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Alkaline earth/rare earth halides and related systems

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Abstract

Halides of di- and trivalent metals of the general formula BX_2 and MX_3 may react with each other forming a fair variety of complex halides in the solid state. Examples for ternary chlorides are: Ba_2ErCl_7 with isolated $[ErCl_7]$ monocapped trigonal prisms, $Ba_2Cl[ScCl_6]$ with isolated octahedra $[ScCl_6]$ and solitary Cl^-, $Ba_8[\{Sm_6Z\}Cl_{32}]$ and $Ba_9[\{Sm_6Z\}Cl_{34}]$ 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- and vertex-connected $[GdCl_8]$ square antiprisms. Two further lines may be followed: Firstly, with $Nd_8[\{Nd_6Z\}Cl_{32}]$ and $Nd_9[\{Nd_6Z\}Cl_{34}]$ isostructural with the above-mentioned chlorides with polyhedral clusters, other intra-rare-earth mixed valence halides may be investigated. ''$Sm_{14}Cl_{33}$'' is one example. Secondly, with the ionic radius of In^{3+} in between those of Lu^{3+} and Sc^{3+}, the $BaCl_2/InCl_3$ system comes into view. With $ZnCl_2$ as the solvent, $Ba_6ZnIn_2Cl_{20}$ and $BaZnCl_4$ ($GaCl_2$ type of structure) were obtained. Following this line further, $SrZnCl_4$ (scheelite type) was obtained as a model for $EuZnCl_4$, and, instead of $BaCoCl_4$, Ba_2CoCl_6 with edge-sharing bioctahedra according to $Ba_2Cl_2[Co_2Cl_{10}]$. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Many efforts have been put into the investigation of alkali halide (AX)/rare-earth(III) halide (MX_3) systems because of their potential applications subject to the special optical and magnetic properties of the trivalent rare-earth cations, M^{3+}. As the basis for all these investigations, academic or applied, the phase diagrams need to be elucidated as a prerequisite for crystal growth and crystal structure determination.

To give an overall picture [1], formula types that occur in the pseudobinary AX/MX_3 type systems are: At the MX_3 rich side there are ''solid solutions'' of the general formula $A_{2x}(A_xM_{2-x})X_6$ which are addition/substitution variants of the UCl_3 type of structure and, therefore, have coordination number nine (CN 9) for M^{3+}. These are followed by AM_2X_7 type halides (CN 8 and/or 7), and further by the formula types AMX_4 (CN 8, 7, 6), $A_3M_2X_9$ (CN 6), A_2MX_5 (CN 7, 6), A_3MX_6 (CN 6) and, finally, A_4MX_7 (CN 6).

Much less is known about alkaline earth halide (BX_2)/rare-earth(III) halide (MX_3) systems. Systematic work has apparently only been carried out for fluorides, especially around the mineral tveitite, i.e., the CaF_2/YF_3 system [2]. Several $BaCl_2/MCl_3$ systems were also investigated by thermal analysis [3]. Three formula types emerged in this work: $BaMCl_5$, Ba_2MCl_7, and Ba_3MCl_9. These are also given for the neighboring $BaCl_2/InCl_3$ system [4]. With the background of the $NdCl_2/NdCl_3$ system [5] and knowledge about the compounds $Nd_8[\{Nd_6Z\}Cl_{32}] \equiv Nd_{14}Cl_{32+x} \approx NdCl_{2.37}$ and $Nd_9[\{Nd_6Z\}Cl_{34}] \equiv Nd_{15}Cl_{34+x} \approx NdCl_{2.27}$ [6,7], it was concluded that, e.g., Ba_2SmCl_7 should be regarded as $(Ba_2Sm)_5(Cl_7)_5 = (Ba,Sm)_{15}Cl_{34+x}$ [8]. This work has also to be seen in close connection with work in the $EuCl_2/EuCl_3$ system, with $Eu_{14}Cl_{33}$ given as one definite phase [9].

2. Large M^{3+} cations

With sufficiently large M^{3+} cations (around La^{3+} through Eu^{3+}), complex chlorides of the just mentioned types $Ba_8[\{M_6Z\}Cl_{32}]$ and $Ba_9[\{M_6Z\}Cl_{34}]$ have been found [10]. In the first case, these occur with M=Pr–Eu, and in the latter for M=La–Eu. Europium is a special case as, in these compounds, it can also be divalent, depending upon the actual preparative conditions. Therefore, to some extent, Ba^{2+} may be substituted by Eu^{2+}.

