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AN IMPROVED METHOD FOR PREPARING
RARE EARTH SESQUICHALCOGENIDES

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W-7405-ENG-82

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-82 between the U.S. Department of Energy and Ames Laboratory.

BACKGROUND OF THE INVENTION

This invention relates to an improved method for preparing rare earth sesquichalcogenides. More specifically, this invention relates to an improved method for preparing high purity rare earth sesquisulfides and sesquiselenides.

10 There is interest in refractory materials which have semiconductive electrical and heat transfer properties, for high temperature electronic applications, and in particular for thermo-electric power generation.

The rare earth sesquichalcogenides are a class of materials which generally meet these requirements. However, to maintain these desirable physical properties, it is important that these materials be as free from impurities as possible.

20 The preparation of these rare earth compounds in a highly pure form has proven to be difficult. Furthermore, it has been found difficult to prepare compounds which

have the precise stoichiometry desired for semiconductor and thermoelectric elements.

The rare earth sesquisulfides and sesquiselenides, have heretofore, been prepared by a variety of methods. Many of these methods are extensively reviewed in U.S. Patent No. 3,748,095, which was issued July 24, 1973. The method of preparation claimed in that patent comprises generally of contacting a metal oxide or salt with a mixture of gases such as hydrogen sulfide and carbon disulfide at a temperature 10 from 900 to 1500°C in the absence of oxygen and water vapor. While the preparation of a number of the rare earth chalcogenides is possible by this method, it has proven difficult to control the content of oxygen and other gaseous impurities in the final product and to remove the free sulfur formed during decomposition of the gaseous reactants. Furthermore, since the ratio of chalcogen to rare earth in some of the compounds may vary over a wide range, it is difficult to prepare a product which is limited to a desired stoichiometry.

Another method currently in use for the preparation of 20 rare earth chalcogenides involves the direct reaction of sulfur or selenium on pieces of rare earth metal in a sealed capsule at temperatures up to 1100 to 1200°C for periods of up to 200 hours. Pieces of metal are used rather than powders because it is easier to control both purity and the speed of reaction in this manner, which is important since the purity of the product is limited by the purity of the starting materials. However, in gas-solid reactions such as this, the reaction product forms as a dense hard skin on the metal surface, and the chalcogen, which is

gaseous at this temperature, must diffuse through this skin into the metal core for the reaction to proceed. This requires long reaction times and, with many metals, will prevent the reaction from going to completion. To overcome the problem, the surface area of the metal is increased, for example by forming the metal piece into a sponge or a thin sheet. However, this can introduce contaminants into the reaction which will affect the quality of the final product and furthermore, reactions involving the heavier rare 10 earths may still not go to completion. Thus, in addition to impurities, control of the final product composition remains difficult.

SUMMARY OF THE INVENTION

A new method has been developed for the preparation of high purity rare earth sesquichalcogenides which eliminates many of the problems of product composition and product purity associated with the prior art methods of preparation.

By the method of the invention for the preparation of high purity rare earth sesquichalcogenides, the rare earth, 20 as one or more pieces of metal, is placed into an inert reaction vessel together with a stoichiometric amount of a chalcogen and a small amount of iodine and the vessel sealed under a vacuum. The sealed vessel is then heated to a temperature above the vaporization temperature of the chalcogen and below the melting point of the rare earth and maintained for a period of time sufficient for the elements to react and form the rare earth sesquichalcogenide. The iodine is then recovered from the vessel and product, whereby the pure rare earth sesquichalcogenide remains.

A number of distinctions are readily apparent between the method of this invention and the prior art. For example, in the present invention, the rare earth is preferably in the form of a single piece or lump of metal, rather than in a form having a high surface area, such as a sponge or thin sheet. This avoids potential product contamination by reducing the possibility of the rare earth metal becoming contaminated with oxygen and other gases from the environment. The reactants are sealed into a reaction vessel so that

10 there is not a continuous flow of gases into the reactor vessel to introduce impurities which can contaminate the product. Here the only impurity added to the reaction is iodine, which is easily removed from the product once the reaction is completed. Product composition is easily controlled because stoichiometric quantities of reactants are placed in the reaction vessel and the reaction goes to completion. Finally, the reaction is completed at temperatures substantially lower than those required by the prior art reducing energy requirements and reducing the possibility of contamination, which increases with increasing

20 temperature.

