Preparation of germanium monosulfide particles by microwave assisted sublimation

ORIGINAL ARTICLE

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Preparation Of Germanium Monosulfide Particles By Microwave Assisted Sublimation

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Abstract

GeS spherical particles in the µm-nm range can be rapidly obtained by sublimation under inert gas flow from a microwave heated mixture of GeS and graphite. The sublimed material has been characterised by XRD, MS and Raman spectroscopy.

Keywords

Germanium sulphide, Spherical particles, Microwave sublimation

Introduction

Methods commonly used for preparing small particles in solution are based on sol-gel techniques or the use of surfactants, which prevent the increase of particle size. Other methods based on gas phase combustion, such as flame hydrolysis, LASER combustion, aerosol process, and vapour phase condensation, take advantage of the properties of molecules in gaseous or vapour phases [1, 2, 3, 4, 5]. A common feature could be represented by the large relative distance between particles, which prevents agglomeration. This can be controlled through an appropriate choice of temperature and concentration. Under these conditions, reagents are dispersed at or about molecular level. We have faced the problem of the preparation of micro- and nano- particles using sublimation, which, due to intrinsic large distance between system constituents, allows the formation of very small particles

In this paper, we describe the first experiments performed for the preparation of particles of germanium monosulfide (GeS) with dimensions ranging from a few micrometers to approximately 100 nanometers as measured from SEM pictures. The choice of germanium sulfide is justified by a number of considerations, such as: a) it could represent a suitable intermediate for the preparation of germanium carbide or of hydrogen free Ge-C alloys; b) together with GeS_2 it shows interesting optical properties when in a vitreous state [6,7]; and, c) it is a semiconductor with an optical gap of 1.7 eV [7, 8]. To our knowledge, no attempt has ever been made to obtain small particles of GeS by any other method.

Microwave heating in organic, organometallic and coordination compounds syntheses and in analytical chemistry, has been proved a powerful instrument for enhancing reaction yields and for reducing reaction time. No such development has been reached by solid-state inorganic chemistry [9,10]. For the above reason, in the attempt to prepare a new "phase" of a well-known material, an innovative and promising method of preparation, i.e. microwave heating, has been chosen.

Experimental

Approximately one gram of GeS (Aldrich) was carefully mixed with 2.5-3 g of graphite (Aldrich) in an agate mortar. The mixture was transferred into an alumina crucible which was placed in a Pyrex container having inlet and outlet connections for gases and a small opening allowing the immersion in GeS of a type K thermocouple contained in an alumina pocket. The entire system was then placed in a modified domestic Whirlpool Talent microwave oven (850W and 2.45GHz). Outside the oven, the outlet tube from the Pyrex container was connected to a series of three gas washing bottles. The first two contained surfactants solution in water to trap the particles in a liquid phase. The third was filled with cotton flocks. The system was washed in a stream of inert gas (Ar) flowing at a rate of 1500-3500 ml/min, for approximately 10 min and then heated for 15 min at 750W power under a continuous gas flow. At measured temperatures higher than 870K, dark-brown fumes started developing from the mixture. Some fumes partially condensed on the walls of the Pyrex container. The remaining fumes were carried by the inert gas into the washing bottles in which they were trapped.

For comparison, an aliquot of GeS was sublimed in a tubular oven (Carbolite MTF) at 870K. The sample was placed in a ceramic combustion boat contained in an alumina tube. The inert gas flow and particles collection system were the same as in the microwave experiments.

The nature and purity of the sublimed matter was controlled by mass spectrometry using a Trace MS plus ThermoFinnigan instrument, by XRD, using a Siemens D5000

(Bragg-Brentano geometry and a Cu kα radiation) instrument, and by Raman spectroscopy using a Bruker RFS 100 FT instrument. SEM images were obtained using a Leica Stereo Scan 420 instrument.

The particle size distributions were evaluated using both a Coulter submicron particle analyzer mod. N4MD and a Brookhaven Instrument equipped with "90 plus particle sizing software."

