Metal sulfide preparation from a sol–gel product and sulfur

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Synthesis of metal sulfides has been demonstrated by the example of monoclinic germanium disulfide produced by reaction of the sol–gel product with sulfur. The elemental sulfur, in turn, was obtained as the result of oxidation of H_2S in the presence of concentrated sulfuric acid. This sulfur was transported into a toluene solution of germanium ethoxide and found to be homogeneously distributed within the gel. Heat treatment of the sol–gel product yielded single-phase GeS_2. Products before and after heat treatment were characterized by IR, XRD, SEM and EDXA measurements.

The electronic and optical properties of semiconducting metal sulfides are strongly affected by impurities and inhomogenities in the material, which may be caused by the preparation process. The sol–gel process is expected to provide a homogeneous product with a low level of impurities, and lead to a product with a controlled structure and stoichiometry.

However, when alkoxides and H_2S gas were used as precursors, the reaction products were mixtures of metal oxides and sulfides,[1–5] since the alkoxides readily react with water. In order to avoid oxide formation, special precautions have to be applied to protect the reaction mixture from contamination by water. Otherwise, an additional reaction has to be undertaken to eliminate the oxide impurity and purify the metal sulfide product.

Kumta and Risbud,[4] for instance, used H_2S gas during heat treatment to obtain single-phase lanthanum sulfide. Sriram and Kumta[5] applied a similar method to produce crystalline TiS_2, *i.e.* heat treating the powder, obtained by sol–gel processing from titanium alkoxide and H_2S gas, in the presence of an H_2S gas flow.

Here, we present an original approach to metal sulfide preparation as demonstrated through the synthesis of monoclinic germanium disulfide. The method is a combination of the sol–gel processing of germanium disulfide previously reported[1,2] and an H_2S oxidation reaction to elemental sulfur and water in the presence of concentrated sulfuric acid. Sulfur forms a colloidal suspension in sulfuric acid, and it can be extracted and homogeneously distributed in a toluene solution of germanium ethoxide by an H_2S gas flow. Since the sol–gel reaction product was a mixture of GeS_2 and GeO_2,[1–3] sulfur converted the oxide to sulfide during heat treatment yielding single-phase monoclinic GeS_2. The reaction product was characterized by various methods before and after heat treatment.

Experimental

Materials and analysis

For the sol–gel processing of GeS_2, germanium ethoxide manufactured by CHEMAT [99.99% $Ge(OEt)_4$] and hydrogen sulfide, produced by Linde Canada (99.6% H_2S), were used as precursors and toluene was used as solvent (Fisher Scientific, HPGC grade). Even though the toluene had a low water content, <0.02%, it was dried by refluxing over Na metal, for 24 h and then distilled. Concentrated sulfuric acid (98%), supplied by Fisher Scientific, was used as the acidic medium for H_2S oxidation. The sol–gel reaction product (before and after heat treatment) was characterized by IR spectroscopy measured in the range 400–4000 cm^{-1} using an FTIR spectrometer (Bruker IFS 113V) equipped with a photoacoustic cell (Princeton Applied Research, model 6003, EG&G). The samples were analysed by X-ray diffraction (XRD) on a Rigaku RU-200B automated powder diffractometer with Cu-Kα radiation. The morphologies of the dried gels and the heat-treated products were examined on a Hitachi S-2700 scanning electron microscope (SEM). Microanalysis of the Ge and S content in the samples was performed by energy dispersive X-ray analysis (EDXA) with a Link analytical eXL incorporated into the electron microscope.

Sol–gel processing

Germanium ethoxide and toluene were mixed under a dried nitrogen atmosphere in a glove box. The toluene : ethoxide ratio was 95 : 5 (vol%). Before introduction into the solution, H_2S was passed through concentrated sulfuric acid that half-filled an Erlenmeyer flask in an air atmosphere. An excess of H_2S carrying elemental sulfur liberated in sulfuric acid was bubbled through the toluene–ethoxide solution until complete gelation had occurred. The obtained gel enclosed in the reactor was aged for 24 h. Samples for analysis were dried in a vacuum oven at room temperature.