The method of the invention is suitable for the preparation of sesquichalcogenides of yttrium and scandium in addition to the rare earth elements: thus the preparation includes elements 21 and 39 in addition to elements 57 to 71 of the periodic table. Chalcogens include both sulfur and selenium.

It is therefore one object of the invention to provide an improved method for the preparation of high purity rare

earth sesquichalcogenides.

It is another object of the invention to provide an improved method for preparing of rare earth sesquichalogenides which have high purity at a controlled stoichiometry.

DETAILED DESCRIPTION OF THE INVENTION

These and other objects of the invention for preparing high purity rare earth sesquichalcogenides may be met by placing the rare earth, as one or more pieces or lumps of high purity metal, into an elongated quartz reaction vessel, 10 adding a chalcogen which may be either sulfur or selenium to the vessel, the amount of chalcogen being a stoichiometric amount sufficient to react with the rare earth metal to form a sesquichalcogenide, and adding an amount of iodine equal to at least 1/1000 by weight of the rare earth metal present, to the vessel. The vessel is then evacuated to at least 10^{-3} torr, sealed and heated to about 750 to 900°C for about 5 hours to 3 days to complete the reaction and form the rare earth sesquichalcogenide.

The sesquichalchogenide can be separated from the iodine 20 by cooling one end of the reaction vessel which does not contain the reaction product, while the other end containing the product is heated to at least 870°C , preferable from 950° to 1000°C to vaporize and drive the iodine from the product. The iodine condenses at the cold end of the reaction vessel, leaving the high purity rare earth chalcogenide at the hot end.

The rare earth is preferably present in the reaction vessel as one or more pieces or lumps of metal having a low surface area rather than as a high surface area powder or

thin metal foil to eliminate possible contamination. The rare earths, as used herein, include scandium and yttrium in addition to the lanthanide rare earths. The physical form of the chalcogens is not critical since they are vaporized during the reaction.

The reaction vessel must contain iodine in an amount equal to at least 1/1000 by weight of the rare earth metal present, in order for the reaction to go to completion.

Amounts greater than this do not affect the reaction, but 10 must be recovered to purify the final product.

The reaction vessel must be of a material which is inert to both rare earth metals and chalcogens at reaction temperatures. The material of choice is quartz although an inert carbon such as vitreous carbon may also be suitable.

The reaction must take place in a vacuum to eliminate possible product contamination from atmosphere gases such as oxygen and nitrogen. The vacuum should be at least 10^{-3} torr. Reaction temperatures will depend upon the particular chalcogen and rare earth being reacted. The 20 temperature must be sufficient to vaporize the chalcogen while remaining below the melting temperature of the rare earth metal which would react with and destroy the reaction vessel. Thus the minimum temperature is about 500°C for sulfur and about 650°C for selenium. Preferably the temperature range is from about 750 to 900°C to ensure completion of the reaction within a reasonable period of time.

Reaction times depend upon the particular reactants and to some extent upon the massiveness or the size of the

piece or pieces of rare earth metal present in the reaction vessel, but must be sufficient to complete the reaction to form the sesquichalcogenide. In general, times have been found to vary from about 5 hours to about 3 days depending upon the particular rare earth metal.

Once the reaction has gone to completion as evidenced by the absence of free chalcogen, it is preferred that the temperature of the product be maintained at 800 to 900° C for a period of time sufficient to drive any free iodine from 10 the product and to decompose any ternary rare earth chalcogenide iodine compound which may have formed. Generally a heating period of from about one to three hours is adequate for this purpose.

While we do not wish to be bound by the following explanation, it appears that the presence of iodine in the sealed reaction vessel serves to prevent formation of the dense hard skin which otherwise forms on the surface of the metal as a result of the reaction between the chalcogen and the rare earth metal. A detailed mechanism of the 20 reaction is not known. There may be several possible explanations for the function of iodine in this reaction. One plausible reaction mechanism would be based on the observation that metal halides dissolve metals and metal compounds. In this reaction the rare earth triiodide is first formed on the metal surface, dissolves the inner metal and transports it to the surface exposed to chalcogen vapor, where metal reacts with the chalcogen forming the chalcogenide. The chalcogenide so formed is porous to diffusion of chalcogen. This permits the vaporized chalcogen

to continue to react with the metal and eventually permits the complete reaction between the vaporized chalcogen and the metal to take place. This results in control of the stoichiometry and results in a high purity product because no impurities have been introduced into the reaction vessel.

The following examples are provided to illustrate the invention and are not to be taken as limiting the scope of the invention as defined by the appended claims.