The crystal structures of these two types of compounds are closely related. Both contain as the main structural feature the $[\{M_6Z\}Cl_{36}]$ polyhedral cluster, Fig. 1. In the

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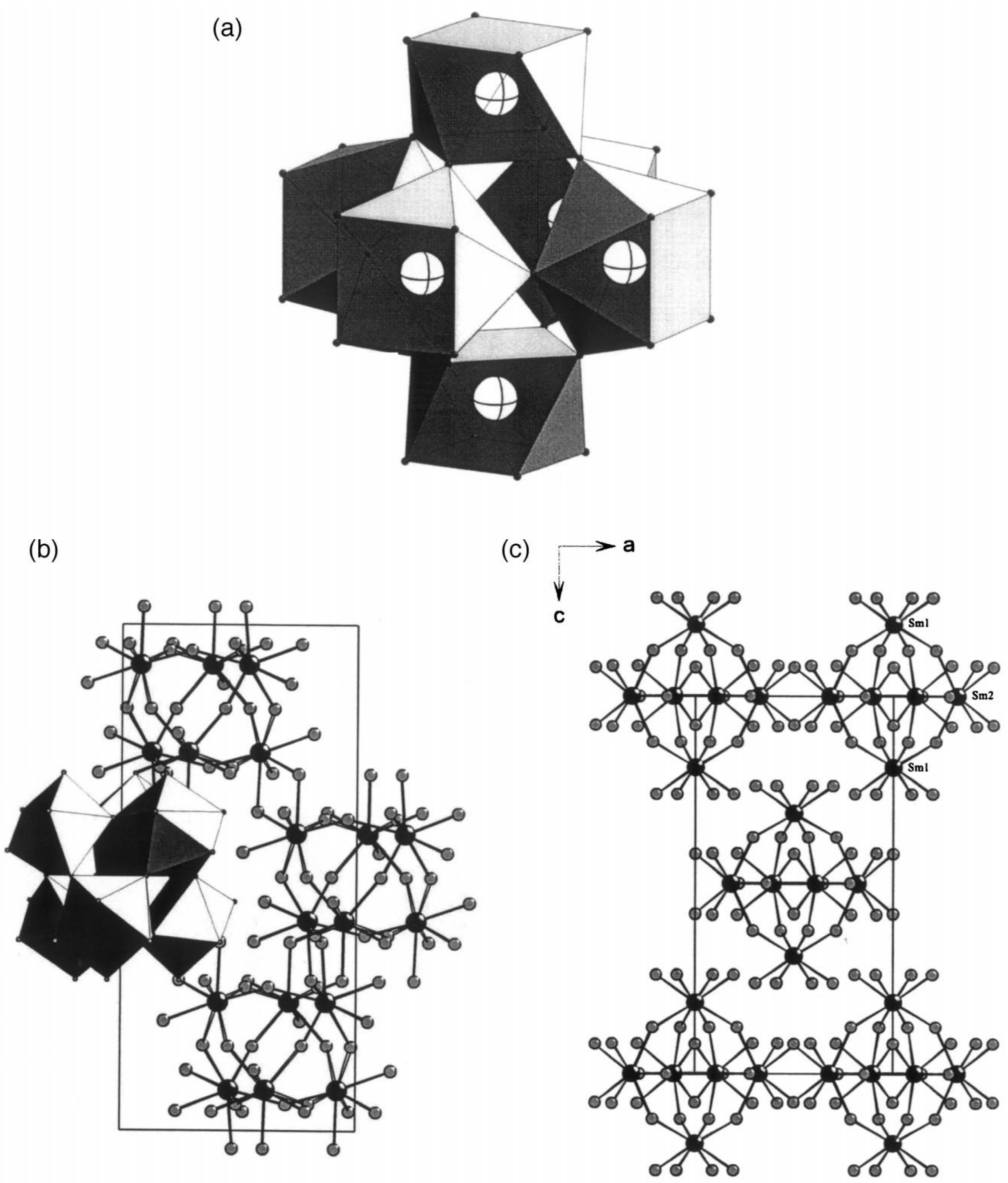

Fig. 1. The polyhedral cluster [$\{M_6Z\}Cl_{36}$] and perspective views of the crystal structures of $Ba_8[\{Sm_6Z\}Cl_{32}]$ and $Ba_9[\{Sm_6Z\}Cl_{34}]$.

case of $Ba_8[\{Sm_6Z\}Cl_{32}]$ for which a crystal structure determination has been carried out, the [$\{Sm_6Z\}Cl_{36}$] ‘‘cluster’’ is connected via four common edges according to [$\{Sm_6Z\}Cl_{28}Cl_{8/2}$] in the fashion of a cubic closest packing of spheres (space group R-3). In the case of $Ba_9[\{Sm_6Z\}Cl_{34}]$ the clusters are connected via two common edges in accordance with the formulation [$\{Sm_6Z\}Cl_{32}Cl_{4/2}$] (space group I4/m).

