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Comparative science of the lanthanide and actinide (lanact) halides

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Abstract

Certain aspects of the chemistries of the binary lanthanide and actinide (lanact) halides are discussed, with main focus on the trivalent chlorides and bromides. These lanact trihalides are the ones most readily prepared, and they exhibit the four different crystal structures known for all lanact trihalides (except trifluorides) at room temperature and pressure (RTP). Formula volumes are correlated with the RTP crystal structures. Correlations with cation radius and/or cationic/anionic radius ratio are used to systematize the structural relationships, including those encountered through the application of pressure. Finally, some unknowns to be addressed in future research are proposed.

Keywords: Halides; Lanthanides; Actinides; Crystal structures; Formula volumes

1. Introduction

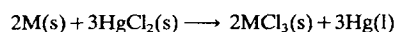
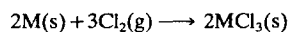
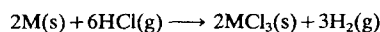
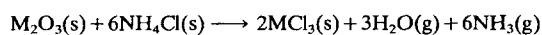
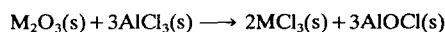
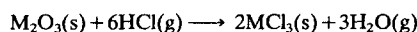
In the development of the chemistries of the lanthanide and actinide (lanact) elements, the halide compounds were often some of the first binary compounds prepared. The number of different lanact halide compounds far exceeds the number of different lanact oxide compounds, the other extensively studied class of lanact compounds. Lanact halides exhibit a wide range of chemical and physical properties – in atmospheric sensitivity, aqueous solubility, redox stability, chemical reactivity, ligand coordination number, metal ion site symmetry, volatility, melting points, etc. Because their melting points are often relatively low, halide samples can be prepared with high optical transparency, including single crystals. Lanact halides are typically used as starting materials for the preparation of the corresponding metals, as hosts for the study of optical and magnetic properties of other f elements doped into them, and as neat compounds for the systematic study of the general chemical and physical properties of these f elements across their respective series. It is in the halide family of compounds that one can stabilize lanact oxidation states both higher and lower than three. These many advantages have led to an extensive literature on the synthesis, characterization and/or physical property determination of f-element halides [1–4].

The present paper will draw attention to certain aspects of this vast knowledge of the binary lanact halides, with main focus on the trivalent chlorides and bromides. These lanact trihalides are the ones most readily prepared, and they exhibit the four different crystal structures known for all lanact trihalides (except trifluorides) at room temperature and pressure (RTP). Following a short summary of selected synthesis routes to trihalides and structural/optical characterization methods, several physical property correlations are discussed. These include melting points, relative stabilities of the di-, tri-, and tetrahalides, RTP crystal structures, formula volumes, and the structural relationships encountered with the application of pressure. In addition, mention is made of some unknowns in lanact halide chemistry to be addressed in future research.

2. Experimental details

A number of the commonly used synthetic methods to produce samples of the lanact trihalides (excluding trifluorides) are given in Fig. 1 in a chemical equation format. Details of a particular preparation scheme depend on the scale of operation (milligrams and up for the lanthanides, milligrams and down for the actinides), whether or not the material is radioactive, and to some degree on the intended use of the product.

Selected synthesis routes



Similar reactions with the corresponding bromide reagents.

Always better to make lanact iodides from a lighter halide or directly by treatment of a lanact metal with $I_2(s)$ or $HgI_2(s)$, e.g.,

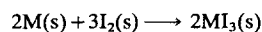
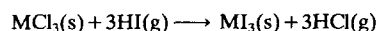


Fig. 1. Commonly used synthetic methods to prepare lanact trihalides (excluding trifluorides).

They are, therefore, best found in the literature for the particular task at hand [1,3,5]. The necessity to provide anhydrous conditions for all the heavier trihalides is constant; they are hygroscopic, becoming more so going from chloride to bromide to iodide. The reasonably high volatilities of most of the lanact trihalides allow single crystals to be grown via vapor transport; their reasonably low melting points allow single crystals to be grown from the melt. The optical clarity of these products makes them ideal hosts for the study of other f elements doped into them [6].

