorides (Table 1), it becomes clear that these positions can only be partially occupied. In general, one finds a maximum occupation of one per cell content, hence the formula AM_2X_6.

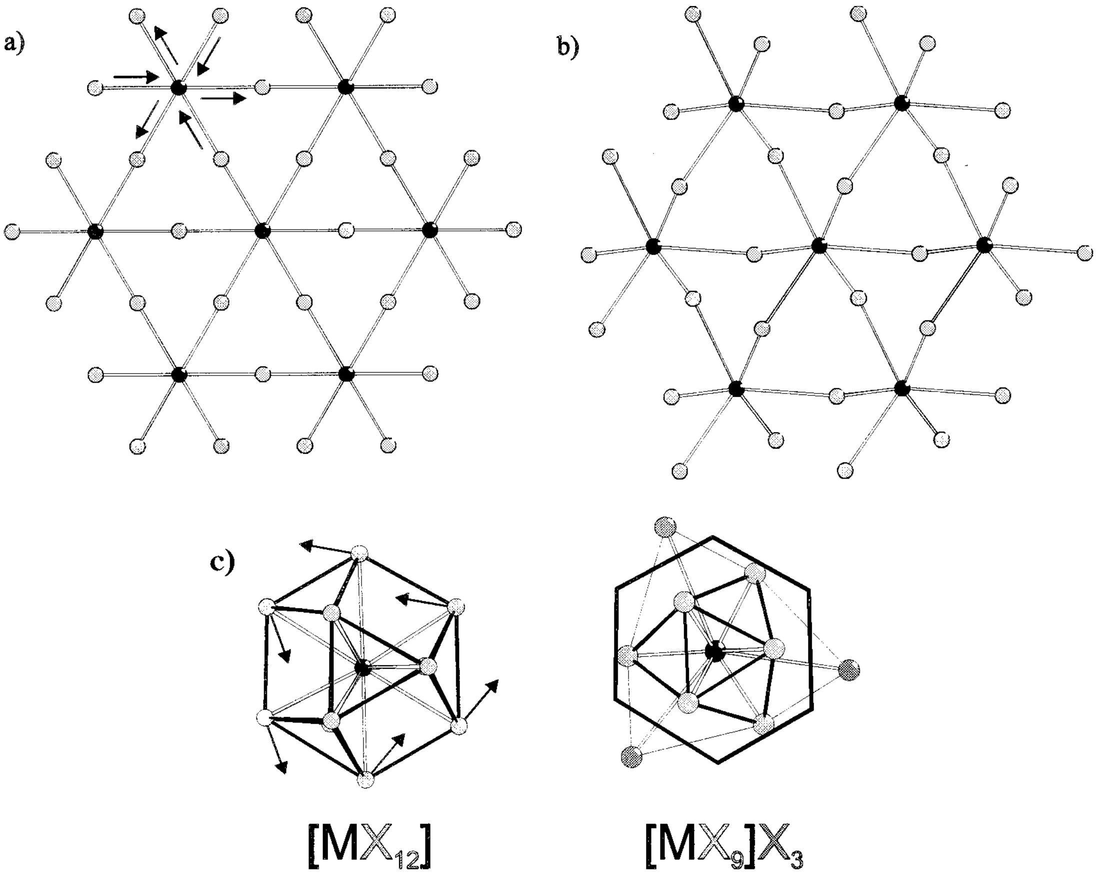


Figure 3. The distortion of one layer of a closest packing of spheres of the composition MX_3 and the accompanying reduction of the coordination number of M from 12 to 9.

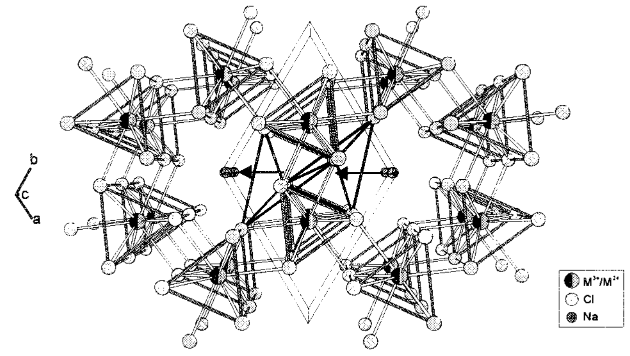


Figure 4. View onto (00.1) exhibiting the $[MX_{9/3}]$ columns and their surrounding in the UCl_3 type of structure. Additional cations in the channels parallel to [00.1] are also shown; the arrows indicate possible pathways for cation diffusion through neighboring tetrahedral interstices.

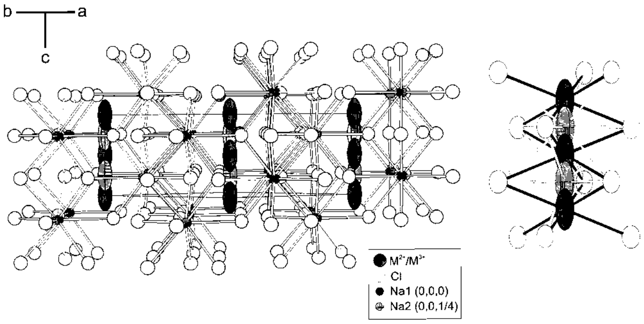


Figure 5. A side view of the crystal structure of UCl_3 with additional Na^+ ions indicated by their elongated thermal ellipsoids in the channels parallel to [00.1] on 2b (0,0,0) and 2a (0,0,$^1/_4$) sites of space group $P6_3/m$.

Table 1. UCl_3 Type Derivative Chlorides

$A(M_2)X_6$	*a*, pm	*c*, pm	ref
$K_{0.64}(K_{0.34}La_{1.66})Cl_6$	785.7(1)	430.9(1)	14
$Na_{0.727}(Na_{0.364}La_{1.637})Cl_6$	759.17(4)	437.91(3)	6
$Na(BaLa)Cl_6$	767.9(4)	454.0(4)	13
$Ag(BaLa)Cl_6$	762.3(5)	452.9(5)	13
$Na_{0.76}(Na_{0.386}Ce_{1.616})Cl_6$	757.07(4)	431.56(3)	5
$Na_{0.70}(Na_{0.349}Ce_{1.651})Cl_6$	756.38(4)	431.79(3)	6
$Na(U^{3+}{}_2)Cl_6$	756.09(3)	431.43(3)	9
$Na_{0.64}(Na_{0.318}Pr_{1.681})Cl_6$	755.4(1)	427.6(2)	6
$Na(Pr^{3+}{}_2)Cl_6$	756.77(5)	429.34(4)	7
$Pr_{0.58}(Pr^{3+}{}_2)Cl_6$	741.7(1)	427.2(1)	11
$Na_{0.608}(Na_{0.305}Nd_{1.789})Cl_6$	754.21(4)	424.00(3)	6
$Na(Nd^{2+}Nd^{3+})Cl_6$	762.60(5)	438.66(4)	7
$Na_{0.491}(Na_{0.246}Sm_{1.754})Cl_6$	750.7(1)	415.9(2)	6
$Na(Sm^{2+}Sm^{3+})Cl_6$	756.14(7)	433.26(6)	6
$Na(SrSm)Cl_6$	758.9(1)	430.2(1)	13
$Ag(SrSm)Cl_6$	757.3(5)	431.8(6)	13
$Na(Eu^{2+}Eu^{3+})Cl_6$	755.74(8)	429.81(5)	12
$Na_{0.75}(Eu^{2+}{}_{0.75}Eu^{3+}{}_{1.25})Cl_6$	753.69(11)	416.3(2)	12
$Na(SrEu)Cl_6$	757.8(1)	429.7(1)	13
$Ag_{0.81}(Sr_{0.79}Eu_{1.21})Cl_6$	749.00(10)	429.00(15)	13

One may consider three categories of derivatives of the UCl_3 type of structure.

Category 1. For those lanthanide chlorides that crystallize with the UCl_3 type of structure ($LaCl_3$ through $GdCl_3$), the systems ACl/MCl_3 are apt to form "solid solutions" at the ACl-poor side of the systems, especially when ACl is NaCl. These have the general formula $Na_{2x}(Na_xM_{2-x})Cl_6$ with, on one hand, Na^+ substituting M^{3+} and, on the other hand, Na^+ ions being incorporated into the channels parallel to [00.1]. The amount of Na^+ substituted and added decreases with decreasing size of the M^{3+} ions, from $x = 0.364$ for M = La to $x = 0.246$ for M = Sm,[5,6] attesting to the fact that the ionic radii of La^{3+} and Na^+ are very similar. In most cases, the additional Na^+ ions occupy statistically the (compressed) octahedral sites parallel to [00.1].