The nature of the interstitial atom Z residing in the center (or a bit off center) of the polyhedral cluster in a cuboctahedral site is not unequivocal. From the size of the hole, a chloride ion could be suited, but from the formulae

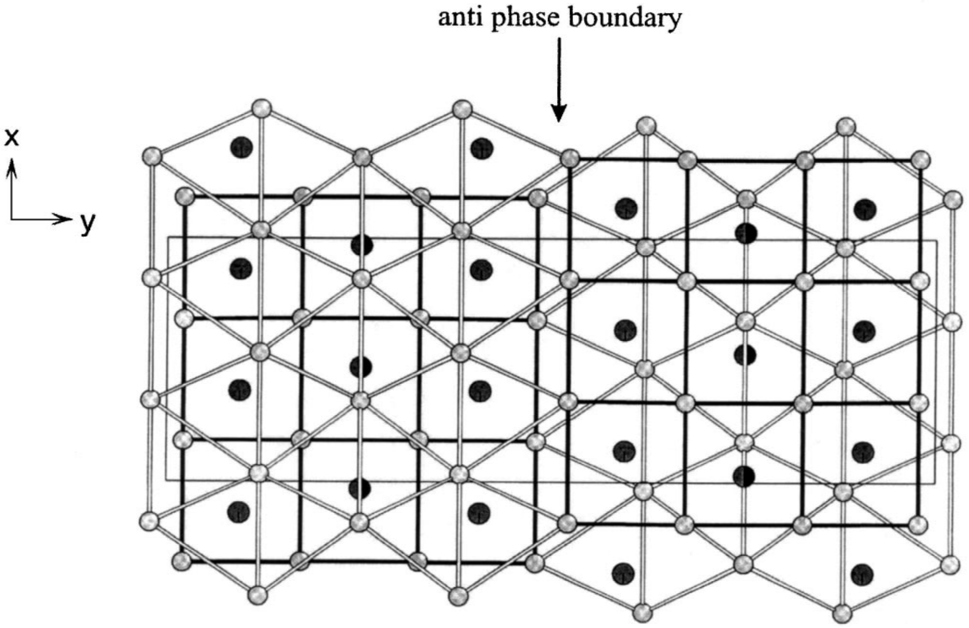

Fig. 2. Crystal structure of Ca_2GdCl_7.

it is clear that there are two negative charges needed. Thus, in cases where the charges of the cations are clear, say in $Ba_9[\{Pr_6Z\}Cl_{34}]$, Z is believed to be an oxide ion. There are other cases, however, like $Sm_{14}Cl_{33}$ [11] where Z appears to be Cl^-, in accordance with $(Sm^{II})_8[\{Sm^{II}Sm_5^{III}Cl\}Cl_{32}]$. A similar case is the phase $Ba_{17}Sm_{10}Cl_{64}$ which may be rewritten as follows: $Ba_{7.5}[\{BaSm_5^{III}Cl\}Cl_{31}]$ [12].

There exists also a number of analogous bromides, $Ba_8[\{M_6Z\}Br_{32}]$ (M=La–Nd) and $Ba_9[\{M_6Z\}Br_{34}]$ (M=La–Sm), respectively [13,14].

Strontium may also be incorporated instead of barium, see Ref. [8]. With even smaller alkaline earth cations like Ca^{2+}, firstly, little is known and, secondly, so-called vernier-type structures come into view. These have been amply found in the $TmCl_2/TmCl_3$ and $YbCl_2/YbCl_3$ and related systems such as, e.g., Sr_4DyCl_{11} [15]. Their compositions may be assigned to the general formula M_nX_{2n+1}. One member is M_3X_7 and an example for this one is Ca_2GdCl_7 (Fig. 2) [16].

3. Smaller M^{3+} cations

In all of the $Ba_8[\{M_6Z\}Cl_{32}]$ and $Ba_9[\{M_6Z\}Cl_{34}]$ type compounds, M^{3+} is eight coordinate (square antiprism).