Results and discussion

It is well known that when microwaves are used for heating purposes on solid samples, the measurement of the temperature of the system is not precise because the sample, in spite of careful milling mixing, is inhomogeneous and this causes the formation of hot spots [11]. For this reason, the expression "measured temperature" has been used. GeS sublimes, under vacuum, at 650-670K [12] and the sublimation temperature at atmospheric pressure reported by the literature is >870K [13]. At 870K, the vapour pressure of GeS, calculated from the equations proposed by Barrow and co-workers, stands in the 20-35-mm/Hg range, high enough to readily observe sublimation [14]. Two different kinds of sublimed GeS have been observed. Near the sublimation crucible, some black crystals with a beautiful metallic sheen are formed. A brown impalpable powder is partially deposited on the walls of the reactor and partially carried to the washing bottles [12].

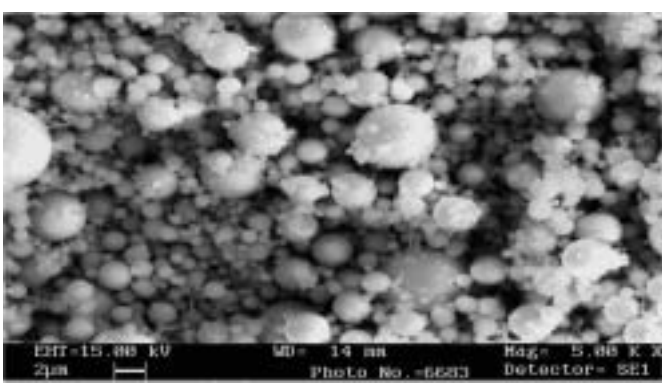

Fig. 1. SEM image of a sample of the sublimed GeS collected on the top of the sublimation apparatus

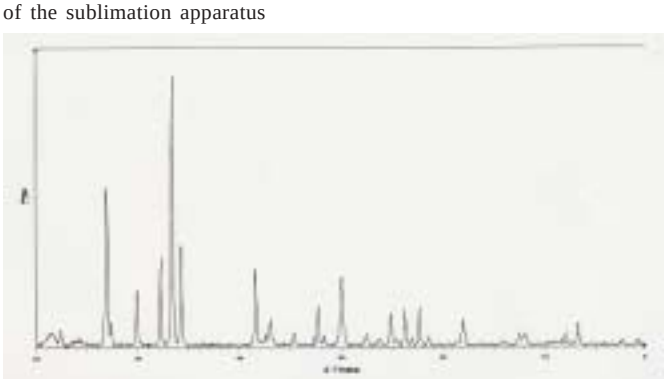

Fig. 2. Powder XRD of the sublimed GeS

Under the microwave-assisted conditions, the sublimation starts after a few minutes.

Figure 1 shows a SEM micrograph specimen of the sublimate, collected from the top surface of the sublimation apparatus, when the sublimation is carried out using a carrier gas flow rate of about 1500 ml/min. The material is in crystal form as shown in Fig. 2 where the powder XRD is reported. The XRD pattern corresponds to that of GeS as reported by the J.C.D. Powder Diffraction File (Swarthmore, P.A.,International Center for Diffraction Data). All the particles show a remarkable spherical symmetry and their diameter distribution ranges from approximately 4 μm to about 100 nm. The most frequent diameters are found to be near 400 nm as reported in the histogram of Fig. 3. The particle size distribution is obtained from SEM images measuring about 350 particles. It is important to point out that the zone where the particles are collected is approximately 1 cm above the surface of the sublimation crucible. Therefore, it is reasonable to think that the deposits consist of the largest particles, which are not easily carried away by the gas stream. Moreover, the temperature of the area from which the particles are taken was held at a temperature in the 370—520K range for the experiment time. Therefore, growth of smaller particles into larger ones is likely to have taken place. The sublimed material is found to be pure GeS by mass spectrometry. The mass spectrum is reported in Fig. 4. Raman spectrum of the material shows scattering at 94, 114, 215, 241 and 270 cm^{-1}, in good agreement with the literature data [15].