EXAMPLE I

10 19.0740 g of Nd as a single piece of metal about 2" long, 6.5282 g of S and 0.2747 g of I were sealed in one end of a degassed quartz ampoule under a vacuum of about 10^{-3} torr. The ampoule, which had a inner diameter of about 23 mm and was about 23 cm long, was placed in a furnace so that one end extended from the furnace. The sample was heated to 700°C , for one hour to initiate the reaction. The temperature of the sample was then raised to 810°C and kept for 16 hours to complete the reaction. In the heating process above, the opposite end of the ampoule was kept at temperature 20 of about 450°C , to control the internal ampoule pressure. Finally the whole ampoule was heated to 860°C for 7 hours to homogenize the product and decompose any ternary compounds which may have formed and then cooled to room temperature. Free iodine was condensed at the cooler end (opposite to the sulfide). The product was a powder of reddish purple color. The powder was zone-melted in a tungsten crucible. The solid obtained by zone-melting was black color with metallic appearance. Rectangular pieces of about 0.3cm x 0.3 cm x 1.5 cm size were cut out from the zoned solid.

Seebeck coefficient and electrical resistivity of the rectangular pieces were measured. These measurements at several temperatures are given in Table I.

TABLE I

Temperature (°C)	Seebeck coefficient (μV/ °C)	Electrical Resistivity (mΩ.cm)
50	-71	2.25
350	-142	4.12
550	-209	5.38
750	-240	7.0
10 950	-256	8.8

The Seebeck coefficient of this sample has a negative sign as is expected for neodymium sesquisulfide and its absolute magnitude is large. Its electrical resistivity is small. These properties show that it is a pure neodymium sesquisulfide and useful for thermoelectric applications, particularly for high temperature uses. X-ray diffraction also showed that the material was a sesquisulfide and contained no impurities.

EXAMPLE II

20 29.1987 g of Ce, as a single piece of metal, 24.6905 g of Se and 0.165 g of I were sealed in one end of a degassed quartz ampoule under a vacuum of about 10^{-3} torr. The ampoule was placed in a furnace as described before, heated to 770 °C, and kept at this temperature for 16 hours to complete the reaction. The temperature was then raised to 860 °C, for 6 hours to homogenize the sample. In the heating process above, the one end of the ampoule (opposite to the metal) was kept at about 750 °C. The whole ampoule was then heated to 950 °C for one and a half hour and cooled to room temperature.

The resulting product was maroon in color and consisted of soft powdery chunks and a rather hard piece. The selenide was ground to powder of 200 mesh or less, and compressed into discs of 5/8" diameter under a pressure of $\sim 80,000$ psi. The discs were heat-treated under an inert atmosphere of argon at 1600°C for 2 hours. The product discs became black, hard, solid, and had metallic luster. Rectangular pieces were cut from discs and Seebeck coefficient and electrical resistivity were measured. These measurements, given in 10 Table 2, indicate that the material has properties suitable for thermoelectric applications. X-ray diffraction showed only the sesquiselenide pattern.

Temperature ($^{\circ}\text{C}$)	Seebeck coefficient ($\mu\text{V/ }^{\circ}\text{C}$)	Electrical resistivity ($\text{m}\Omega\text{.cm}$)
50	-66	2.4
550	-190	7.2
1050	-310	(11.2)

EXAMPLE III

13.3862 g of La, as a single piece of metal along with 20 11.3581 g of Se and 0.1839 g of I were sealed in one end of a degassed quartz ampoule under a vacuum of 10^{-3} torr. The ampoule was placed in a furnace as before. The metal end was heated to 870°C for 23 hours. The one end (opposite to the metal) was kept at about 750°C in this operation. Then the whole ampoule was placed in the furnace and the temperature was set at 1050°C , and kept at this temperature for 17 hours, and cooled to room temperature. The product had maroon color and was in the form of brittle pieces which could easily be crushed into fine powder. The product

selenide was melted in a tungsten crucible. Rectangular pieces were cut out from the solid. Seebeck coefficient and electrical resistivity measurements given in Table 3, indicate the material would have good thermoelectric properties. X-ray diffraction showed only the lanthanum sesquiselenide peaks.