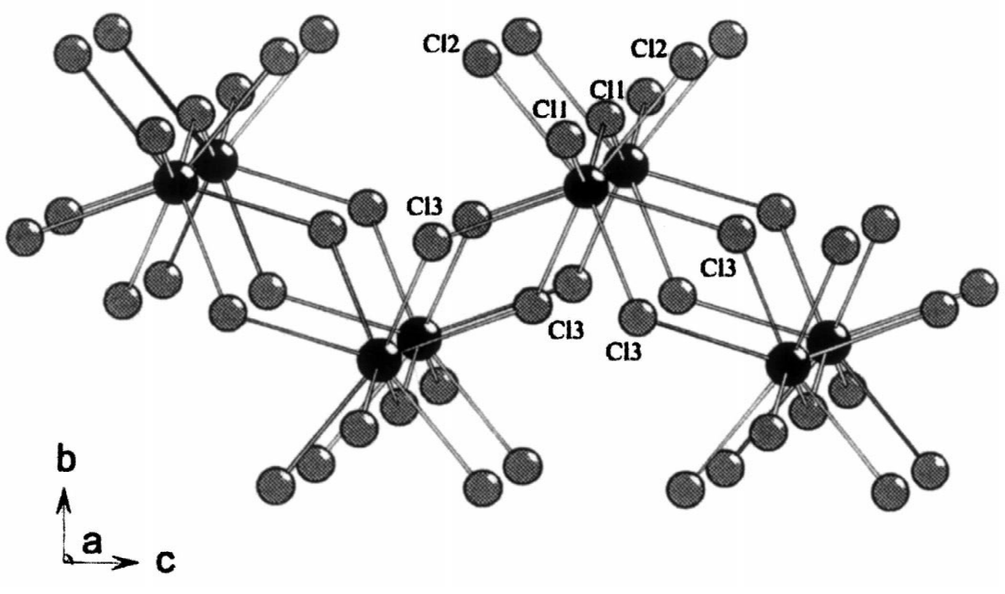

Fig. 3. Corrugated layers $[GdCl_{2/1}Cl^{c}_{2/2}Cl^{e}_{4/2}]\equiv[GdCl_5]$ in $BaGdCl_5$.

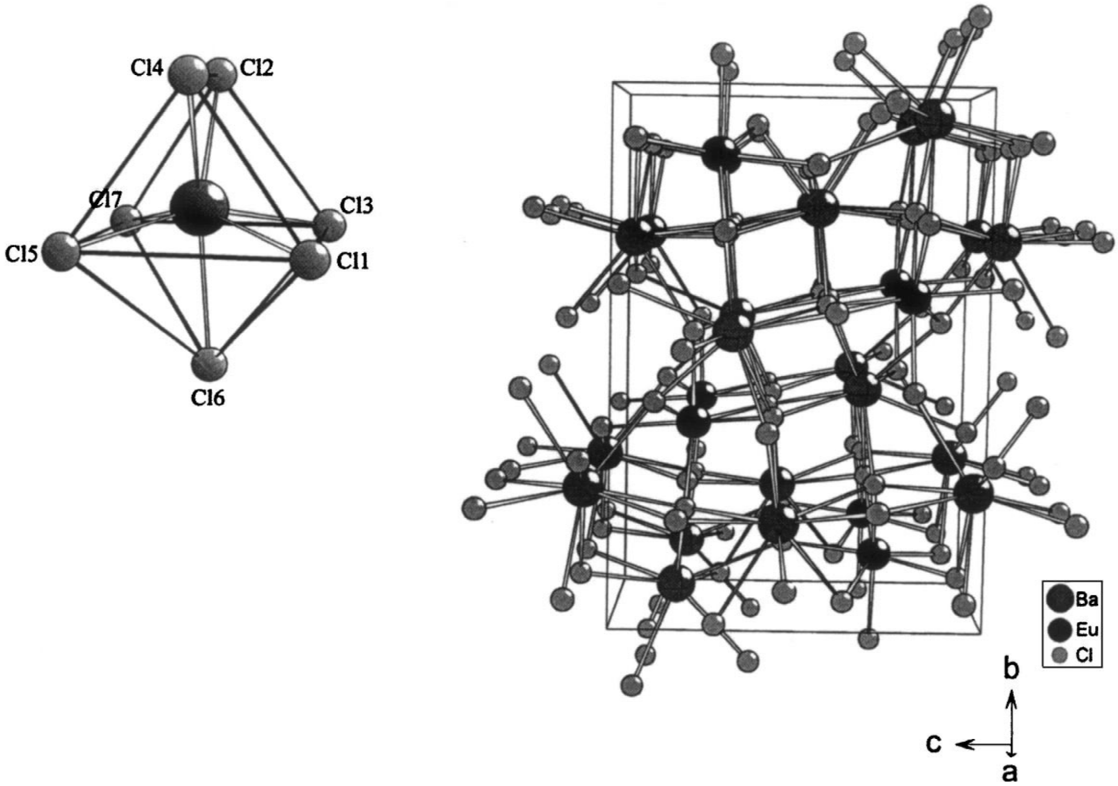

Fig. 4. A monocapped trigonal prism $[EuCl_7]$ and a perspective view of the crystal structure of $Ba_2[EuCl_7]$.