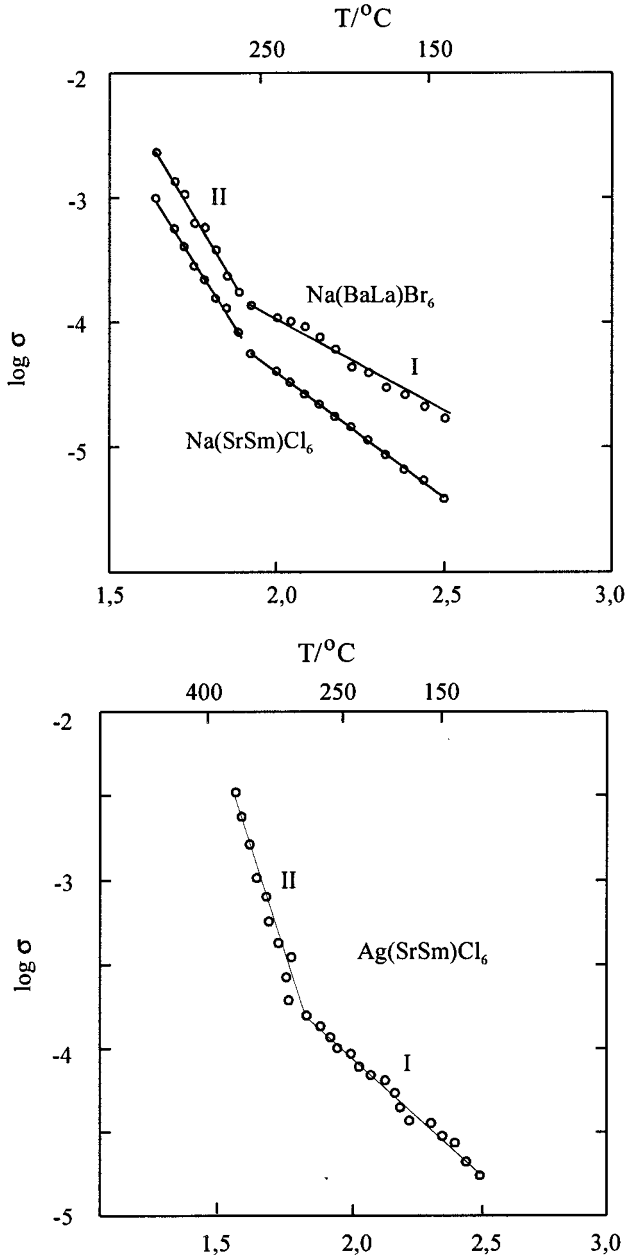


Figure 6. Ionic conductivity of $NaBaLaBr_6$, $NaSrSmCl_6$, and $AgSrSmCl_6$ in the log σ versus $1/T$ representation (σ in Ω^{-1} cm^{-1}; T in K). The origin of the "phase transition" (I → II) at higher temperatures is not clear.

Table 2. Lattice Constants of $Ba_8[\{(M_6)Z\}Cl_{32}]$ ($R-3$, $Z = 3$) and $Ba_9[\{(M_6)Z\}Cl_{34}]$ ($I4/m$, $Z = 2$) Type Chlorides from Powder Diffraction Data

M	*a*, pm	*c*, pm	V_m, cm^3/mol
Pr	1337.9(3)	2499.0(5)	777.7(6)
Nd	1335.8(3)	2496.1(4)	774.4(5)
Sm	1332.0(2)	2491.3(3)	768.5(4)
Eu[a]	1325.4(3)	2481.2(5)	757.8(5)
La	1137.7(4)	2179.9(6)	849.7(9)
Ce	1134.8(3)	2172.9(5)	842.7(6)
Pr	1134.1(3)	2172.1(4)	841.3(6)
Nd	1132.9(5)	2167.6(7)	837.8(10)
Sm	1130.8(2)	2160.9(4)	832.1(5)
Eu[b]	1121.57(7)	2149.2(2)	814.1(2)

[a] $(Ba,Eu^{II})_8[\{(Eu^{III}{}_6)Z\}Cl_{32}]$. [b] $(Ba,Eu^{II})_9[\{(Eu^{III}{}_6)Z\}Cl_{34}]$.

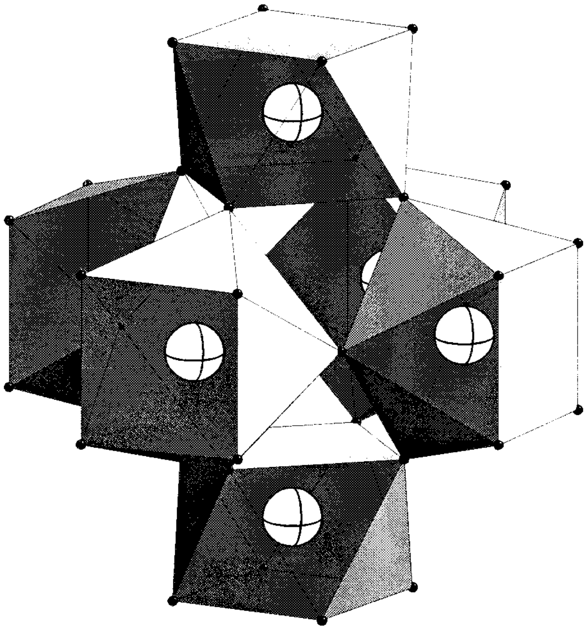


Figure 7. The "polyhedral cluster" $[\{M_6Z\}X_{36}]$.

Category 2. Derivatives of the type $A(M_2)X_6$, where no substitution takes place on the M sites, occur when the electron added from the added atom A either reduces one-half of the M^{3+} ions to M^{2+}, as in $NaNd_2Cl_6 \equiv (Na^+)(Nd^{2+}Nd^{3+})(Cl^-)_6$ with statistical distribution of Nd^{2+} and Nd^{3+},[7] or the electron is delocalized into a band as in $NaPr_2Cl_6 \equiv (Na^+)(Pr^{3+})_2(Cl^-)_6(e^-)$.[7,8] The former is a mixed-valent salt; the latter a semiconductor or metal. NaU_2Cl_6, obtained by reduction of uranium trichloride with sodium, is another example of the latter case.[9] The once enigmatic phase $PrCl_{2.31}$[10] also belongs to this group of compounds where 0.58 Pr^{3+} occupy the (compressed) octahedral holes parallel to [00.1], in accord with the formulation $(Pr^{3+})_{0.58}(Pr^{3+})_2(Cl^-)_6(e^-)_{1.74}$.[11]

Category 3. The divalent lanthanide cations in the chlorides $NaNd_2Cl_6$,[7] $NaSm_2Cl_6$,[6] and $NaEu_2Cl_6$[12] might be substituted by other divalent cations of similar size; most important are Sr^{2+} and Ba^{2+}. Of course, the remaining M^{3+} cations can now also be M = La, Ce, Pr. Examples of this third category of UCl_3 type derivatives are $NaSrSmCl_6$ and $NaBaLaCl_6$, with statistical distribution of the di- and trivalent cations.[13]

Table 1 summarizes our present knowledge of UCl_3 type derivative chlorides.

It has already been mentioned that chlorides such as $NaPr_2Cl_6$ with excess electrons that reside in a band are semiconductors or metals. From Figures 4 and 5 it is obvious that the cations in the channels parallel to [00.1], of which a maximum of one is statistically distributed over four sites per formula unit AM_2Cl_6, are apt for high mobility; hence, these chlorides should be good cationic conductors. This is indeed the case. Even powder samples show specific conductivities of, for example, $4 \cdot 10^{-4}$ S/cm at 360 °C for $NaSrSmCl_6$ (Figure 6). However, the ionic conductivity should be highly anisotropic; it should be excellent in the [00.1] direction and rather poor in the (00.1) plane (cf. Figure 4). As usual, when Na^+ is substituted for Ag^+, as in $AgSrSmCl_6$, the conductivity is considerably better (10^{-3} S/cm at 350 °C).[13]