The primary characterization methods used on the lanact halides are X-ray diffraction (both powder and single-crystal analyses) and spectroscopic (both electronic and scattering). In addition, for many of them, thermodynamic values (e.g. melting point, enthalpy of formation, vapor pressure) and their magnetic behavior have been determined. Again, the details of these various kinds of measurements are available in the literature, accessible somewhat through the references given in this paper.

3. Results and discussion

Correlations of the physical and chemical properties of the lanact halides provide insights into the systematic behavior of these materials as a function of their position in the Periodic Chart, f-electron configuration, lanact oxidation state, etc. In addition, determination of a trend in properties across a series permits more accurate interpolation and/or extrapolation to the corresponding property of a halide not yet studied or even prepared; this extrapolation becomes more important in the actinide series. In this section several such correlations are presented and discussed.

3.1. Melting points

The range of melting points exhibited by the known lanact trichlorides, tribromides and triiodides is 525 to 1050 °C (see Figs. 2 and 3). Eliminating the extremes, one finds that the majority of these compounds melt between 600 and 950 °C, with most melting points across a series first decreasing to a minimum and then increasing. As already mentioned, it is this property that makes this class of compounds so amenable to the preparation of single crystals and optically clear macrocrystalline samples that are so useful to the experimentalist.

3.2. Relative stabilities of the di-, tri- and tetrahalides

All the lanact elements have been shown to exhibit at least one trihalide compound, except for the trans-actinides. The availability of salt-like di-

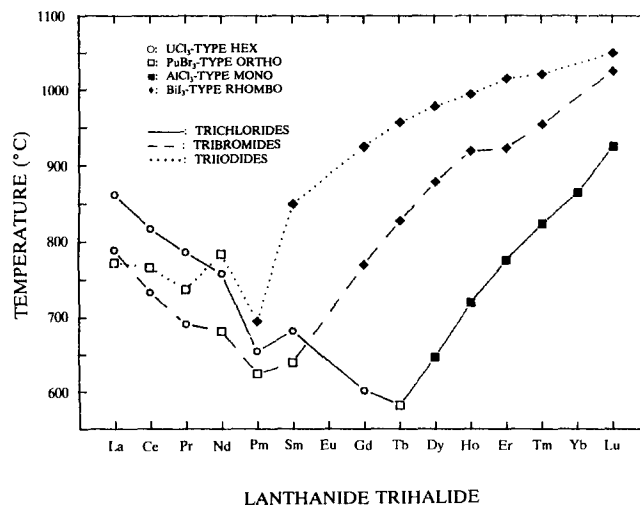


Fig. 2. Melting points of the lanthanide trichlorides, tribromides, and triiodides.

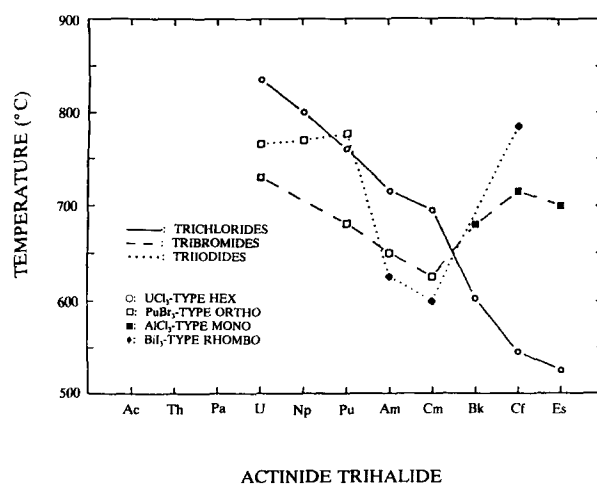


Fig. 3. Melting points of the actinide trichlorides, tribromides, and triiodides.

halides allows one to draw the solid lines given in Fig. 4 (adapted from Ref. [7]) to represent the standard III–II reduction potentials for the limits of existence of difluorides ($X=F$) and dichlorides and dibromides ($X=Cl,Br$) at RTP. The lanact species below the respective lines drawn (more positive III–II potential) should form salt-like dihalides, while those above these lines will not. A line for $X=I$ would appear only slightly above the one shown for $X=Cl,Br$; the salt-like diiodide situation is clouded by the existence of “metallic” ($M^{3+}(I^-)_2e^-$) diiodides. Such correlations provide predictive capabilities (e.g. all the transberkelium actinides should form dihalides) as well as experimental challenges along the lines of demarcation (e.g. might $PmBr_2$ and CfF_2 be prepared?). Only salt-like trihalides (or perhaps diiodides) of the lanact species above the upper solid line exist.