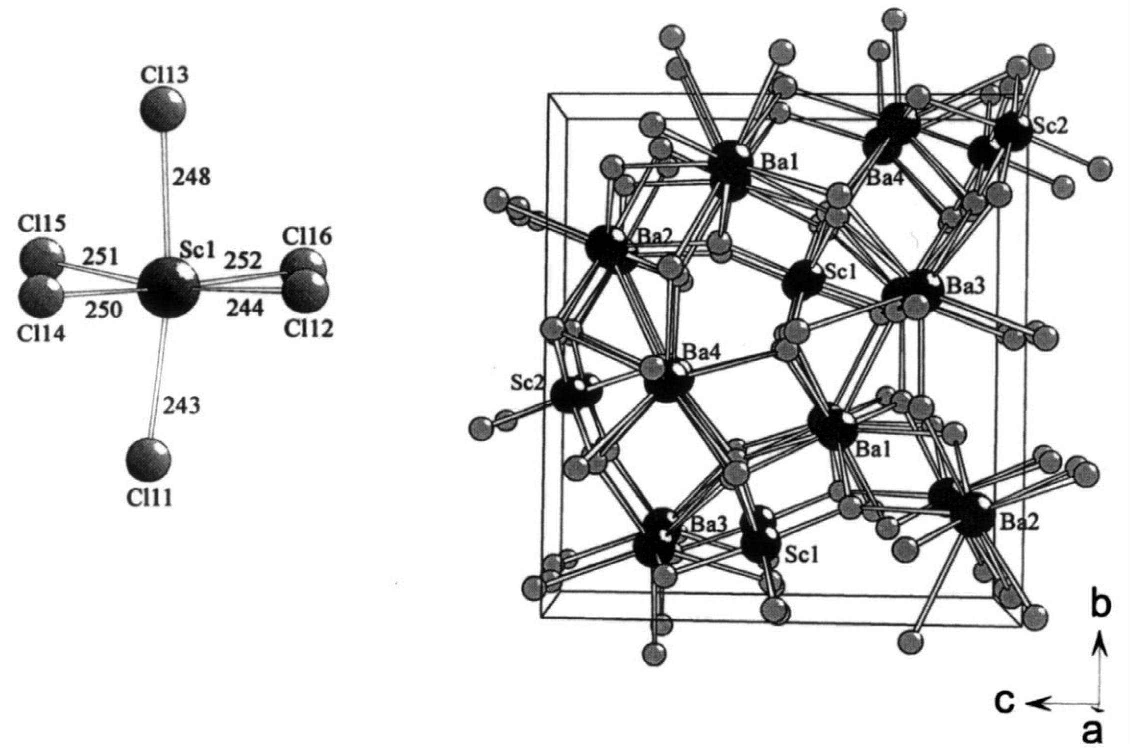

Fig. 5. One of the two crystallographically independent $[ScCl_6]$ octahedra and a perspective view of the crystal structure of $Ba_2ScCl_7=Ba_2Cl[ScCl_6]$.

This has to do with the polyhedral cluster [M_6X_{36}] and its origin from the parent fluorite type of structure.

In the structure of $BaGdCl_5$ [17], which is also adopted for $BaEuCl_5$ and $BaTbCl_5$, Gd^{3+} is still eight coordinate. The square antiprisms are now, apparently subject to the M:X ratio of only 1:5, connected via two common edges and two common corners to form corrugated layers (Fig. 3).

With rare-earth cations equal to and smaller than Eu^{3+}, the $BaCl_2/MCl_3$ type systems contain Ba_2MCl_7 type compounds [3,4]. For these, the crystal structure of Ba_2ErCl_7 was first determined [18]; chlorides with M= Eu–Lu,Y are isostructural [10,19,20]. These all contain isolated [MCl_7] monocapped trigonal prisms (Fig. 4).