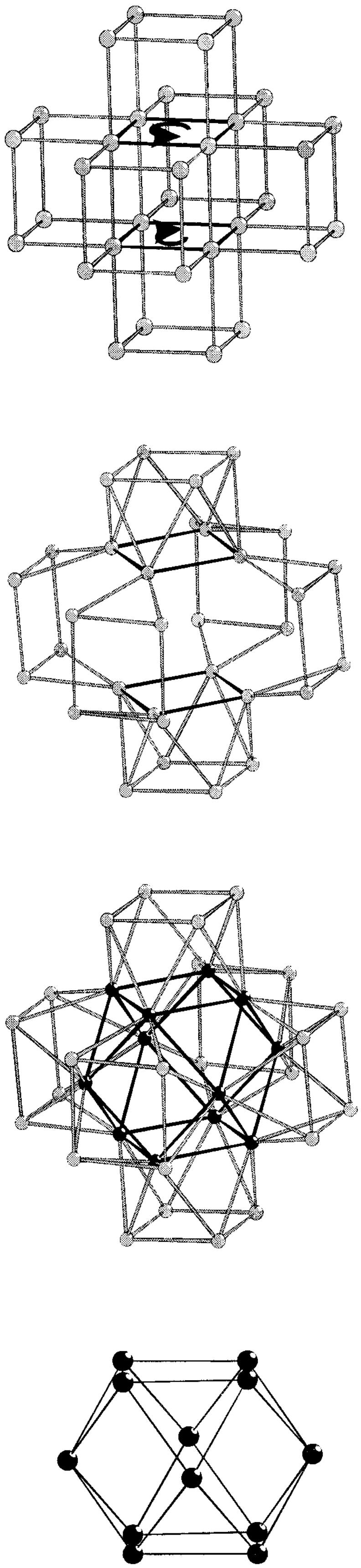


Figure 8. The formation of a $[\{M_6Z\}X_{36}]$ polyhedral cluster from an M_6X_{32} structural fragment of the fluorite type by rotation of two square faces and the addition of four X^- anions whereby a cuboctahedron for the interstitial Z is built.

In contrast to $PrCl_{2.31}$, which is the only phase in the system $Pr/PrCl_3$ with the UCl_3 type derivative structure

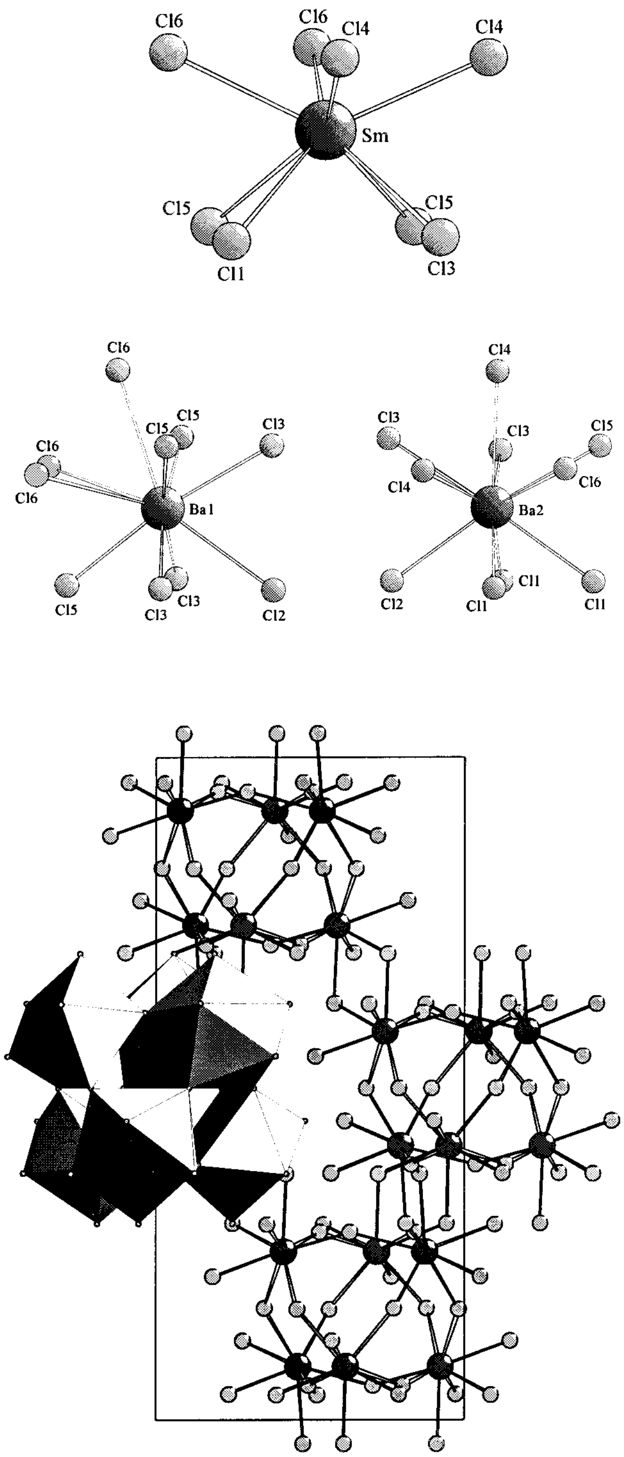


Figure 9. The crystal structure of $Ba_8[\{Sm_6Z\}Cl_{32}]$ (trigonal, $R{-}3$, $Z = 3$). The square-antiprismatic $[SmCl_8]$ polyhedron, the two types of $[BaCl_{10}]$ polyhedra, and the arrangement and connection of the $[\{Sm_6Z\}X_{36}]$ polyhedral clusters.

according to $(Pr^{3+})_{0.58}(Pr^{3+})_2(Cl^-)_6(e^-)_{1.74}$, two compositions were found in the $NdCl_2/NdCl_3$ partial system, i.e., $NdCl_{2.27}$ and $NdCl_{2.37}$.[15] These are mixed-valent compounds, and contrary to the topologically identical structures of $NaPr_2Cl_6$ and $NaNd_2Cl_6$, neither of them belongs to the UCl_3 derivative family. Their formulas may be written as $NdCl_{2.27} \equiv (Nd^{2+})_8[\{(Nd^{3+})_6(Z^-)\}(Cl^-)_{32}]$ and $NdCl_{2.37} \equiv (Nd^{2+})_9[\{(Nd^{3+})_6(Z^-)\}(Cl^-)_{34}]$, respectively.[16] Both have structures that may be grasped as superstructure derivatives of the fluorite (CaF_2) type of structure. These will be discussed in the following section.

$Ba_8[\{(M_6)Z\}X_{32}]$ and $Ba_9[\{(M_6)Z\}X_{34}]$ Type Chlorides

Fluorite Superstructure Derivatives. Phase diagram determinations of the systems $BaCl_2/MCl_3$ (M = La, Sm)[17] revealed incongruently melting phases that were assigned to the compounds Ba_2LaCl_7, Ba_2SmCl_7, and $BaSmCl_5$, although with considerable phase widths. The formation of mixed crystals between the rare-earth chlorides and the high-temperature modification of $BaCl_2$ (fluorite type of structure)[18] was thought to be responsible for these phase widths. Indeed, further investigations made clear that these chlorides belong structurally to three-dimensional superstructures of the fluorite type with the general composition M_nX_{2n+5}.[19]

Yellow single crystals of $Ba_8[\{(Sm_6)Z\}Cl_{32}]$ were obtained from a 1:1 equimolar mixture of $BaCl_2$ and $SmCl_3$ in a silver chloride flux (mp of AgCl, 455 °C) at 560 °C in a silica ampule. These silver chloride fluxes were first designed for the synthesis of UCl_3 type derivatives like, in the present case, $Ag(BaSm)Cl_6$. This compound appears, however, not to exist, and neither does $BaSmCl_5$ nor Ba_2SmCl_7. Mixtures (2:1) of $BaCl_2$ and $SmCl_3$ at slightly higher temperatures (620 °C) yield $Ba_9[\{(Sm_6)Z\}Cl_{34}]$, also from a AgCl flux. If no AgCl is added that may act as a flux, only powder samples are obtained. Analogous europium-containing chlorides were from green to blue colored in both cases. This is explained with some substitution of Ba^{2+} by Eu^{2+} (see below for $(Ba,Eu^{II})_9[\{(Eu^{III}{}_6)Z\}Cl_{34}]$). Mixed-valence Eu^{II}/Eu^{III} halides are always blue to green; see, for example, $Eu_4Cl_9 \equiv (Eu^{II})_3Eu^{III}Cl_9$[20] and $Na_{0.75}Eu_2Cl_6$.[12]

Only the mentioned two types of $(B+M)_nX_{2n+5}$ type chlorides (B = Ba) were obtained, i.e., with $n = 14$, $B_8[\{(M_6)Z\}Cl_{32}]$, M = Pr, Nd, Sm, Eu (note that $2n + 5$ equals 33, which is 32 Cl + Z; for a comment on the nature of Z, see below), and with $n = 15$, $B_9[\{(M_6)Z\}Cl_{34}]$, M = La, Ce, Pr, Nd, Sm (see Table 2).

