Preparation and Processing of Rare Earth Chalcogenides*

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Rare earth chalcogenides are initially prepared by a direct combination of the pure rare earth metal and the pure chalogen element with or without a catalyst. The use of iodine (10 to 100 mg) as a fluxing agent (catalyst), especially to prepare heavy lanthanide chalcogenides, greatly speeds up the formation of the rare earth chalcogenide. The resultant powders are consolidated by melting, pressure assisted sintering (PAS), or pressure assisted reaction sintering (PARS) to obtain near theoretical density solids. Mechanical alloying is a useful technique for preparing ternary alloys. In addition, mechanical alloying and mechanical milling can be used to form metastable allotropic forms of the yttrium and heavy lanthanide sulfides. Chemical analysis techniques are also described because it is strongly recommended that samples prepared by melting should have their chemical compositions verified because of chalogen losses in the melting step.

1. Introduction

A large number of compounds with a variety of stoichiometries exist in the rare earth, R, chalcogenide, X, systems (Ref 1). The most common compounds are the RX, R_3X_4, R_2X_3, and RX_2 compositions. The focus of this review will be concerned with the R_3X_4 and R_2X_3 phases, with R primarily being lanthanum, cerium, praseodymium, and neodymium, and X primarily being sulfur. The preparation and processing of some rare-earth-chalcogenide ternary compounds will also be discussed.

The major scientific and technological interest in the rare earth chalcogenides are the compositions near the R to S ratio of 2 to 3 because these phases are narrow gap semiconductors (Ref 2). In addition, the light lanthanides (lanthanum, cerium, praseodymium, neodymium, and samarium) form a solid solution region from R_3X_4 and R_2X_3 in which there is a continuous transition from a metallic conductor (R_3X_4) to a semiconductor (R_2X_3). These alloys are known as the γ-phase. Concomitant with this change in the electrical conductivity, a metal atom vacancy is introduced from the completely filled lattice of the R_3X_4 phase (which has the cubic Th_3P_4-type structure) as the composition changes toward the R_2S_3 composition (where there are 4.76 at.% vacancies). For the formula units expressed as RX_x (that is, x = 1.3333 for R_3X_4 and 1.5000 for R_2X_3) the number of vacancies, N_V, is given by

$$N_V = (3x - 4)/7x \qquad (Eq\ 1)$$

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and the number of conduction electrons per atom, N_e, is given by

$$N_e = (3 - 2x)/(1 + x) \qquad (Eq\ 2)$$

More details can be found in the review by Gschneidner et al. (Ref 2).

There are a variety of ways to prepare the rare earth chalcogenides. These methods include (a) direct reaction of the components, (b) reaction of the metal with H_2X, (c) reaction of the oxide with the chalcogenide, (d) reaction of the oxide with H_2X gas, (e) reaction of the oxide with CX_2, (f) reaction of the chloride with H_2X, and (g) reduction of the rare earth chalcogenate with $H_2 + H_2X$.

The main problem with most of these reactions, especially (c) through (g), is that the conversion of the oxide (or chloride) is generally incomplete. Furthermore, there is a lack of control of (and thus the knowledge of) the exact final composition. This is especially true for the compositions near R_2X_3 because many of the physical properties are quite sensitive to the exact R to S ratio (Fig. 1, 2). This could account for the wide divergence in the reported experimental results found in the literature. Chemical analyses of the samples after preparation would be helpful, but few investigators have bothered to make them. The author believes that the first method is the best way to prepare the RX_x phases, provided R is fairly pure to begin with, that is, >99 at.% pure with respect to all elements in the periodic table. Typical analyses (in ppm atomic) of the Ames Laboratory light lanthanide metals are 250 H, 75 C, 60 N, 350 O, and 50 F, with the remaining elements <10 for an overall purity of ~99.9 at.% (Ref 4). Commercial metals generally are only 95 to 98 at.% pure with the major impurities being the interstitial elements with a reported wide range of concentration levels (in atomic ppm): 5,000 to 20,000 H, 3000 C, 500 to 8000 N, 12,000 to 35,000 O, and 2000 to 4000 F (Ref 5, 6).

Because of these facts and because most of the author's experience at Ames Laboratory has been on the preparation and processing of the rare earth chalcogenide materials using the direct combination of the elemental components, this paper will concentrate on variations of the first method. These include the direct combination without an iodine catalyst, direc-

tion combination in the presence of a trace of iodine, pressure assisted sintering, pressure assisted reaction sintering, and mechanical milling and alloying. Finally, this paper concludes with two sections dealing with the preparation and processing of ternary phases and a brief summary on chemical analyses of rare earth chalcogenides.