Heat treatment

The gel was placed into a quartz ampoule evacuated to 10^{-4} Torr pressure, heat-treated isothermally in a furnace at 630 °C for 24 h to homogenize the solid mixture and then quenched in water to room temperature. The cooling rate was $>17\,°C\,s^{-1}$.

Results

The obtained gel was yellow and of smooth appearance. The XRD pattern of the gel [Fig. 1(a)] shows the presence of two crystalline phases. One was identified as hexagonal GeO_2,[6] while the other was orthorhombic sulfur.[7] The XRD pattern of the gel after heat treatment [Fig. 1(b)] is identical to that of monoclinic GeS_2.[8]

The peak positions from this XRD pattern were matched with a standard[8] using software PDF-2 Database sets 1–42. The 2*θ* and *d*-spacings for the heat-treated product and the standard are shown in Table 1 along with their absolute deviations.

The IR spectrum of the gel in the range 400–1000 cm^{-1} is shown in Fig. 2(a). In the range 400–450 cm^{-1} shoulders at

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Table 1 XRD peak positions (2θ) and d-spacings of the heat-treated product and of standard GeS_2[8] with absolute deviations

	2θ/degrees			d/Å		
hkl	standard GeS_2	heat-treated product	$\Delta(2\theta)$	standard GeS_2	heat-treated product	Δd
200	15.479	15.477	−0.002	5.7200	5.7208	0.0008
111	16.372	16.377	0.005	5.4100	5.4082	−0.0018
211	21.239	21.245	−0.006	4.1800	4.1788	−0.0012
002	26.555	26.551	−0.004	3.3540	3.3544	0.0004
151	31.832	31.839	0.007	2.8090	2.8084	−0.0006
260	36.978	36.975	−0.003	2.4290	2.4292	0.0002
−332	39.223	39.228	0.005	2.2950	2.2947	−0.0003

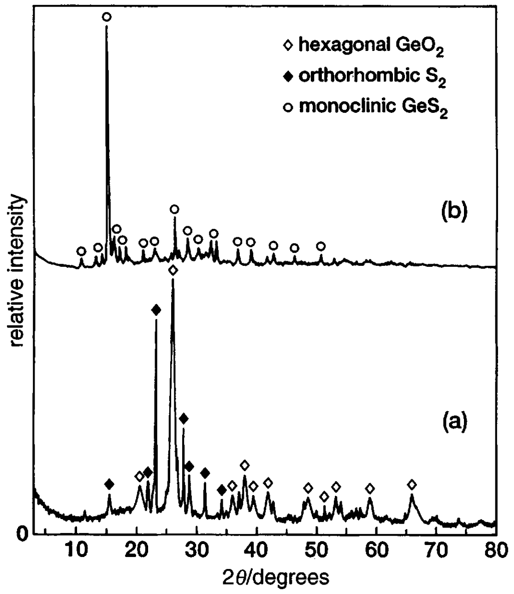

Fig. 1 XRD pattern of (a) the gel and (b) monoclinic GeS_2 obtained after heat treatment

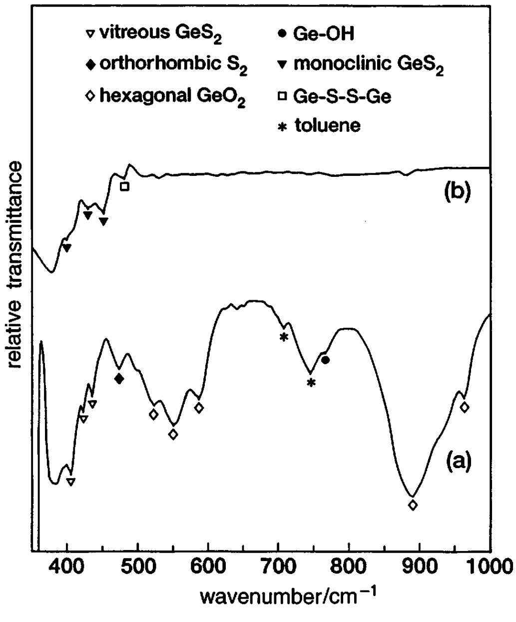

Fig. 2 IR spectrum of (a) the gel and (b) monoclinic GeS_2 obtained after heat treatment