For a rapid and easier determination of the particle size

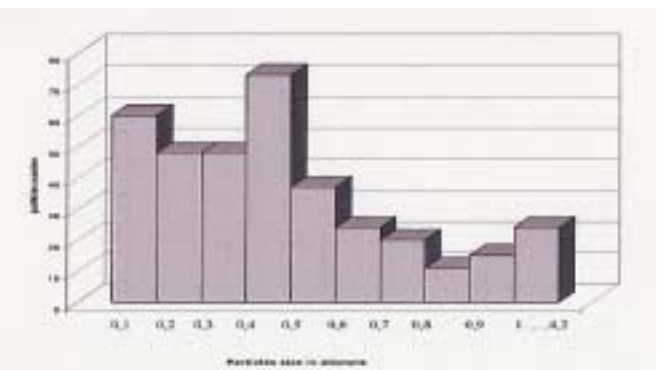

Fig. 3. Particle size distribution of the sublimed GeS, calculated over 350 particles

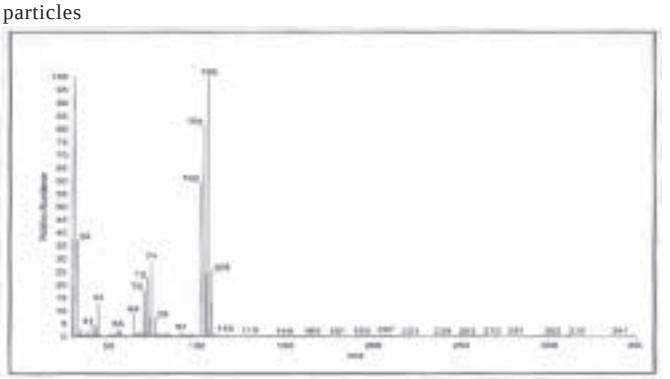

Fig. 4. Mass spectrum of the sublimed GeS

distribution by light scattering, the following surfactant solutions have been used as trapping agents for the particles carried out by the argon flow:

- Sodium dodecyl sulfate
- Polyoxyethylene(4)lauril ether (Brij 30)
- Dodecyl trimethylammonium bromide (DTAB)
- N,N'- dihexadecyl-N,N,N',N-tetramethylpropandiammoniumdibromide (RB1)

The concentrations of the surfactants are kept lower than or at least equal to, the CMC (Critical Micellar Concentration) to avoid spurious scattering by the latter. Unfortunately, all the surfactants used are unable to prevent particle agglomeration. In fact, light scattering measurements repeated two to seven days after the sublimation give particle diameters ranging from two to four times the original value.

A parameter which could be a reasonabe determinant on the size of the particles is the carrier gas flow rate. The experiments performed using different argon flow rates show that the mean diameters of the particles do not change in a significant way as the flow rate increases, at least in the 1200—3500-ml/min range. The material obtained by traditional heating in a tubular oven shows the same characteristics of the material obtained using the microwave oven: crystalline, spherical particles. The two materials differ only in the particle size. The non-microwave generated particles are larger by approximately 20—30%.

Conclusions

Sublimation under controlled conditions (mainly carrier gas flow rate) is a good method for obtaining very fine spherical crystal particles of GeS. The method is also quite rapid if the heating tool allows a rapid achievement of the sublimation temperature, by means of microwave radiation. The rapid heating of the material causes the rapid nucleation of the particles. The flowing inert gas causes rapid cooling of the particles and hence high supers saturation of the subliming vapour. Rapid heating, rapid nucleation, and super saturation are among the conditions that promote the formation of small particles [3, 5]. Further studies are in progress on the selection of better surfactants and/or surfactant concentration to prevent particles agglomeration.

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