2. Direct Combination (Ref 3, 7, 8)

The direct combination method without the presence of a catalyst is generally limited to the light lanthanide sulfides, especially lanthanum and cerium. The reason for this is the fact that when the chalogen reacts with the rare earth metal it forms a tenacious coating, which in many cases prevents the reaction from being completed in any reasonable time frame (that is, less than one month). Although with patience and some modifications of the procedures described in the following paragraphs, the authors have successfully prepared many of the heavy lanthanide sesquisulfides, R_2S_3 and Y_2S_3, without using a catalyst or fluxing agent (Ref 7). In the case of lanthanum and cerium the volume of the LaS_x phase formed on the surface is

sufficiently large that it spalls off and continuously exposes a fresh metal surface to react with the chalogen gas.

In this procedure thin electropolished strips of lanthanum or cerium are reacted with sulfur in a sealed quartz tube. The metal and sulfur are carefully weighed to ±0.0001 g to give the desired stoichiometry. The quartz tube is outgassed before loading with the two components, then evacuated and backfilled with helium to 650 torr and fused closed with a flame. The sealed tube is heated from room temperature to 600 ± 10 °C in approximately six hours and held there until all of the sulfur reacts, usually several days. It is important not to raise the temperature too fast or too high at this stage because the direct combination of the two elements is an extremely exothermic reaction; the reaction can run away breaking the quartz tube and emitting unreacted sulfur to the atmosphere. For this reason, all the operations are carried out in hoods.

After all of the sulfur is reacted, the furnace temperature is increased to ~900 °C and held there for about one week. If studying or using the low temperature phases, that is, α-La_2S_3, no further heat treatment is carried out (Ref 7). To obtain the high temperature γ-phases (i.e., those with the Th_3P_4-type structure) the alloys are melted in a tungsten crucible under 1 atm of argon (Ref 3, 8). Because most of these alloys (the exception being R_2S_3) melt incongruently, they are annealed after melting at 1700 °C for 4 h and then quickly cooled to room temperature. But because some sulfur is lost in the melting and possibly the annealing steps, the alloys were all chemically analyzed for their rare earth content (see the section "Chemical Analysis").

3. Direct Combination in the Presence of Iodine (Ref 9, 10)

As noted previously, most of the sulfides and selenides (and presumably the tellurides too) cannot be prepared by direct combination without the presence of a catalyst or fluxing agent.
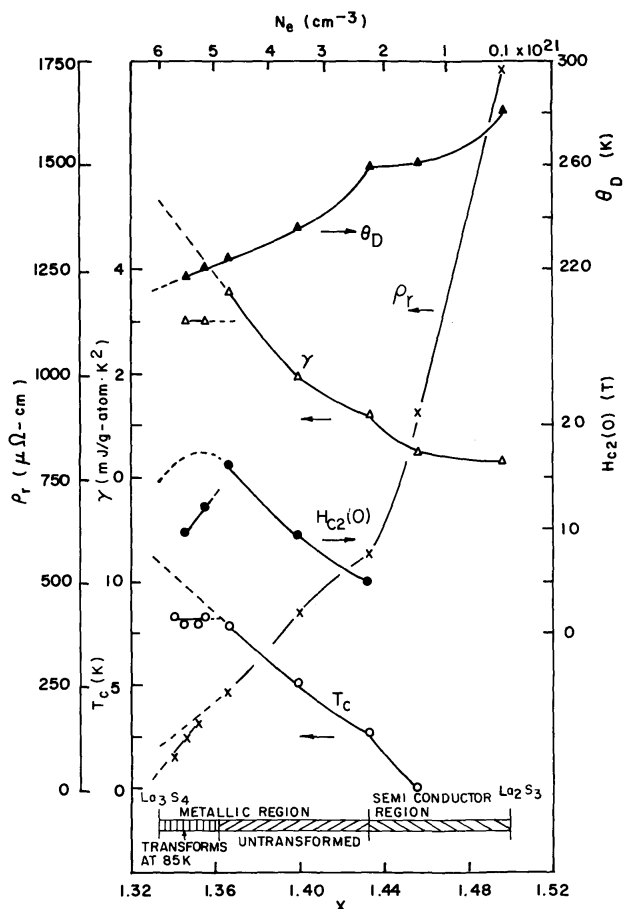