Three-dimensional fluorite type superstructures were known for quite a while for ternary fluorides[21-23] and for mixed-valent rare-earth halides.[16,19] Especially noteworthy are the two phases in the system $NdCl_2/NdCl_3$ with the compositions $NdCl_{2.37}$ and $NdCl_{2.27}$,[15] which, according to very thorough structure determinations,[16] are in fact $Nd^{II}{}_8[\{(Nd^{III}{}_6)Z\}Cl_{32}]$ and $Nd^{II}{}_9[\{(Nd^{III}{}_6)Z\}Cl_{34}]$, respectively (see above).

The most important, characteristic building unit of this family of structures is the so-called polyhedral cluster of the composition $[M_6X_{36}]$ (Figure 7). It is built from six square antiprisms $[MX_8]$ that share four corners with four like square antiprisms leading to the formulation $[MX_{4/1}X_{4/2}] \times 6 \rightarrow [M_6X_{24/1}X_{24/2}] \equiv [M_6X_{36}]$. The six "metal" centers (M^{3+}) are at the corners of a regular octahedron. The $[M_6X_{36}]$ polyhedral cluster may be derived from a structural fragment of the fluorite (CaF_2) aristotype: six cubes with their centers (M) forming an octahedron, of the composition $[M_6X_{32}]$. When two inner square faces are rotated by 45° to form two apical square antiprisms, four X^- anions need to be added equatorially to build four additional square antisprisms. A cuboctahedron of X^- anions is thereby

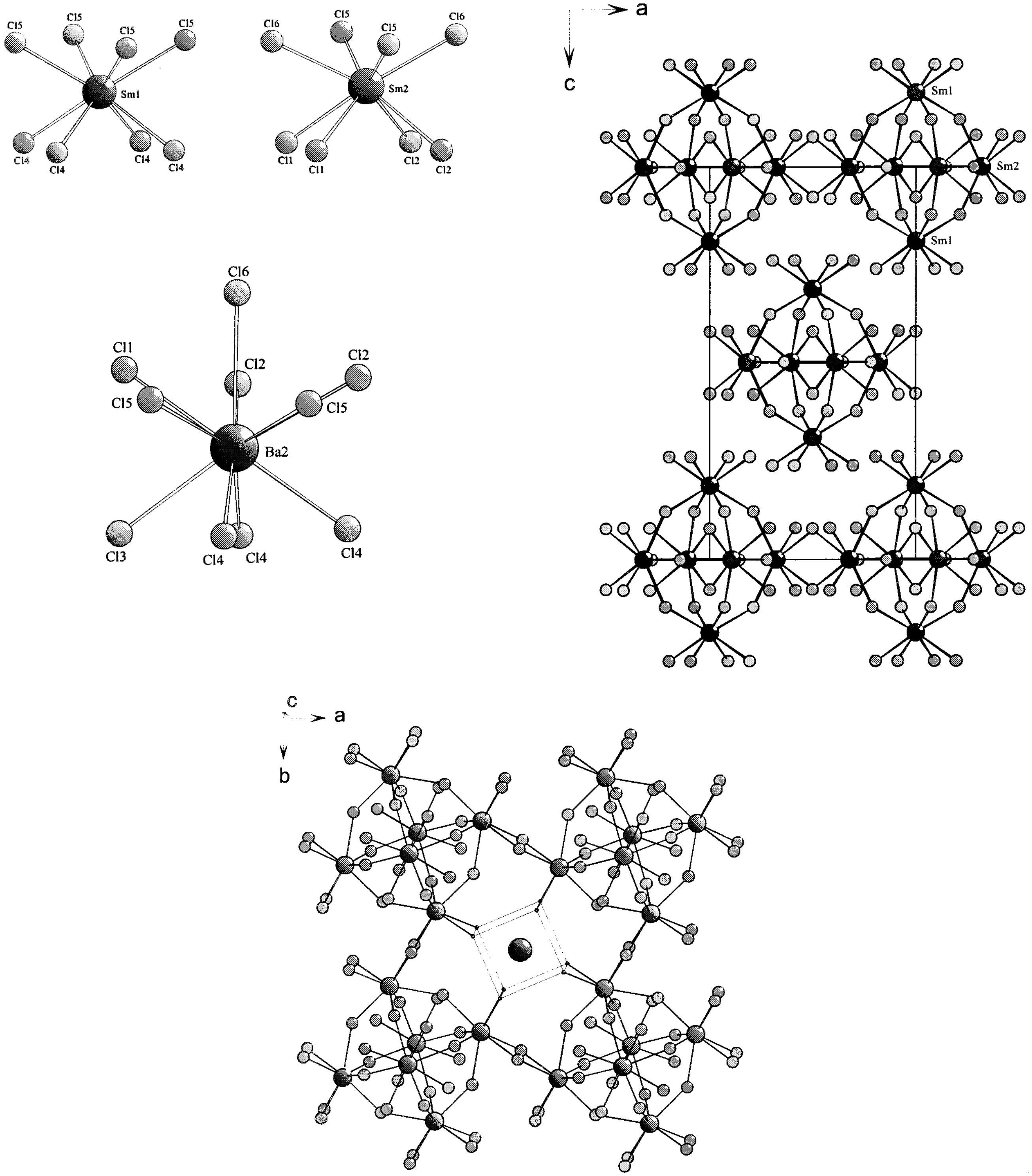


Figure 10. The crystal structure of $Ba_9[\{Sm_6Z\}Cl_{34}]$ (tetragonal, *I*4/*m*, $Z = 2$). The two symmetrically inequivalent square antiprismatic $[SmCl_8]$ polyhedra, the $[BaCl_{10}]$ polyhedron, the $[BaCl_8]$ cube and its surrounding, and the arrangement and connection of the $[\{Sm_6Z\}X_{36}]$ polyhedral clusters.

formed which leaves much space for an interstitial atom Z, $[\{M_6Z\}X_{36}]$ (Figure 8). To achieve electroneutrality, the interstitial ion needs to be an anion, of which an oxide anion would be most likely, judging from the charge balance, but a chloride ion would be more feasible judging from the size of the hole.

The $[\{M_6Z\}X_{36}]$ polyhedral clusters are connected with each other in accord with the point groups -3 (space group $R-3$) and $4/m$ (space group $I4/m$) via six and four outer edges, respectively. Thereby the compositions $Ba_8[\{M_6Z\}Cl_{32}]$ ($R-3$) and $Ba_9[\{M_6Z\}Cl_{34}]$ ($I4/m$) are obtained (see Figures 9 and 10).

$Ba_8[\{M_6Z\}Cl_{32}]$. A crystal structure determination was undertaken for the example $Ba_8[\{Sm_6Z\}Cl_{32}]$. Distances $Sm^{3+}-Cl^-$ within the square antiprism are an average of 288 pm (Table 3). The $[\{M_6Z\}X_{36}]$ "clusters" are connected via common edges and arranged in the fashion of a cubic-closest packing of spheres (Figure 9). This leaves space for two crystallographically independent Ba^{2+} cations with multiplicities of 6 (Ba1) and 18

Table 3. Distance Ranges and Mean Distances for the Crystallographically Independent B and M Sites for Some Chlorides in the BCl_2/MCl_3 Systems

chlorides	CSD no.	table no.[a]	B sites[b]	M sites[b]
$Ba_2[EuCl_7]$	408502	S1	Bal [9] 308.6(2)−332.5(2); 321.5(2) Ba2 [9] 308.7(2)−331.5(2); 322.0(2)	Eu [7] 269.6(2)−281.0(2); 275.1(2)
$Ba_9[\{Sm_6Z\}Cl_{34}]$	408480	S2	Bal [8] 310.3(2) Ba2 [10] 311.6(1)−359.3(1); 329.5(2)	Sm1 [8] 289.7(2)−290.7(2); 290.2(2) Sm2 [8] 279.4(3)−292.9(2); 288.8(2)
$(Ba,Sr)_9[\{Sm_6Z\}Cl_{34}]$	408478	S3	Sr/Bal [8] 302.5(2) Ba3 [10] 308.8(2)−356.3(1); 327.3(2)	Sml [8] 285.4(2)−286.9(3); 286.2(3) Sm2 [8] 276.9(4)−293.0(3); 286.9(3)
$(Ba,Eu^{II})_9[\{Eu^{III}{}_6Z\}Cl_{34}]$	408479	S4	Eu/Bal [8] 303.5(1) Ba2 [10] 309.0(1)−356.3(1); 327.8(2)	Eul [8] 284.2(2)−286.0(2); 285.1(2) Eu2 [8] 277.0(2)−295.0(2); 287.4(2)
$Ba_8[\{Sm_6Z\}Cl_{32}]$	408481	S5	Bal [10] 307.0(3)−363.0(4); 328.9(3) Ba2 [10]314.1(2)−354.2(3); 328.8(3)	Sm [8] 280.4(3)−292.7(3); 288.4(3)
$BaGdCl_5$	407832	S6	Ba [10] 318.8(2)−354.1(1); 328.6(2)	Gd [8] 274.4(2)−292.9(1); 281.4(2)
$Ba_2Cl[ScCl_6]$	408056	S7	Bal [9] 302.7(2)−357.5(2); 323.9(2) Ba2 [9] 303.7(2)−349.0(2); 322.0(2) Ba3 [10] 295.5(2)−363.1(2); 338.5(2) Ba4 [9] 299.2(2)−363.3(2); 335.9(2)	Scl [6] 242.9(3)−252.1(3); 247.9(3) Sc2 [6] 241.6(3)−251.6(2); 247.9(2)

[a] Table number of Supporting Information. [b] Coordination numbers are in brackets.