In a similar manner, but in the opposite direction, we can see the relative stabilities of the lanact tetrahalide species in Fig. 5 (adapted from Ref. [7]). The lanact species above the $X=F$ solid line all exhibit salt-like tetrafluorides at RTP, whereas only those lanact species above the $X=Cl,Br$ line are known to exhibit RTP tetrachlorides and tetrabromides. A line for $X=I$ could be drawn just above the zero-volt tick marks, consistent with the existence among the lanact elements of only Th, Pa and U tetraiodides. The same type of comments as given in the previous paragraph applies here as well with respect to prediction and experimental challenge.

3.3. Crystal structures

The six crystal structures exhibited by the various lanact trihalides at RTP are listed in Table 1 along with their space group, *International Tables of Crystal-*

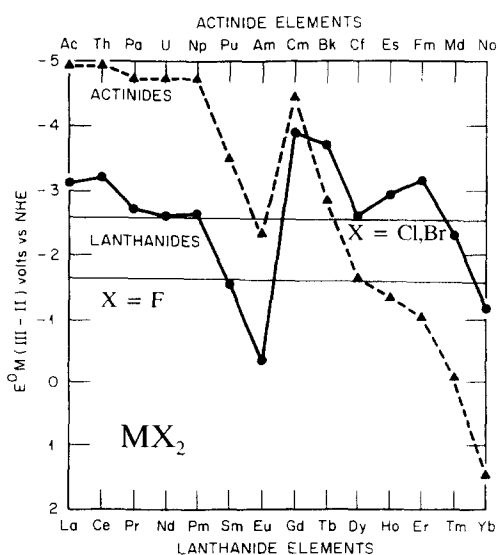


Fig. 4. Relative stabilities of the lanact difluorides, dichlorides, and dibromides correlated with the standard lanact (III–II) reduction potentials.

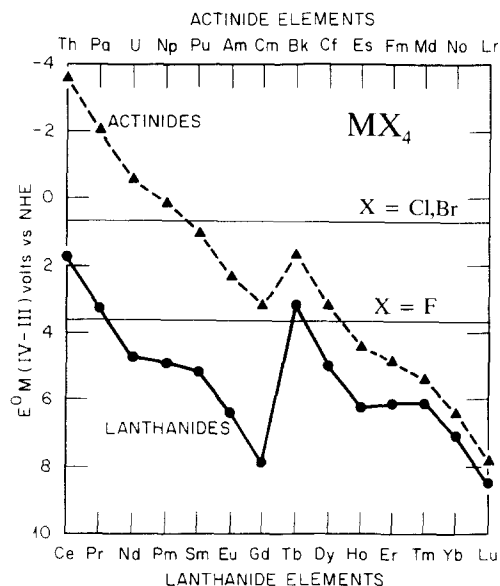


Fig. 5. Relative stabilities of the lanact tetrafluorides, tetrachlorides, and tetrabromides correlated with the standard lanact (IV–III) reduction potentials.

lography (ITC) number, ranges of existence by halide, and coordination number (CN), atomic position in Wyckoff notation, and site symmetry of the lanact³⁺ ion. Certainly the reason that there are so few structures accommodating such a large number of individual compounds is that the lanact³⁺ radii (CN=6) cover a similar range of values: Ln³⁺ ions from 1.03 to 0.861 Å; An³⁺ ions (through Es³⁺) from 1.12 to 0.925 Å. It is the cation/anion radius ratio that is dominant in determining which of these trihalide crystal structures will be exhibited by a particular lanact trihalide.

