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NOTE

A New Method for Preparing Rare-Earth Monosulfides

The rare earth monosulfides (*Ln*S) have attracted a great deal of attention recently due to the semiconductor–metal transition in phases such as SmS. The aim of this note is to describe a novel method for the preparation of rare-earth monosulfides by a double decomposition reaction between lead sulfide and the rare earth metal (*Ln*): $PbS + Ln \rightarrow Pb + LnS$.

Several methods of preparation of this monosulfide have been described in the literature:

(1) By aluminothermal reaction of a mixture of the sesquisulfide with oxysulfide or oxide: $3Ln_2O_2S + 3Ln_2S_3 + 4Al \rightarrow 12LnS + 2Al_2O_3$ at 1350°C; the highly volatile aluminum suboxide species is eliminated by sublimation under vacuum at this temperature (*1*).

(2) By direct reaction between sulfur and metal in a sealed evacuated silica tube heated between 500 and 700°C, followed by heat treatment at higher temperature (1100°C).

(3) By reduction of the sesquisulfide Ln_2S_3 with an excess of metal in a furnace between 500 and 800°C under vacuum, the excess of rare-earth metal being removed by sublimation between 1000 and 1200°C (*2*).

In attempts to study crystalline solution formation among different rare earth monosulfides and with metallic sulfides (crystallized in the cubic, NaCl type system) we found that it was impossible to obtain a crystalline solution between *Ln*S ($Ln =$ Y, Sm, Gd, Nd) and PbS at any concentration. It was noted that the lead sulfide was always decomposed with deposit of lead on the walls of the quartz tube. Either monosulfides, or higher sulfides, of the rare-earth metal (depending on the temperature of the reaction and the concentration of lead sulfide) were formed simultaneously. It therefore seemed to be of interest to try to use this reaction to obtain the rare earth monosulfide. We have studied in detail the conditions for the formation of GdS, SmS, NdS, and YS and crystalline solutions of various cations therein using the following procedure.

High purity lead sulfide is mixed with powdered rare earth metal in stoichiometric proportions; the powder is degassed by heating at 500°C under vacuum and then pressed into a pellet and placed in a graphite tube in a cleaned quartz tube and sealed. The charge is reacted for 48 hr between 600 and 700°C. The X-ray patterns show that, at this stage, the exchange reaction is complete, yielding Pb and *Ln*S. (If the reaction is carried out at higher temperatures (750 to 900°C), one obtains the cubic sesquisulfide Ln_2S_3.) The lead formed is removed from the pellet by distillation in a horizontal furnace with a temperature gradient. The high temperature side is kept at 950°C, the cool end at about 200°C. After 24 to 48 hr, all the lead is deposited at the cool end of the quartz tube and the monosulfide obtained is very well crystallized. The X-ray patterns of most of the *Ln*S phases (especially with Gd, Y) show the presence of a small amount of the oxysulfide formed simultaneously with the monosulfide, but no PbS or Pb can be detected in the X-ray patterns. The source of the oxygen is undoubtedly in the starting materials, especially the metal (which can *hardly* be obtained "pure" at all under these conditions).

Explanations for the success of this double decomposition are to be found in the lattice energy terms and the electronegativities of the compounds and ions concerned. The ΔG° (300°K) for PbS is −36 kcal/mole, and for CeS it is −226 kcal/mole (only rare-earth phase for which data are available (*4*)).

A second interesting possible application of this reaction between lead sulfide and the rare-earth metal is the potential of obtaining at "low temperatures" (i.e., without melting the mixtures) a crystalline solution between various rare earth monosulfides. One application for such crystalline solutions would be to permit adjusting the pressure of the metal–semiconductor transition in SmS(*3*) to convenient values such as 1 atm at ambient temperature. In order to obtain such crystalline solutions between SmS and *Ln*S (*Ln* = Y, Nd, Gd) the following procedure was used. Appropriate amounts of Sm and *Ln* were reacted with PbS at 700°C for 48 hr. The proportion of Sm and *Ln* was always chosen in order to obtain the collapsed (= metallic) phase in SmS (Sm = 0.75, *Ln* = 0.25). At this stage the X-ray pattern showed the presence of lead not yet removed from the pellet, SmS and extra X-ray lines displaced from the SmS lines. The lattice parameter can be attributed to a collapsed metallic $Sm_{1-n}Ln_nS$ phase, although there is no evidence for excess *Ln*S lines in the patterns. By heating the pellet at 1100°C the SmS lines disappear progressively, and the lines corresponding to the solid solution increase. After approximately 2 or 3 days, the sample obtained is golden-yellow and the X-ray pattern shows only the presence of the diffraction lines of the collapsed crystalline solution phase of $Sm_{0.75}Ln_{0.25}S$. It should be noted that in these experiments also some oxysulfide phases are found simultaneously, especially the oxysulfide corresponding to the "doping" metal (Gd, Nd, Y) and only a very small amount of Sm_2O_2S. We attribute the oxygen again to handling of the original metal phase in air.

The literature reports that by mixing preformed *Ln* monosulfides, formation of the crystalline solution is only possible after melting (at temperatures higher than 2000°C). For comparison of this procedure to our PbS exchange method, a pellet was made of 0.25 GdS and 0.75 SmS and heated under the same conditions (3 days at 1100°C). The X-ray pattern from the final product showed only a weak line indicating the beginning of the formation of a crystalline solution and mainly unreacted monosulfides.

Our new method of preparation of rare-earth monosulfides by the exchange reaction between lead sulfide and the rare earth is therefore especially interesting for preparing crystalline solutions in *Ln*S at low temperature. Further experiments are in progress in order to extend this method to other systems.

Acknowledgments

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