(Ba2). Both have 10 nearest neighbors (Figure 9) with mean distances of 329 pm. With all samarium atoms in the trivalent state (to which the light yellow color attests) and full occupation on all cationic sites, the interstitial Z needs to be divalent to achieve electroneutrality. This is most preferably the ubiquitous oxide anion.

$Ba_9[\{M_6Z\}Cl_{34}]$. Crystal structure determinations were undertaken for the examples of $Ba_9[\{Sm_6Z\}Cl_{34}]$, $(Ba,Sr)_9[\{Sm_6Z\}Cl_{34}]$, and $(Ba,Eu^{II})_9[\{Eu^{III}{}_6Z\}Cl_{34}]$. There are two crystallographically independent sites for M^{3+} cations with mean $Sm^{3+}-Cl^-$ distances between 286 and 290 pm (Table 3), much the same as in $Ba_8[\{Sm_6Z\}Cl_{32}]$, and $Eu^{3+}-Cl^-$ distances a little shorter (average 286 pm), as the lanthanide contraction requests. The coordination number for Ba2 is 10, with an average $Ba^{2+}-Cl^-$ distance around 328 pm (as above). The 8-coordinate Ba1, however, is special in that there are eight equal distances at 310 pm; the coordination polyhedron is a cube (Figure 10). This position may at least be partly substituted by Sr^{2+} and Eu^{2+}, leading to much shorter distances of 303 and 304 pm, respectively. Full occupation of these sites by Sr^{2+} and Eu^{2+}, respectively, would lead to the formulas $SrBa_8[\{Sm_6Z\}Cl_{34}]$ and $Eu^{II}Ba_8[\{Eu^{III}{}_6Z\}Cl_{34}]$. Again, the nature of the anion Z in the cuboctahedron of the $[\{M_6Z\}Cl_{36}]$ "cluster" is not clear. The existence of $Ba_9[\{Sm_6Z\}Cl_{34}]$ with all samarium atoms trivalent would request one O^{2-} or two Cl^- for electroneutrality. There is indeed electron density in the cuboctahedron, although not right in the center, but one may refine four split positions, because of the space group symmetry *I*4/*m*. With the cations out of the center of the square antiprisms directed to these split positions, $M^{3+}-$"O^{2-}" distances are 326 pm. These are certainly too large to be normal, for example, $Sm^{3+}-O^{2-}$ distances. Note that even in a compound with divalent samarium, $[Sm_4O]Cl_6$,[24] the $Sm^{2+}-O^{2-}$ distance is only around 237 pm.

$BaMCl_5$ Type Chlorides (M = Eu−Tb)

The phase diagram of the system $BaCl_2/GdCl_3$ has been determined and shows that $BaGdCl_5$ melts incongruently at about 560 °C.[17] Colorless single crystals of $BaGdCl_5$ were obtained together with those of $GdCl_3$ from the melt (560 °C) of a 1:2 equimolar mixture of $BaCl_2$ and $GdCl_3$ in a silica ampule by slow cooling at 1 K/h to 520 °C, where the solid was kept for 10 days. The composition of the melt was between that of the eutectic (~30 mol % $BaCl_2$) and the intersection of the peritectic with the liquidus curve (~35 mol % $BaCl_2$). Pure powder samples of $BaGdCl_5$ and of $BaEuCl_5$ and $BaTbCl_5$ may be obtained by heating equimolar mixtures of $BaCl_2$ and MCl_3 (M = Eu, Gd, Tb) in silica ampules at 480 °C for about 2 weeks. Attempts to prepare $BaDyCl_5$ failed.

The crystal structure of $BaGdCl_5$[25] (Figure 11) with which $BaEuCl_5$ and $BaTbCl_5$ are isostructural (for lattice constants see Table 4) contains rather regular square antiprismatic polyhedra $[GdCl_8]$ with $Gd^{3+}-Cl^-$ distances between 274.4(2) and 292.9(1) pm ($\bar{d} = 281.4(2)$ pm). Note that $Gd^{3+}-Cl^-$ distances are 285 pm on average in UCl_3 type $GdCl_3$ (coordination number of 9).[26] The polyhedra $[GdCl1_2Cl2_2Cl3_4]$ are connected parallel to [001] via two common edges and in the [100] direction via two common corners yielding corrugated layers according to ${}^2_\infty[GdCl1_{2/2}Cl2_{2/1}Cl3_{4/2}]$ (Figure 11). The Ba^{2+} cations have eight rather close Cl^- neighbors at distances between 318.8(2) and 330.2(2) pm and two more distant neighbors at 354.1(1) pm with an average of 328.6(2) pm for coordination number 10 (or better as 8 + 2). The $[BaCl_{10}]$ polyhedra are connected via two common edges parallel to [001] and likewise [100] according to $[BaCl2_{6/2}Cl3_{2/1}]$ to corrugated layers that alternate in the [010] direction with $[GdCl1_{2/2}Cl2_{2/1}Cl3_{4/2}]$ layers and are, of course, connected with these via common chloride ions where the two more distant chloride ligands of the $[BaCl_{8+2}]$ polyhedra play an important role.

Ba_2MCl_7 Type Chlorides (M = Eu−Lu, Y)

The first hints at the existence of "true", incongruently melting Ba_2MCl_7 type chlorides came from phase diagram determinations of the systems $BaCl_2/MCl_3$ (M = Gd,Yb, Y).[17,27] Quite recently, single crystals were grown making use of the Bridgman technique, and the crystal structure was determined for the example of Ba_2ErCl_7.[28] The chlorides Ba_2MCl_7 with M = Gd−Yb,Y were found to be isostructural;[29] for lattice constants, see Table 5. From single-crystal data, the existence of Ba_2EuCl_7 was verified, and from X-ray powder data so was that of Ba_2LuCl_7.[4]