Only the four rightmost structures in Table 1 are required to account for all the known RTP forms of the lanact trichlorides, tribromides, and triiodides. It is seen that no actinide trichloride exhibits the $AlCl_3$ -type monoclinic structure at RTP, because the actinide³⁺ radius through Es³⁺ is still large enough to be accommodated in the $PuBr_3$ -type orthorhombic structure. When the actinide³⁺ radius is 0.91 Å and smaller, then one should expect the RTP trichloride structure to be the $AlCl_3$ -type monoclinic one. Also note that the RTP lanthanide tribromides do not exhibit the $AlCl_3$ -type monoclinic structure, in contrast to the RTP actinide tribromides, which exhibit all four of these structures in accord with the changing cation/anion radius ratio across the series. This suggests that one might find the $AlCl_3$ -type structure in $EuCl_3$ and/or $GdCl_3$ prepared under special circumstances.

3.4. Formula volumes

The formula volumes of the lanact trichlorides and tribromides at RTP were calculated from available lattice parameters [1,4] and are plotted in Figs. 6 and

Table 1
Lanact trihalide crystal structures, their ranges of existence, and associated crystallographic information

Prototypic structure	LaF ₃ trig	YF ₃ ortho	UCl ₃ hex	PuBr ₃ ortho	AlCl ₃ mono	BiI ₃ rhombo
Space group (ITC No.)	$P\bar{3}c1$ (165)	$Pnma$ (62)	$P6_3/m$ (176)	$Cmcm$ (63)	$C2/m$ (12)	$R\bar{3}$ (148)
Fluorides	La–Eu; Ac, U–Cf	Sm–Lu; Bk, Cf				
Chlorides			La–Gd; Ac, U–Cf	Tb; Bk–Es	Dy–Lu	
Bromides			La–Pr; Ac, U, Np	Nd–Eu; Np–Bk	Bk–Es	Gd–Lu; Bk, Cf
Iodides				La–Pm; Pa–Pu		Sm, Gd–Lu; Am–Es
Lanact ³⁺ coordination number	11	9	9	8	6	6
Lanact ³⁺ atomic position	6f	4c	2d	2c	2g	2c
Lanact ³⁺ site symmetry	C ₂	C _s ^z	C _{3h}	C _{2v}	C ₂	C ₃

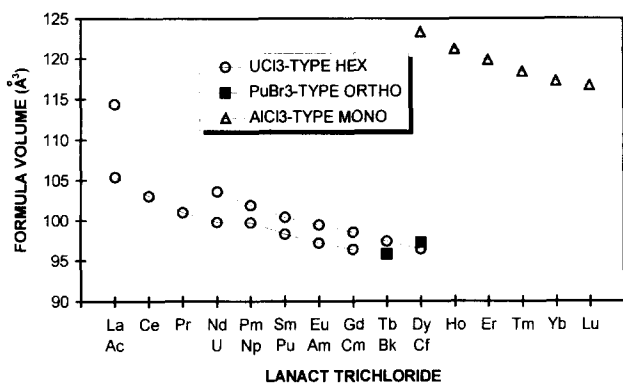


Fig. 6. Formula volumes of the lanact trichlorides at RTP. Solid lines connect lanthanides; dashed lines connect actinides.

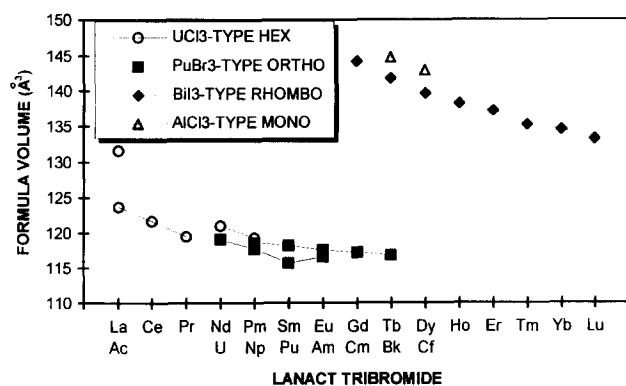


Fig. 7. Formula volumes of the lanact tribromides at RTP. Solid lines connect lanthanides; dashed lines connect actinides.