Fig. 1 Low temperature properties of LaS_x alloys as a function of x (or N_e). T_c is the superconducting transition temperature, $H_{c2}(0)$ is the upper critical field required to quench superconductivity, and γ is the electronic specific heat constant, ρ_r is the residual electrical resistivity, and θ_D is the Debye temperature (Ref 3). Courtesy of *Physical Review*
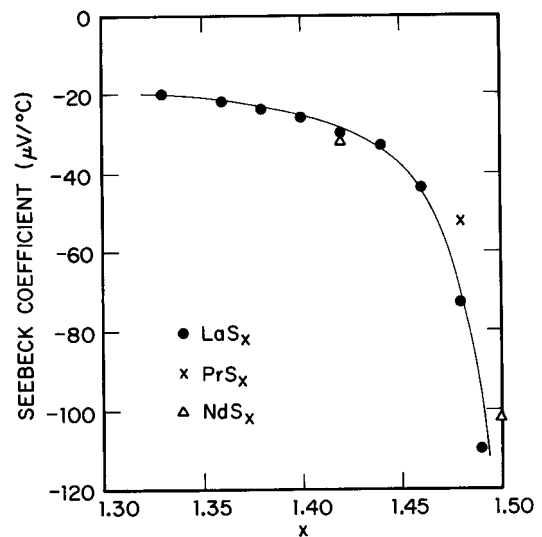

Fig. 2 The room temperature Seebeck coefficient as a function of composition for some RS_x phases (Ref 2). Courtesy of Materials Research Society

The addition of ~100 mg of iodine to a 10 to 30 g reaction mixture of R plus X is sufficient to allow the reaction to go to completion. The temperatures and procedures outlined in the previous section are also followed in this modification of the direct combination reaction.

The iodine is thought to react with the rare earth metal to form the triiodide, which serves as a flux and dissolves the chalogen. This enables the chalogen to decompose the triiodide to form a RX_x phase and free the iodine, which in turn reacts with the metal to form more triiodide, allowing the process to continue. Takeshita, Beaudry, and Gschneidner (Ref 10) noted that the reaction time for the complete form of the RS_x phase was 2 h for lanthanum and 2 days for lutetium, which is much faster than the direct combination without a fluxing agent, especially for lutetium. They also noted that the reaction time increased with increasing the atomic number of the lanthanide metal. The same authors found that the iodine flux worked quite well for preparing the sesquisulfides of scandium, erbium, and lutetium (Ref 11) and ytterbium (Ref 12), and the substoichiometric sesquiselenides of cerium and praseodymium (Ref 9), while Han, Gschneidner, and Cook (Ref 13) presented details for successfully preparing η-Dy_2S_3 (orthorhombic phase) by this technique.

4. Pressure Assisted Sintering (PAS) (Ref 11)

Because the main emphasis of the Ames Laboratory research was to study the electrical, thermoelectric, and thermal conductivity properties of these rare earth chalcogenides, it was necessary to have solid compacts, which had densities close to theoretical. But because the preparation techniques described previously generally yield powders, except in cases where the materials are melted, it was necessary to develop a process to obtain these compacts. It was found that simple cold pressing of the powder and then sintering would not yield viable specimens for making reliable physical property measurements; the samples contained too many voids (Ref 14). Thus, a high (modest) pressure technique for making such compacts was developed (Ref 11). This process is called pressure assisted sintering (PAS). The rare earth chalcogenide powder was molded into a 0.6 cm diameter by 1.9 cm high cylinder by sintering in a dynamic volume of ~10^{-3} torr (10^{-1} Pa) under a pressure of ~41.4 MPa (~6000 psi) and at a temperature of ~1350 °C. The die and plunger were fabricated from high purity graphite. There was no evidence of reaction between the rare earth chalcogenide and the graphite. The use of PAS technique to prepare physical property measurement specimens was described for the sesquisulfides of scandium, erbium, and lutetium (Ref 11), and ytterbium (Ref 12), and some ytterbium ternary sulfides containing calcium, barium, or vanadium (Ref 12).

4. Pressure-Assisted Reaction Sintering (PARS) (Ref 14-16)

The pressure assisted reaction sintering (PARS) method was developed to more reliably obtain alloy compositions in the solid solution region between $LaS_{1.333}$ and $LaS_{1.500}$ (Ref 14).