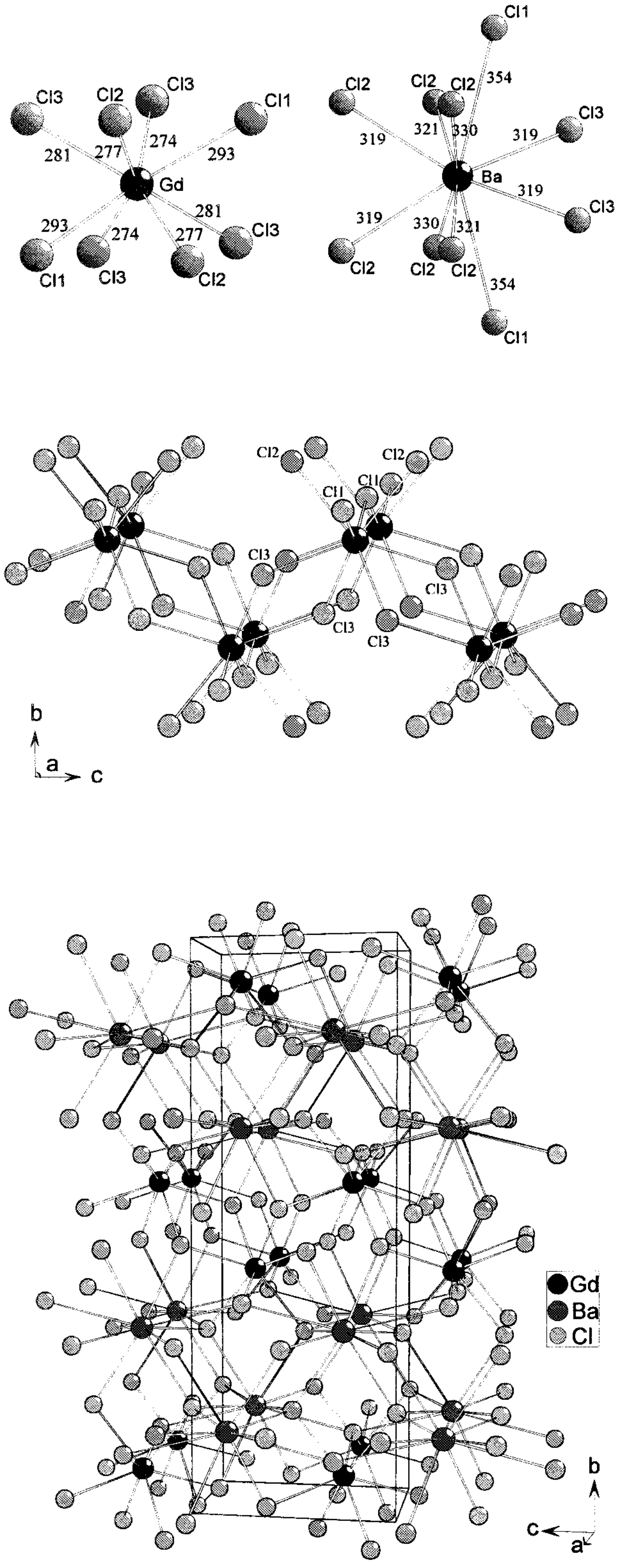


Figure 11. The crystal structure of $BaGdCl_5$ (monoclinic, *C*2/*c*, Z = 4); perspective views of the coordination polyhedra around Gd^{3+} and Ba^{2+}, of a corrugated $[GdCl_5]$ layer and of the unit cell.

Table 4. Lattice Constants of $BaMCl_5$ Type Chlorides (monoclinic, *C*2/*c*, *Z* = 4; from powder data)

M	*a*, pm	*b*, pm	*c*, pm	*β*, grd	V_m, cm^3/mol
$BaEuCl_5$	553.8(2)	1934.3(7)	689.0(4)	93.38(6)	110.9(2)
$BaGdCl_5$	551.8(3)	1923.9(6)	686.2(4)	93.18(5)	109.5(2)
$BaTbCl_5$	551.1(3)	1915.3(7)	684.4(5)	93.11(7)	108.6(2)

Table 5. Lattice Constants and Molar Volumes of $Ba_2[MCl_7]$ Type Chlorides (monoclinic, *P*2_1/*c*, *Z* = 4)[a]

M	*a*, pm	*b*, pm	*c*, pm	*β*, grd	V_m, cm^3/mol
Eu	681.7(2)	1558.6(3)	1055.2(2)	90.66(2)	168.8(2)
Gd	681.9(2)	1557.8(3)	1055.1(2)	90.66(1)	168.8(2)
Tb	681.0(2)	1555.3(3)	1053.6(2)	90.61(2)	168.0(2)
Dy	680.1(3)	1554.0(4)	1051.7(3)	90.56(3)	167.4(2)
Ho	679.6(1)	1552.1(2)	1049.1(1)	90.54(1)	166.6(1)
Er	679.2(1)	1551.4(2)	1048.9(1)	90.50(1)	166.4(1)
Y	679.4(2)	1552.8(3)	1050.0(2)	90.49(2)	166.8(2)
Tm	677.9(2)	1550.1(2)	1048.3(2)	90.43(2)	165.9(2)
Yb	676.4(1)	1548.4(2)	1046.5(1)	90.41(1)	165.0(1)
Lu	675.8(2)	1546.9(3)	1046.2(2)	90.38(2)	164.7(1)

[a] For M = Gd−Yb, Y, see ref 29.

Yellow single crystals of Ba_2EuCl_7 were obtained from a $ZnCl_2$ flux (mp of $ZnCl_2$, 283 °C; the $ZnCl_2/MCl_3$ systems (M = rare-earth elements) appear to be simply eutectic; the $BaCl_2/ZnCl_2$ system contains the ternary chloride $BaZnCl_4$).[4,30] A mixture of $BaCl_2$, $EuCl_3$, and $ZnCl_2$ with 4:2:3 equimolar amounts was held at 520 °C for 2 weeks in a silica ampule, followed by slow cooling at 4 K/h. Powder samples of Ba_2LuCl_7 were obtained from a 2:1 mixture of $BaCl_2$ and $LuCl_3$ at 540 °C in a silica ampule (2 weeks).

The characteristic feature of the crystal structure of, for example, Ba_2EuCl_7 is an isolated monocapped trigonal prismatic $[EuCl_7]$ polyhedron (Figure 12) with $Eu^{3+}-Cl^-$ distances of 275 pm on average, approximately 11 pm shorter than those found for 8-coordinate $(Ba,Eu)_9[\{Eu^{III}{}_6Z\}Cl_{34}]$ (Table 3). There are two crystallographically independent 9-coordinate Ba^{2+} cations in the structure with typical $Ba^{2+}-Cl^-$ distances around 322 pm on average. The $[BaCl_9]$ polyhedra are connected with each other via two edges, forming linear and zigzag chains, respectively (Figure 12). The chains are connected with each other through triangular faces so that a three-dimensional network arises in which the Eu^{3+} cations are embedded (Figure 12).

The Chloride $Ba_2ScCl_7 \equiv Ba_2Cl[ScCl_6]$

With the smallest of the rare-earth cations, Sc^{3+}, the chloride of composition Ba_2ScCl_7 was obtained as colorless single crystals together with $ScCl_3$ from a 1:1 mixture of the binary chlorides at 580 °C in a silica ampule (2 weeks, slow cooling at 1 K/h).[31] For pure powder samples, a 2:1 mixture of $BaCl_2$ and $ScCl_3$ is heated at 540 °C for 2 weeks.

Ba_2ScCl_7 crystallizes in the monoclinic crystal system with $a = 688.88(7)$ pm, $b = 1349.4(1)$ pm, $c = 1207.3(1)$ pm, $\beta = 94.92(1)°$ and a molar volume of 168.3(1) cm^3 mol^{-1}. The space group is noncentrosymmetric ($P2_1$). This could be verified through the second harmonic generation of the fundamental of a Nd:YAG laser (1064 nm).

Characteristic of the crystal structure of Ba_2ScCl_7 are isolated $[ScCl_6]$ octahedra; the seventh Cl^- only belongs to polyhedra around Ba^{2+}, so the formula should be written as $Ba_2Cl[ScCl_6]$. As Figure 13 shows, the two symmetrically inequivalent $[ScCl_6]$ are very similar with equal mean $Sc^{3+}-Cl^-$ distances of 248 pm (Table 3) much as those in $ScCl_3$.[32,33] Four symmetrically inequivalent Ba^{2+} cations are surrounded by 9 or 10