In contrast, although of the same formula type, Ba_2ScCl_7 does not contain an isolated $ScCl_7$ polyhedron. Rather, when rewritten as $Ba_2Cl[ScCl_6]$ [21], it becomes clear that it contains isolated octahedra and one solitary chloride per formula unit that is not coordinated to Sc^{3+} (Fig. 5).

4. Related systems

The ionic radius of the In^{3+} ion lies in between those of the smallest lanthanide ion, Lu^{3+}, and the smallest rare-earth ion, Sc^{3+}. Therefore, the investigation of the analogous systems with $InCl_3$ is usually helpful to get the entire picture. The system $BaCl_2/InCl_3$ does indeed contain three ternary chlorides, $BaInCl_5$, Ba_2InCl_7, and Ba_3InCl_9 [4]. None of these have been structurally characterized. One reason for this might be that crystal growth appears to be difficult because they all melt incongruently.

As we had good success with the solvent AgCl in the

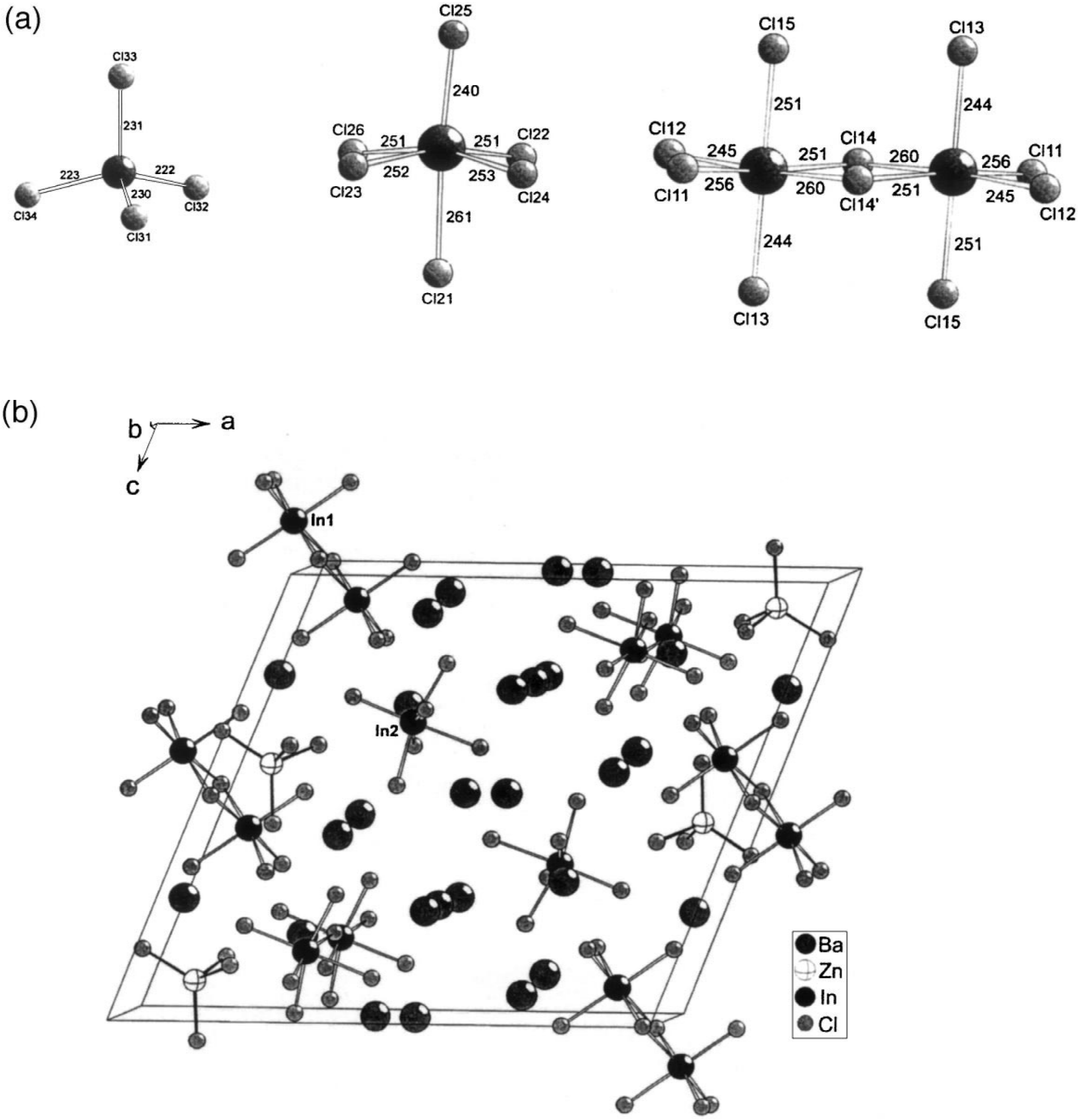

Fig. 6. The polyhedra surrounding Zn^{2+} and In^{3+} in $Ba_6ZnIn_2Cl_{20}$ and a perspective view of the unit cell.