Subsequently, the PARS technique has been successfully used to prepare a number of other binary and ternary compounds. The method involves the mixing of the stoichiometric La_2S_3 and LaH_3 powders in the desired proportions to give the desired composition and reacting them in a hot press (Ref 14).
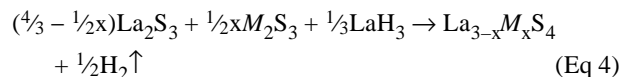
The La_2S_3 is prepared as described previously and then ground into a fine powder (<150 mesh). The LaH_3 was synthesized by hydriding freshly electropolished lanthanum metal in a stainless steel container under ~10 atm of H_2 at room temperature. The reaction starts anywhere from a few minutes to a few hours depending on the cleanliness of the metal surface (Ref 14). Once the H_2 starts to react with the lanthanum, the exothermic nature of the hydriding process assures that the reaction rapidly proceeds to completion. The LaH_3 is cooled to room temperature and crushed to a <150 mesh powder. Because LaH_3 is quite reactive, all procedures must be carried out in a glove box. The two powders are intimately mixed and then placed in the graphite die described previously in the section on the PAS method. The die, sample, and plunger are evacuated to 10^{-3} torr (10^{-1} Pa) and then heated by an induction furnace, while a ~41.4 MPa (~6000 psi) pressure is maintained. When the temperature reaches ~800 °C a large amount of H_2 is released because of the decomposition of LaH_3. At ~900 °C a rapid shrinking of the sample was observed. The pressure was maintained during this stage, and after the shrinkage slowed the temperature was increased to ~1450 °C, and the sample was held at this temperature and 41.4 MPa (6000 psi) for 2 h. The resultant materials had a density greater than 97% of theoretical; in most cases it was much closer to 99%.

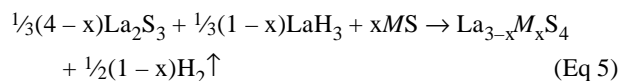In the PARS method the following overall chemical reaction occurred:

$$\tfrac{1}{3}yLa_2S_3 + (1 - \tfrac{2}{3}y)LaH_3 \rightarrow LaS_y + (\tfrac{3}{2} - y)H_2\uparrow \quad \text{(Eq 3)}$$
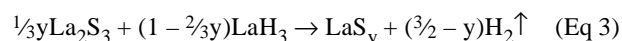
In reality the reaction occurs in two steps. First, the LaH_3 is decomposed, and the H_2 is pumped from the system leaving behind a fine reactive powder of lanthanum metal. The second reaction occurs when the temperature reaches ~920 °C, and the molten lanthanum metal (its melting point is 918 °C) will fill in the cavities between the La_2S_3 grains and react with La_2S_3 to form LaS_y. There are two other important factors. One factor is the presence of H_2 gas, which helps to protect the highly oxidizable lanthanum metal that would react with any oxygen present to form a La_2O_3 coating. The oxide coating will prevent the molten metal from flowing between the La_2S_3 grains and slow down the reaction between lanthanum and La_2S_3. The second factor is the applied pressure on the compact, which helps to squeeze the shrinkage cavities and voids that develop during this process.

The PARS method has also been successfully used to prepare YbS by reaction of Yb_2S_3 with YbH_2 (Ref 12), and also a number of ternary compounds of the general formula $La_{3-x}M_xS_4$ where M = Sm, Eu, Yb (Ref 15), and also M = Ca, Sr, Hg (Ref 16). In the ternary sulfide case the overall chemical reaction is:

$$(\tfrac{4}{3} - \tfrac{1}{2}x)La_2S_3 + \tfrac{1}{2}xM_2S_3 + \tfrac{1}{3}LaH_3 \rightarrow La_{3-x}M_xS_4$$
$$+ \tfrac{1}{2}H_2\uparrow \quad \text{(Eq 4)}$$

for M = Sm and Yb, but for the divalent cations (i.e., M = Eu, Ca, Sr, Hg), the chemical reaction is:

$$\tfrac{1}{3}(4-x)La_2S_3 + \tfrac{1}{3}(1-x)LaH_3 + xMS \rightarrow La_{3-x}M_xS_4$$
$$+ \tfrac{1}{2}(1-x)H_2\uparrow \qquad (Eq 5)$$

The basic procedure for preparing the ternary sulfides is essentially the same as described previously for the preparation of the LaS_x phases, although somewhat lower pressures (31 MPa, or 4,500 psi) were used in preparing the ternary compounds (Ref 15, 16). The binary sulfides (La_2S_3, Sm_2S_3, EuS, Yb_2S_3, CaS, and SrS) were prepared by the direct combination of the respective metal and sulfur following one of the procedures described earlier. The HgS was purchased from commercial sources (Ref 16).