TABLE 3

<u>Temperature (°C)</u>	<u>Seebeck coefficient (μV/ °C)</u>	<u>Electrical resistivity (mΩ.cm)</u>
50	-50	1.6
10 550	-220	3.6
1050	-380	6.4

EXAMPLE IV

10.6345 g piece of Pr metal along with 3.6295 g of S and 0.0603 g of I were sealed in a degassed quartz ampoule as before. The ampoule was placed in the furnace, and the sample heated to about 800 °C while the opposite end was kept at about 450 °C. This temperature was maintained for 20 hours. The reaction finished and free iodine condensed at the cold end as the temperature of the ampoule was cooled 20 to room temperature. The product sulfide consisted of brittle pieces, maroon in color, which could be powdered easily. The powder x-ray diffraction pattern showed only presence of praseodymium sesquisulfide which indicates that the product is the desired material.

EXAMPLE V

19.4784 g of Gd metal, 5.9754 g of S and 0.11 g of I were sealed in a degassed quartz ampoule under a vacuum of 10^{-3} torr as before. The ampoule was placed in a furnace and sample metal temperature was set to 850 °C, and kept

at this temperature for 20 hours. The one end of the ampoule was kept at about 450°C in this operation. The product had brown color and consists of brittle pieces. Powder x-ray diffraction showed only the presence of gadolinium sesquisulfide.

EXAMPLE VI

23.5594 g of Dy metal, 6.9931 g of S and 0.0507 g of I were sealed in a degassed quartz ampoule under a vacuum of 10^{-3} torr. The heating schedule was the same as example 10 5. The product had dark brown color and consisted of brittle pieces which were easily powdered. The product sulfide were ground into powder of 200 mesh or less and compressed into discs under pressure of 80,000 psi. The discs were heat-treated at 1500°C for 5 hours under an inert atmosphere of argon and the discs became black metallic. Rectangular pieces were cut out from the discs and physical properties were measured. This material had a Seebeck coefficient of $-160 \mu\text{V}/^{\circ}\text{C}$, and electrical resistivity of $23 \text{ m}\Omega\text{.cm}$ at 50°C . Powder x-ray diffraction showed only the presence of dysprosium 20 sesquisulfide.

EXAMPLE VII

12.2297 g of Y, 6.6407 g of S and 0.081 g of I were sealed in a degassed quartz ampoule under a vacuum of 10^{-3} torr. The heating process was the same as Example VI. The product had white color and consisted of brittle pieces which were easily ground into fine powder (200 mesh or less). Powder x-ray diffraction showed only the presence of yttrium sesquisulfide.

EXAMPLE VIII

7.6106 g of Sc and 8.1415 g of S, and 0.050 g of I were sealed in a degassed quartz ampoule under a vacuum of 10^{-3} torr. The ampoule was placed in a furnace and the sample metal temperature was set 950°C while the opposite end of the ampoule was kept at about 450°C . This heat treatment lasted 5 days, and the reaction was 99% complete, and the product consisted of yellow brittle pieces and small hard black piece. The product sulfide was ground into 10 powder of 200 mesh or less, and compressed into pellets. The pellets were heat-treated at 1500°C for 5 hours under an inert atmosphere. The pellet became black metallic. Rectangular pieces were cut out from discs and physical properties were measured. Seebeck coefficient and electrical resistivity were $-50 \mu\text{V}/^{\circ}\text{C}$ and $7 \text{ m}\Omega\text{.cm}$ at 50°C , respectively.

EXAMPLE IX

15.8336 g of Lu, 4.3611 g of S and 0.0348 g of I were sealed in a degassed quartz ampoule under a vacuum of 10^{-3} torr. The ampoule was placed in the furnace, and the sample 20 metal temperature was set to $\sim 950^{\circ}\text{C}$ while the opposite end was kept at about 450°C . This heating process was carried out over 2 days, and the reaction was completed. The product had white color and consisted of brittle pieces which were easily ground into fine powder (<200 mesh).

As can be seen from the preceding discussion and Examples, the process of the invention provides a simple and effective method for preparing high purity rare earth sesquichalcogenides, having properties suitable for thermo-electric applications.

ABSTRACT OF THE DISCLOSURE

An improved method for the preparation of high purity rare earth sesquichalcogenides is described. The rare earth, as one or more pieces of the metal, is sealed under a vacuum with a stoichiometric amount of sulfur or selenium and a small amount of iodine into a quartz reaction vessel. The sealed vessel is then heated to above the vaporization temperature of the chalcogen and below the melting temperature of the rare earth metal and maintained until the product has been formed. The iodine is then vaporized off leaving a pure product. The rare earth sulfides and selenides thus formed are useful as semiconductors and as thermoelectric generators.