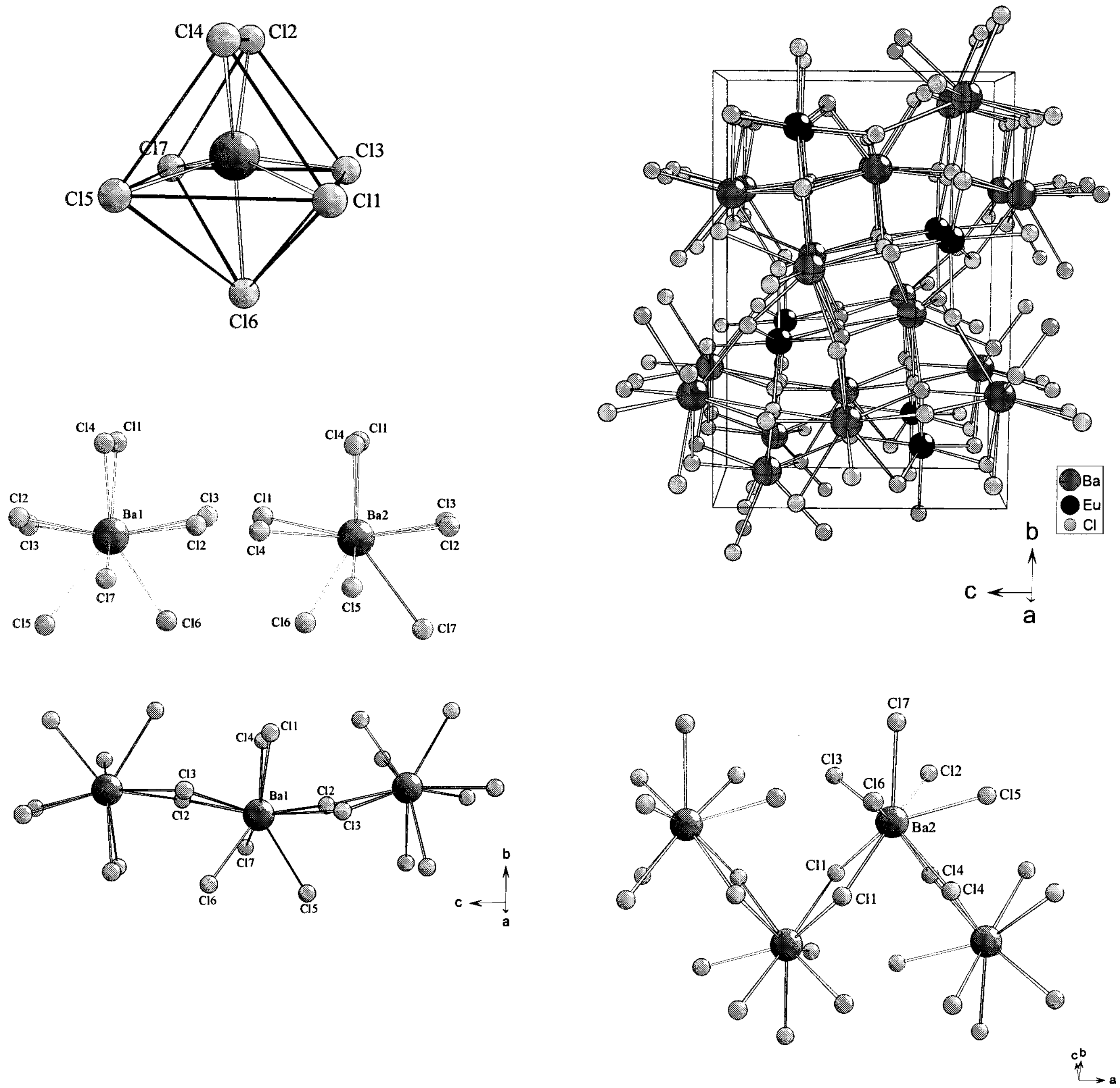


Figure 12. The crystal structure of $Ba_2[EuCl_7]$ (monoclinic, $P2_1/c$, $Z = 4$). The isolated monocapped trigonal prism $[EuCl_7]$, the two symmetrically inequivalent $[BaCl_9]$ polyhedra, two types of their connection via common edges, and a perspective view of the unit cell.

nearest chloride neighbors with average distances falling into two groups, around 323 and 337 pm, respectively.

Properties and Potentials

Alkali chlorides, ACl, when "mixed" with rare-earth chlorides offer a wide variety of complex halides. With the rare-earth ions in the divalent state, a rather common valence now,[8] ternary chlorides exist with the formula types AB_2Cl_5, $ABCl_3$, and A_2BCl_4.[34,35] These B^{2+} cations have pure $6s^05d^04f^n$ electronic configurations. The element B may be Nd, Sm, Eu, Dy, Tm, and Yb, but not, for example, Pr, because an electronic configuration crossover takes place to, generally, $6s^05d^14f^{n-1}$. The "excess" 5d electron is either delocalized into a band, giving rise to semiconductingor metallic behavior, or it may be localized in multicenter bonds, as is apparently the case in Pr_2Br_5, where triangles of praseodymium atoms occur with one-electron−three-center bonds.[36,37] This halide exhibits a rather complicated mixed ferro- and antiferromagnetic behavior below 50 K and is a semiconductor. It also shows a metallic luster, as does $NaPr_2Cl_6$ but not $NaNd_2Cl_6$ (see above for a reason). The latter two compounds fall in the category of the derivatives of the UCl_3 type of structure according to $2MX_3 \rightarrow M_2X_6 \rightarrow ABMX_6$ (see above). Neither their magnetic and spectroscopic properties nor their electronic conduction properties have yet been explored. Chlorides of the $ABMCl_6$ type with A = Na, Ag are highly anisotropic, essentially one-dimensional cationic conductors, for example, $NaBaLaCl_6$ and $AgSrSmCl_6$ (see above).

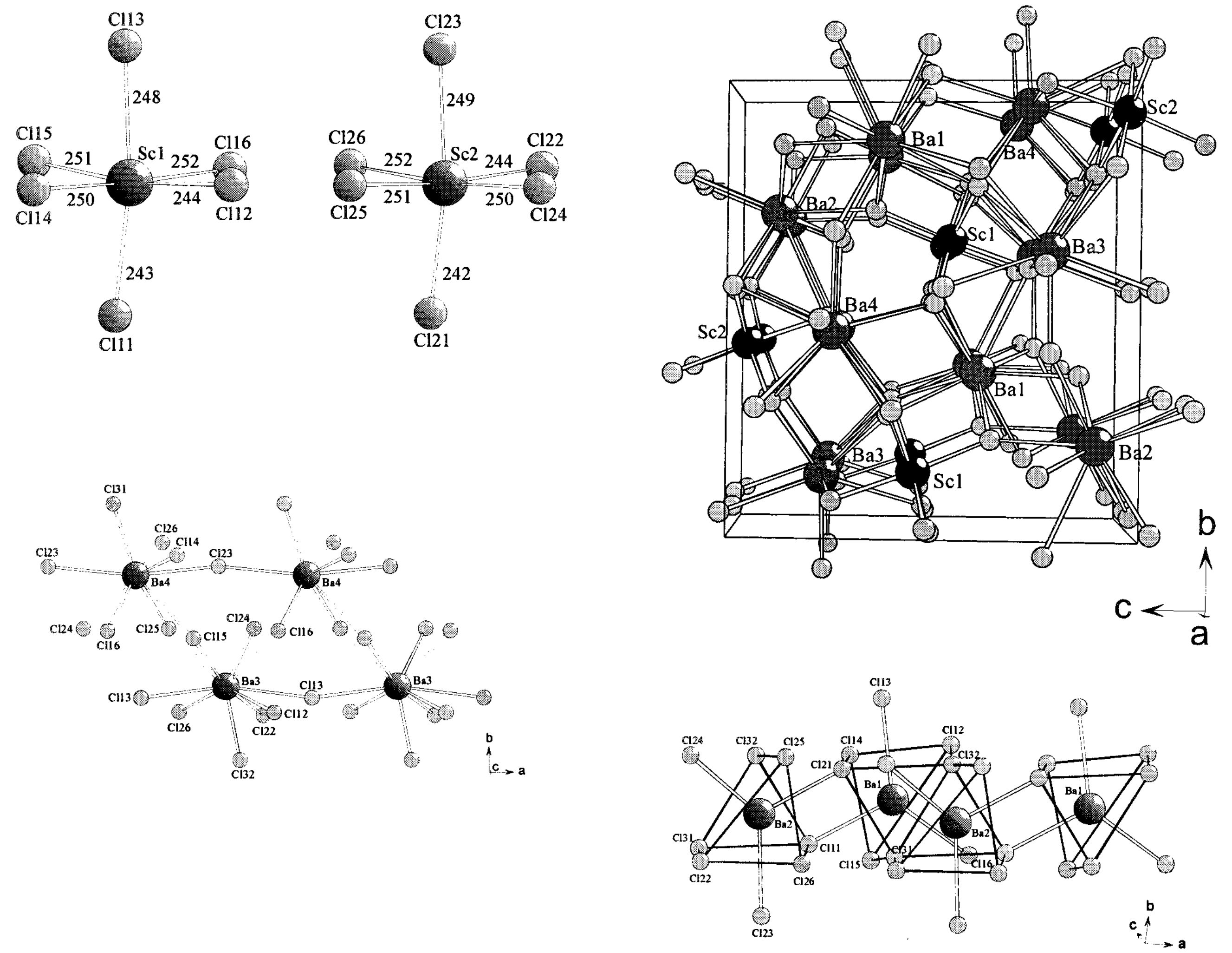


Figure 13. The crystal structure of $Ba_2ScCl_7 \equiv Ba_2Cl[ScCl_6]$ (monoclinic, $P2_1$, $Z = 4$). The two symmetrically inequivalent isolated octahedra $[ScCl_6]$, the connection of the two plus two types of symmetrically inequivalent polyhedra surrounding Ba^{2+}, and a perspective view of the unit cell.

In these chlorides, as in $NaNd_2Cl_6$, the rare-earth ion might be di- and trivalent. The alkali chloride/rare-earth trichloride systems, ACl/MCl_3, are even richer in compound types. At the alkali chloride-poor side and with the larger M^{3+} ions (La^{3+} through Sm^{3+}), UCl_3 type derivatives also occur with the general formula $A_{2x}(A_x\text{-}M_{2-x})Cl_6$ that are addition/substitution variants. Nothing is known about their properties, other than their crystal structure and exact compositions. A number of other compound types in the “pure” alkali chloride/rare-earth(III) chloride systems are known, namely AM_2Cl_7, $AMCl_4$, $A_3M_2Cl_9$, A_2MCl_5, A_3MCl_6, and A_4MCl_7, for which at least one example of the crystal structure has been determined. For an ample review of these compounds, see ref 3.