5. Mechanical Milling and Alloying (Ref 17, 18)

Mechanical alloying is an excellent method for preparing alloys when one component is a low melting phase with respect to a second component. Thus, Han et al. (Ref 17) explored the use of this method to prepare a solid solution alloy of copper (the low melting phase, 1083 °C) dissolved in α-Dy_2S_3 (the high melting phase, 2010 °C). Much to their surprise, after mechanically alloying the α-Dy_2S_3 and copper powders for 4 h in a Spex mill, the resultant solid solution alloy $(Dy_{2-x}Cu_x)S_3$ had the cubic γ-R_2S_3 structure (i.e., the defect Th_3P_4-type structure). In the case of Dy_2S_3, the γ-phase is the thermodynamically stable phase above 1190 °C. The authors soon found that by mechanically milling Dy_2S_3 by itself, the metastable γ-phase is formed in 1 h, indicating that the copper is not necessary to stabilize the γ-phase (Ref 17). Similar results were found for Y_2S_3, but in this case the room temperature δ-Y_2S_3 (monoclinic) phase exists all the way to the melting point, and the γ-phase only exists at high pressure. Nevertheless, the cubic γ-phase was formed in pure Y_2S_3 by mechanical milling and in the $(Y_{2-x}Cu_x)S_3$ alloy by mechanical alloying δ-Y_2S_3 and copper powders (Ref 17). In both cases the α-Dy_2S_3 and δ-Y_2S_3 powders were prepared by direct combination of the pure metal and sulfur.

When the R_2S_3 or $(R_{2-x}Cu_x)S_3$ powders were consolidated to make a compact for physical property measurements by heating to 1100 °C for 1 h under a pressure of 75.9 MPa (10,800 psi) they reverted to their respective equilibrium phase (Ref 17). One exception to this observation was reported by Han et al. (Ref 13). In this case, they started with the η-Dy_2S_3 (orthorhombic-U_2S_3 type) phase and added various amounts of copper (0 to 15 at.%). Again after mechanically alloying, the γ-phase was formed, and during the high-pressure, high-temperature heat treating, all alloys reverted to the η-form, except for the alloy containing 2.5 at.% Cu, which transformed to α-$(Dy_{2-x}Cu_x)S_3$ structure (i.e., the orthorhombic-Gd_2S_3 type).

In a later paper Han et al. (Ref 18) also prepared the metastable high pressure, γ-R_2S_3 form for R = Er, Tm, Yb and Lu. However, for Tm_2S_3 and Lu_2S_3 the γ-phase coexisted with the corresponding equilibrium ambient polymorphic phase, monoclinic δ-Tm_2S_3, and rhombohedral ϵ-Lu_2S_3 phases, respectively.

6. Chemical Analysis (Ref 3, 7, 8)

In procedures in which the rare earth chalcogenide is melted, it is quite possible that some of the chalogen is lost to vaporization because of the high melting points of the compounds. So in these cases it is important that a chemical analysis is made of the sample. But for compounds that have been prepared by PAS or PARS the need for a chemical analysis is not nearly as strong and in general no such results have been reported.

The first step is to dissolve the sulfide in 4.8 M hydrochloric acid. The rare earth content is determined by titrating with ethylenediamine-tetraacetic acid (EDTA), which had been freshly standardized against a pure rare earth sample dissolved in hydrochloric acid. The titration was completed at a pH of 5.5 using xylenol orange as the indicator (Ref 3). The sulfur content was determined by collecting the hydrogen sulfide gas when the rare earth sulfide was dissolved in the initial step. The sulfide gas was collected in a solution of hydrogen peroxide and sodium hydroxide. The sulfate that was formed was determined as barium sulfate (Ref 7, 8). Analyses have been reported for yttrium sulfides (Ref 7), lanthanum sulfides (Ref 3), cerium sulfides (Ref 8), and lutetium sulfides (Ref 7). The precisions reported varied from ±0.002 to ±0.006 in x for RS_x.

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