$BaCl_2/MCl_3$ systems, we have used $ZnCl_2$ to attempt to grow crystals in the $BaCl_2/InCl_3$ system. The solvent was, however, not as inert as we had hoped. Rather than a ternary barium indium chloride, two hitherto unknown compounds emerged these attempts, $Ba_6ZnIn_2Cl_{20}$ [22,23] and $BaZnCl_4$ [24].

$Ba_6ZnIn_2Cl_{20}$ contains besides for $[ZnCl_4]$ tetrahedra two types of In/Cl polyhedra, $[InCl_6]$ and $[In_2Cl_{10}]$ groups built from two octahedra sharing a common edge. The formula is best written as follows: $Ba_{12}Cl_{10}[ZnCl_4]_2[InCl_6]_2[In_2Cl_{10}]$ showing that there is a fair number of chloride that do not belong to cations of higher net charges, Zn^{2+} and In^{3+} (Fig. 6).

That solitary ligands occur is becoming a more common feature. As these are very rarely seen in systems with alkali halides, the higher charged alkaline earth cations seem to compete more severely for the halide ligands. One striking example for this is Ba_2CoCl_6 [25] which could just simply contain isolated $[CoCl_6]$ octahedra. It was obtained when chlorides analogous to $BaZnCl_4$ were searched, i.e., $BaCoCl_4$. Surprisingly, this chloride appears not to exist. In Ba_2CoCl_6, as in part of $Ba_6ZnIn_2Cl_{20}$, two octahedra share one common edge so that the formula needs to be rewritten as $Ba_2Cl_2[Co_2Cl_{10}]$ (Fig. 7).

$BaZnCl_4$ crystallizes with the $GaCl_2$ type of structure [24] with Ba^{2+} residing on the eight coordinate sites of Ga(I) and Zn^{2+} occupying the tetrahedral sites of Ga(III) (Fig. 8). This together with $SrZnCl_4$ [24] are the first examples of AMX_4 type compounds with divalent cations. $SrZnCl_4$ belongs to the scheelite type of structure ($CaWO_4$; Fig. 8). We have seen this structure as an antitype for $LiGdCl_4$ [26] already, according to $CaWO_4 \equiv GdLiCl_4$. $EuLiCl_4$ has the same structure [27].

Thus, we see that Eu^{3+} may reside on eight coordinate sites in these structures and so should Eu^{2+} as it has practically the same ionic radius as Sr^{2+} and may in many cases also substitute for Ba^{2+} in halides. These systems are, therefore, model systems for compounds with Sm^{2+}/Sm^{3+}, Eu^{2+}/Eu^{3+} and also, if properly designed, for Dy^{2+}/Dy^{3+} and Tm^{2+}/Tm^{3+}. There are many open questions in these systems, not only concerning the synthesis and the structures but also their optical properties.

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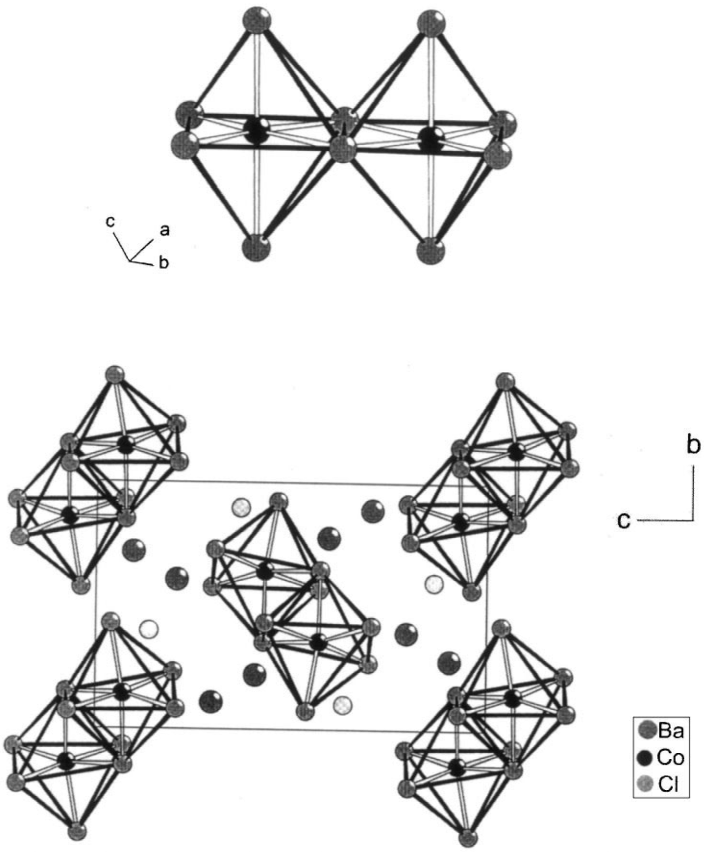