There is an increasing interest in the magnetic and optical properties of these compounds. Especially halides with confacial bioctahedra of the $Cs_3M_2X_9$ type were investigated for magnetic ordering at low temperatures. Ordering temperatures are rather low, around 230 mK for the antiferromagnetic ordering of the ferromagnetically coupled dimers in $Cs_3Er_2I_9$.[38] This is attributed to the rather shielded 4f states. Therefore, in K_2PrCl_5 with chains of edge-connected monocapped trigonal prisms,[39] magnetic ordering could not be detected, while in the isostructural K_2UCl_5, one-dimensional and three-dimensional magnetic ordering occur at 15 and 4 K, respectively.[40]

More prolific is the incorporation of rare-earth ions in luminescent materials.[41] There is a wide variety of uses as phosphors and scintillators. The most well-known popular example is the use of Eu^{3+} as the luminescent ion in the Y_2O_2S:Eu^{3+} red phosphor in color television screens. Tb^{3+} gives green and Tm^{3+} blue emission. Another interesting ion is Er^{3+}, as it may yield near-infrared to near-ultraviolet upconversion. For example, Ba_2ErCl_7 shows a surprisingly intense luminescence at room temperature at 380 nm when excited at 803 nm.[28,29] It might find its way in a new upconversion solid-state laser operating in the near-ultraviolet. Chlorides and even better bromides and iodides are promising as they are low-phonon materials that are needed for intense luminescence.

The greatest hindrance for ample exploration of these materials is their sensitivity against moisture. This is especially the case for alkali halide/rare-earth halide systems, although there might be some hope in further explorations because, surprisingly, some of these phases are known to crystallize even from aqueous solutions, for example, some of the elpasolites of the Cs_2NaMCl_6[42] type or a chloride like Cs_4YbCl_7.[43] Halides with divalent lanthanides are also sensitive to the oxygen in the air, especially at elevated temperatures. Halides with the (also divalent) alkaline-earth elements appear to be more stable against moist air. This has been an important reason for the new interest in these materials. We hope that our above reviewed study of some BX_2/MX_3 systems (see Figure 2 for the actual occurrence of $BaCl_2/MCl_3$ type chlorides) will further stimulate research in this area. One of the next steps must certainly be the growth of large optically pure crystals, doped or undoped. This is a veritable problem because most of these phases melt incongruently or even decompose in the solid state, especially when the smaller alkaline-earth ions are used. Flux growth is certainly a possibility, as we have shown, for example, for Ba_2EuCl_7, where $ZnCl_2$ was used. In other cases AgCl proved to be a good solvent.

Supporting Information Available: Crystal structure data for Ba_2EuCl_7, $Ba_9[\{(Sm_6)Z\}Cl_{34}]$, $(Ba,Sr)_9[\{(Sm_6)Z\}Cl_{34}]$, $(Ba,Eu^{II})_9[\{(Eu^{III}{}_6)Z\}Cl_{34}]$, $Ba_8[\{(Sm_6)Z\}Cl_{32}]$, $BaGdCl_5$, and Ba_2ScCl_7 (16 pages). Ordering information is given on any current masthead page.

References

(1) *Gmelin Handbook of Inorganic Chemistry, system no. 39: Sc, Y, La-Lu, Selten-Erd-Elemente;* Springer-Verlag: Berlin, 1976/78.
(2) Meyer, G. *Prog. Solid State Chem.* **1982**, *14*, 141.
(3) Meyer G.; Wickleder, M. S. *Handbook on the Physics and Chemistry of the Rare Earths*, North-Holland: Amsterdam, The Netherlands, in press.
(4) Masselmann, S. Dr. rer. nat. thesis, Universität zu Köln, 1998.
(5) Krämer, K.; Meyer, G. *Z. Anorg. Allg. Chem.* **1990**, *589*, 96.
(6) Lissner, F.; Krämer, K.; Schleid, Th.; Meyer, G.; Hu, Z.; Kaindl, G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 444.
(7) Schleid, Th.; Meyer, G. *Inorg. Chim. Acta* **1987**, *140*, 113.
(8) Meyer, G.; Meyer, H.-J. *Chem. Mater.* **1992**, *4*, 1157.
(9) Schleid, Th.; Meyer, G. *Naturwissenschaften* **1989**, *76*, 118.
(10) Druding, L. F.; Corbett, J. D.; Ramsey, B. N. *Inorg. Chem.* **1963**, *2*, 869.
(11) Meyer, G.; Schleid, Th.; Krämer, K. *J. Less-Common Met.* **1989**, *149*, 67.
(12) Wickleder, M. S.; Meyer, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 593.
(13) Wickleder, M. S.; Meyer, G. *Z. Anorg. Allg. Chem.* **1998**, *624*,.
(14) Seifert, H. J.; Fink, H.; Thiel, G. *J. Less-Common Met.* **1985**, *110*, 139.
(15) Druding, L. F.; Corbett, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 2462.
(16) Bärnighausen, H.; et al. Unpublished research; see also: (a) Löchner, U. Dr. rer. nat. thesis, University Karlsruhe 1980. (b) Eitel, M. Dr. rer. nat. thesis, University Karlsruhe 1985; A. Lumpp, A. Dr. rer. nat. thesis, University Karlsruhe 1988.
(17) Blachnik, R.; Alberts, G.; Enninga, E. *Z. Anorg. Allg. Chem.* **1985**, *522*, 207.
(18) Haase, A.; Brauer, G. *Z. Anorg. Allg. Chem.* **1978**, *441*, 181.
(19) Löchner, U.; Blachnik, R. *Z. Kristallogr.* **1988**, *183*, 207.
(20) Bachmann, R. Dr. rer. nat. thesis, University Karlsruhe 1987.
(21) Burns, J. H.; Ellison, R. D.; Levy, H. A. *Acta Crystallogr.* **1968**, *B24*, 230.
(22) Bevan, D. J. M.; Greis, O.; Strähle, J. *Acta Crystallogr.* **1980**, *A36*, 889.
(23) Bevan, D. J. M.; McCall, M. J.; Ness, Sh. E.; Rossell, H. J.; Taylor, M. R. *Eur. J. Solid State Inorg. Chem.* **1988**, *25*, 509.
(24) Schleid, Th.; Meyer, G. *Z. Anorg. Allg. Chem.* **1987**, *553*, 231.
(25) Masselmann, S.; Meyer, G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 357.
(26) Morosin, B. *J. Chem. Phys.* **1968**, *49*, 3007.
(27) Blachnik, R.; Alberts, J. E. *Z. Anorg. Allg. Chem.* **1982**, *490*, 235.
(28) Egger, P.; Rogin, P.; Riedener, T.; Güdel, H. U.; Wickleder, M. S.; Hulliger, J. *Adv. Mater.* **1996**, *8*, 668.
(29) Wickleder, M. S.; Egger, P.; Riedener, T.; Furer, N.; Güdel, H. U.; Hulliger, J. *Chem. Mater.* **1996**, *8*, 2828.
(30) Sandonnini, C. *Gazz. Chim. Ital.* **1914**, *44I*, 353.
(31) Masselmann, S.; Meyer, G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 551.
(32) Klemm, W.; Krose, E. *Z. Anorg. Allg. Chem.* **1947**, *253*, 218.
(33) Fjellvag, H.; Karen, P. *Acta Chem. Scand.* **1994**, *48*, 294.
(34) Meyer, G. *Chem. Rev.* **1988**, *88*, 93.
(35) Schilling, G.; Meyer, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 759.
(36) Krämer, K.; Meyer, G.; Fischer, P.; Hewat, A.; Güdel, H. U. *J. Solid State Chem.* **1991**, *95*, 1.
(37) Meyer, H.-J.; Hoffmann, R. *J. Solid State Chem.* **1991**, *95*, 14.
(38) Krämer, K. Personal communication; Hehlen, M. P.; Krämer, K.; Güdel, H. U.; McFarlane, R. A.; Schwartz, R. N. *Phys. Rev. B*, **1994**, *49*, 12475.
(39) Meyer, G.; Soose, J.; Moritz, A.; Vitt, V.; Holljes, Th. *Z. Anorg. Allg. Chem.* **1985**, *521*, 161.
(40) Krämer, K.; Güdel, H. U.; Meyer, G.; Heuer, Th.; Edelstein, N. N.; Jung, B.; Keller, L.; Fischer, P.; Zych, E.; Drozdzynski, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1339.
(41) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin, 1994.
(42) Morss, L. R.; Siegal, M.; Stenger, L.; Edelstein, N. *Inorg. Chem.* **1970**, *9*, 1771.
(43) Reuter, G.; Sebastian, J.; Frenzen, G. *Acta Crystallogr.* **1996**, *C52*, 1859.

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