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Exploratory synthesis of reduced rare-earth-metal halides, chalcogenides, intermetallics New compounds, structures, and properties☆

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Abstract

A new direction in reduced rare-earth-metal (R) compounds opened up when tantalum (and niobium) were adapted to use as virtually faultless containers for these reactions, as these gave immediate access to many new metal-rich phases and structures. Examples are summarized for the new binary dihalides (e.g., Pr, Nd, Dy, Ho, Tm), metallic diodides (Sc, La, Ce, Gd), and metal–metal bonded chains (Sc, Y, Gd, Lu) that were so discovered. Furthermore, a large array of condensed metal cluster, chain, and sheet halides arise when a stoichiometric amount of a diverse variety of nonmetal or metal atoms is included to serve as an interstitial, the earliest examples originating with traces of common impurities. A change in anion charge type to telluride affords a whole new regime of condensed metal-rich cluster compounds and structures, including such remarkable examples as (Sc, Gd, Dy)$_2$Te, $Lu_{11}Te_4$, Lu_8Te, and Sc_6PdTe_2. Also, a number of novel Zintl phases, interstitial derivatives of the type R_5Ge_3Z, quasicrystals, and their approximants are generated in other intermetallic systems. Generalities in structures and bonding are described along the way.

Keywords: Reduced rare-earth-metal compounds; Chemical synthesis; Crystal structures; Synthesis; Halides; Tellurides; Bonding

1. Introduction

My involvement in reduced rare-earth-metal chemistry originated with a nice combination of luck, imagination, and environment. I arrived in Ames in 1952 with a joint appointment in the Ames Laboratory and the Department of Chemistry and an interest in reduced metal halides, particularly for the post-transition metals cadmium, gallium, and bismuth. Although I was aware of early reports of the remarkable solutions of significant amounts of more active metals in their molten halides, La, and Ce in their trichlorides in particular [1,2], I was not then actively interested in these. But by a stroke of luck, my office and laboratory were directly above those of Adrian Daane who headed the metallurgy research and development part of Spedding's broad rare-earth production and research programs. I became aware of their use of tantalum containers for casting these metals and their alloys and of their facilities for welding Ta apparatus in many forms. A few years later I asked Len Druding, a recent MIT undergraduate, "what if" we were to try to reduce some of the traditional trivalent rare-earth-metal halides by their respective metals at higher temperatures under "neat" conditions, that is, in RX_3–R systems in tantalum. Adrian readily helped us to get acquainted with the techniques and furnished us some pure metals, and in a short while we had made $NdCl_2$ and NdI_2 [3], this element being a reasonable near-neighbor of the traditional divalent Sm, Eu, Yb for which the dihalides could be made in solution or at least in glass apparatus at moderate temperatures. The Ta container method [4] is now standard around the world, although in fact the lower density and cheaper Nb is satisfactory for most rare-earth-metal systems, especially at temperatures well-below the melting points of the pure metals.

2. Binary halides

The initial studies were on RX_3–R phase diagrams, and two landmark examples are reproduced in Fig. 1, namely for $NdCl_3$–Nd [5] and LaI_3–La [6]. The series of thermal analy-

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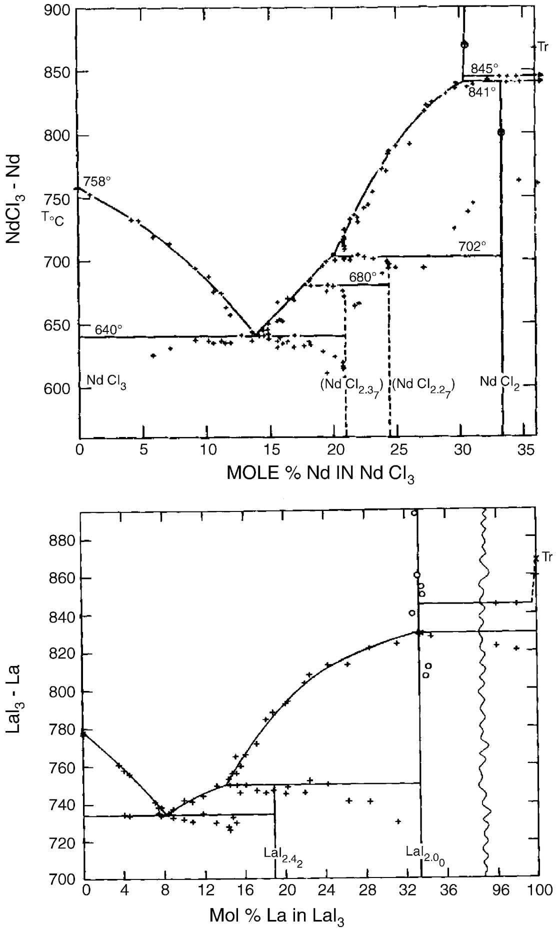