Fig. 7. The $[Co_2Cl_{10}]$ double octahedron and a perspective view of the crystal structure of $Ba_2CoCl_6 \equiv Ba_2Cl_2[Co_2Cl_{10}]$.

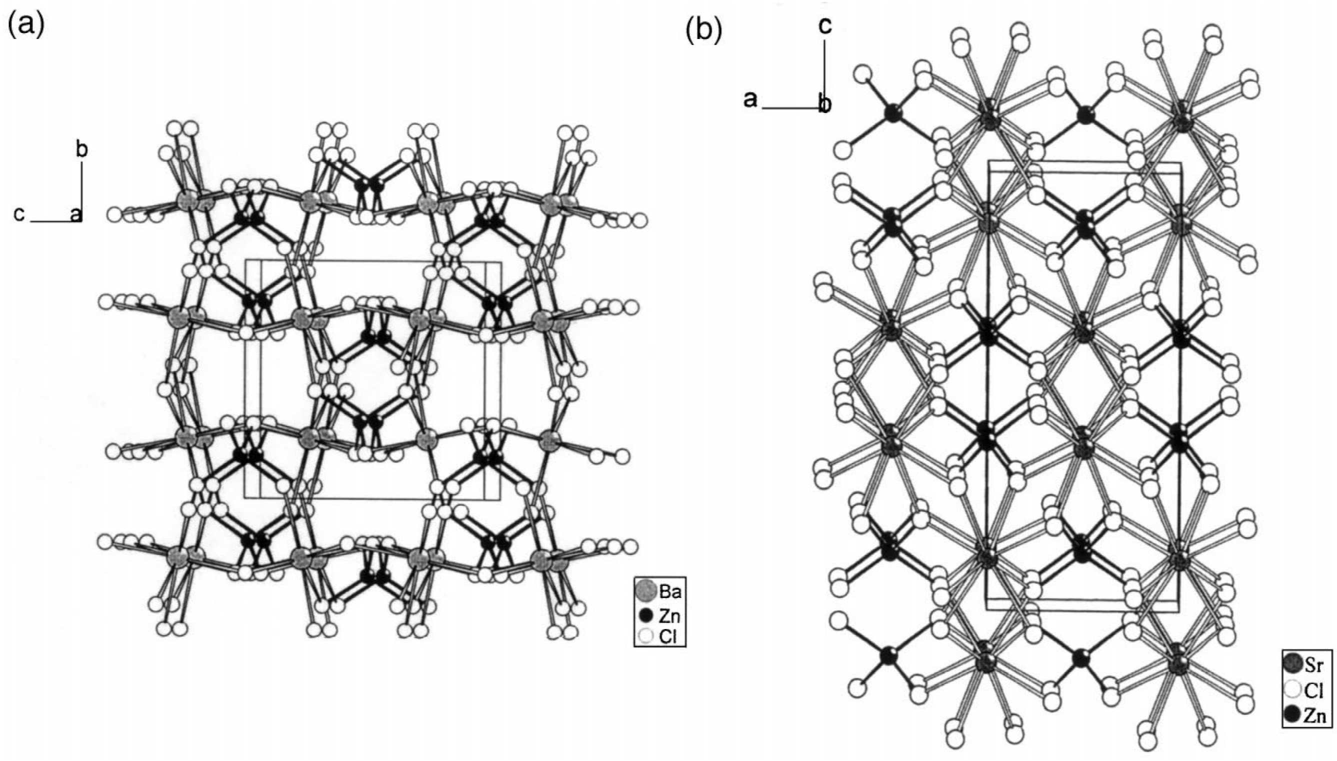

Fig. 8. Perspective views of the crystal structures of $BaZnCl_4$ ($GaCl_2$ type) and $SrZnCl_4$ (scheelite type).

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