7, respectively. Solid lines connect the points relating to the lanthanides; dashed lines the same for the actinides. Again, the progression of crystal structures exhibited is evident, with clear ranges of formula volumes being associated with a particular crystal structure. The expected contractions across both series are obvious; the hump at $PmCl_3$ suggests radiation-induced expansion or an inaccurate experimental measurement. Choosing the trichloride data, where the lanact³⁺ ion has a more significant effect in determining the metal–halide distances, one finds the formula volume of a lanthanide

trichloride equal to that of the homologous actinide plus about 3, i.e. $NdCl_3$ and $AmCl_3$ have about the same formula volume, and therefore about the same trivalent ionic radius. It is clear from the plots in Figs. 6 and 7 that the efficiencies of space filling in the $AlCl_3$ - and BiI_3 -type structures are considerably lower than those in the UCl_3 - and $PuBr_3$ -type structures. This fact plays a dominant role in determining the structural phase behavior of a lanact trihalide under pressure. This aspect is discussed below.

3.5. Structural relationships with the application of pressure

If one considers the pressurization of a lanact trihalide at RTP, one should expect its formula volume to decrease and its cation/anion radius ratio to increase. From a structure-field diagram for the lanact trihalides, one finds the progression of RTP crystal structures with increasing cation/anion radius ratio to be the following [8]: BiI_3 -type rhombohedral \rightarrow $AlCl_3$ -type monoclinic \rightarrow $PuBr_3$ -type orthorhombic \rightarrow UCl_3 -type hexagonal. From the work of others [8,9] and looking at Fig. 7, one sees that the efficiency of space filling (i.e. packing efficiency = $(\sum Volume_{ions})/Volume_{unit\ cell}$) increases in the order of trihalide crystal structures given in Fig. 8. Also included are the corresponding metal

CRYSTAL STRUCTURE vs. PACKING EFFICIENCY ($\sum V_{ions}/V_{cell}$)

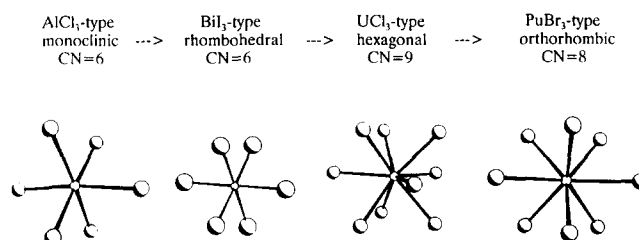


Fig. 8. Lanact trihalide crystal structures in order of increasing efficiency of space filling, shown with the corresponding first coordination sphere geometries.

ion coordination numbers (CN) and first coordination sphere geometries. Interestingly, all experimental results obtained from lanact trihalides under pressure are in agreement with this sequence of crystal structures [8–10]. A more detailed discussion of this observation is available elsewhere [10]. A theoretical explanation for a sequence of crystal structures with increasing pressure increasing to a maximum cation coordination number and then decreasing is given there as well [10]. Also, a suggestion for the existence of a still more efficiently packed lanact trihalide crystal structure has been offered [10].

3.6. Unknowns in lanact halide chemistry to be addressed in future research

Although the wide availability of halides across the lanact series has facilitated the determination of many more physico-chemical properties than reviewed in this paper, there are still experimental challenges to be met. These include the determination of the crystal structures exhibited by the halides of einsteinium ($Z=99$) at RTP, a monumental experimental challenge considering the 20.5-day half-life of the most readily available isotope ($A=253$) and its alpha decay energy of 1.5×10^4 kJ mol⁻¹ min⁻¹. We hope to use optical probes to aid in the identification of the unknown or only semi-quantitatively known einsteinium halide crystal structures. Knowledge of these einsteinium halide crystal structures is important as well for understanding of the physical consequences of alpha decay in the bulk-phase solid state.

A second challenge is the preparation and characterization of a dihalide of berkelium, e.g. BkBr₂. It appears that nature has prepared this material via the alpha decay of EsBr₂, as evidenced by the recognizable CfBr₂ granddaughter ingrowth into EsBr₂ samples with time. However, no direct characterization of a berkelium dihalide has yet been made. A third unknown to be addressed in future lanact halide research comes from

the discussion in the previous section, i.e. the determination of the crystal structure of a lanact trihalide that is more efficiently packed than that in the PuBr₃-type orthorhombic structure. Possible evidence for such transformations at high pressures has been obtained in experiments with PrBr₃, NdBr₃, CmCl₃ and CfCl₃ [10].

Acknowledgments

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