Fig. 1. The original phase diagrams for the $NdCl_3$–Nd and LaI_3–La systems.

sis results shown were achieved by sequentially opening the Ta container in the glovebox, adding weighed metal, rewelding, and re-equilibrating. The procedures revealed the formation of three incongruently melting compounds in the first, $NdCl_{\sim 2.37}$, $NdCl_{\sim 2.27}$, and $NdCl_2$, the first two compositions being estimated from the thermal analysis results and powder patterns, and the last, analytically following equilibration of the salt phase with excess bulk metal below its (peritectic) melting point, 841 °C. The LaI_3–La results revealed the very surprising formation of the congruently melting LaI_2 as well as an intermediate we assigned as $LaI_{2.42}$. The striking neodymium results first demonstrated the ready stability of Nd^{II} when Nd^{III} is reduced by its own metal, the optimum reducing agent when disproportionation of the intermediate state is limiting. The formation of the iconoclastic LaI_2, but not the analogous chloride, represented another novel facet of the solid state, a layered metallic diiodide that can in a very simplified way be represented as $La^{3+}(I^-)_2e^-$ in which delocalization of the third electron among many La^{3+} cores in some sort of a d conduction band is the main feature. Earlier examples of TiO and CeS come to mind.

2.1. Observed phases

We will now return to a more systematic presentation of such results, first, the more or less straightforward examples of simple R^{II} oxidation states, with mention of additional evidence for these states in the melts. In fact, these simple dihalides represent only a fraction of the new and novel reduced phases found in these systems. Many subsequent investigations and characterizations, often by others, have been published on many of these, on their structures and electronic and magnetic phenomena in particular, but we will not attempt to include many of these. The binary metallic halides will also be described before moving on to even more novel phases that exhibit direct metal–metal bonding, first in a few binary systems and then in the large family of interstitially-stabilized ternary and higher phases with cluster, chain, sheet, and network structures.

Table 1 summaries the compositions and structure types of the lowest (most reduced) binary halides among the rare-earth elements, which usage is understood to include Sc and Y. All pertain to equilibrium systems. Data for the better known dihalides of Sm, Eu, Yb and the unknown Pm are omitted. References are also included for systems investigated that do not contain solid reduced products, but only as solutions of R in RCl_3 melt. The number of intermediate RX_{2+x} phases that also form in these systems will not be detailed, although some can be recognized when the same structure type also appears in less reduced systems, i.e., only Pr_2I_5-types as La_2Br_5 and Ce_2Br_5 and the Dy_5Cl_{11}-type for Ho_5Cl_{11}. A general process of reduction of R^{III} to R^{II} appears appropriate to all of these RX_3–R systems as long as we set aside those novel products in which the differentiating electrons are not localized on specific metal centers to yield clearly larger reduced cations (below). Common R^{II} states can also be inferred from solution properties, including in systems in which the reduced solids are not stable enough to allow a new phase to form, e.g., in $LaCl_3$–La, $CeCl_3$–Ce, YI_3–Y, and all RX_3–R systems for Er and Lu. Depressions of the freezing points of liquid RX_3 by added R have been found to be generally consistent with the formation of R^{2+} cations [19,28,37,38]. EMF studies on melts of Ce, Pr, Nd in their trichlorides also support the formation of the dipositive cations [39]. Doping Ce into solid $NdCl_{2x}$ phases can also be achieved to an extent that requires some Ce^{2+} be present [5]. Melt conductivities show an increasing localization of the added valence electrons from La to Nd, the conductances in all cases being activated processes [38].

There is nothing in the melt properties that distinguishes between chloride, bromide or iodide solutes although two other novel phase types separate from some bromide and iodide systems in which the differentiating electrons are structurally invisible insofar as they have a no discernable effect on the cation radii, viz., for R_2X_5 and RI_2 phases that derive from $4f^{n-1}$ $5d^1$ states for the nominal R^{II}. The monoclinic Pr_2I_5-type structure, also formed as La_2I_5 and Ce_2I_5 and for bromides of all three, is best regarded as a "free electron" type $(R^{3+})_2(X^-)_5e^-$ in which the extra electron is presumed to be trapped in a polymetal-centered bonding state and thence not readily conducting. Thus, "$LaI_{2.4}$", Pr_2Br_5, Pr_2I_5, and Ce_2Br_5 are poor semiconductors [40–42], the lanthanum example being paramagnetic but not that of a classic $5d^1$ state. Likewise, only the X-ray absorption near-edge structure of Pr^{3+} is found for Pr_2Br_5 as well as $PrCl_{2.33}$ [43]. Theoretical analyses suggest that these are Mott insulators