ca. 405, 415 and 430 cm^{-1} can be assigned to Ge—S vibrational absorptions by vitreous GeS_2.[9] This spectrum shows a vibrational absorption triplet of hexagonal GeO_2 at 515, 555 and 587 cm^{-1}.[10] The gel also has a strong absorption peak at *ca.* 885 cm^{-1}, assigned to the asymmetric stretching of Ge—O—Ge,[10] which confirms the presence of hexagonal GeO_2. A shoulder at 780 cm^{-1} suggests the existence of a Ge—OH vibration.[10] An absorption band at 473 cm^{-1} is characteristic of an S—S bond stretch of elemental sulfur;[11] absorption peaks due to toluene are also observed at *ca.* 694 and 730 cm^{-1}.[11]

The IR spectrum of the heat-treated gel is shown in Fig. 2(b) and has absorption peaks close to those of monoclinic GeS_2 at *ca.* 405, 430 and 450 cm^{-1}.[9] Furthermore, an absorption band at 483 cm^{-1} can be assigned to S—S vibrational absorption.

A scanning electron micrograph of the dried gel [Fig. 3(a)] reveals that the gel is colloidal, *i.e.* formed by linking of spherical colloidal particles into a porous network. From the micrographs, it is evident that particles of *ca.* 0.4 µm are linked by necks. As well as the gel network, the micrograph of the gel obtained at lower magnification [Fig. 3(b)] reveals large crystals of dimension *ca.* 60 µm. The morphology of the heat-treated gel is shown in Fig. 3(c) and indicates a fused structure with large grains and the absence of macropores.

Energy dispersive X-ray analysis (EDXA) shows that the particles have a Ge:S atomic ratio of 1:3.7. However, the large crystals with a ratio 1:46.5 are almost pure sulfur.

The microstructure changes after heat treatment, with the sulfur crystals completely disappearing and a homogeneous structure being formed. EDXA revealed that the atomic ratio Ge:S was constant when measured at different spots on the sample, not deviating significantly from the average value of 1:2.9.

Discussion

The IR spectrum of the gel has well defined absorption peaks, typical of hexagonal GeO_2 the presence of which is also confirmed by the sharp peaks in the XRD pattern of the gel.

Although the XRD pattern of the gel does not indicate amorphous GeS_2, its presence was confirmed by IR spectroscopy. However, both the IR spectrum and the XRD pattern of the gel confirmed the presence of crystalline orthorhombic sulfur.

The overall reaction for H_2S oxidation can be proposed as:

$$H_2S + \tfrac{1}{2}O_2 \xrightleftharpoons{H^+} S^0 + H_2O \qquad (1)$$

The sulfur formed by reaction (1) was carried into the reaction mixture by the H_2S gas flow and crystallized into the stable orthorhombic structure within the gel. The influence of the acid on the H_2S oxidation can be explained by the following electrochemical reactions:

$$H_2S \rightleftharpoons 2H^+ + S^0 + 2e \qquad (1a)$$

$$2H^+ + \tfrac{1}{2}O_2 + 2e \rightleftharpoons H_2O \qquad (1b)$$

If reaction (1b) is the slow step then the presence of the concentrated acid aids the oxidation of H_2S. The oxygen involved in reaction (1b) probably comes from air trapped above sulfuric acid in the Erlenmeyer flask. Since the gel contains both GeO_2 and GeS_2,[1–3] the sol–gel processing of these compounds occurred simultaneously. Reactions (2)–(4) describe the formation of GeO_2:

$$\equiv Ge{-}OR + H_2O \rightleftharpoons \equiv Ge{-}OH + ROH \qquad (2)$$

$$\equiv Ge{-}OR + HO{-}Ge\equiv \rightleftharpoons Ge{-}O{-}Ge\equiv + ROH \qquad (3)$$

$$\equiv Ge{-}OH + HO{-}Ge\equiv \rightleftharpoons \equiv Ge{-}O{-}Ge\equiv + H_2O \qquad (4)$$

The Ge—OH bond was identified in the IR spectrum of the gel, providing evidence for this reaction mechanism during the sol–gel processing of GeO_2. Water involved in the reaction was formed according to reaction (1) and was introduced into the mixture by the H_2S gas flow.[3]

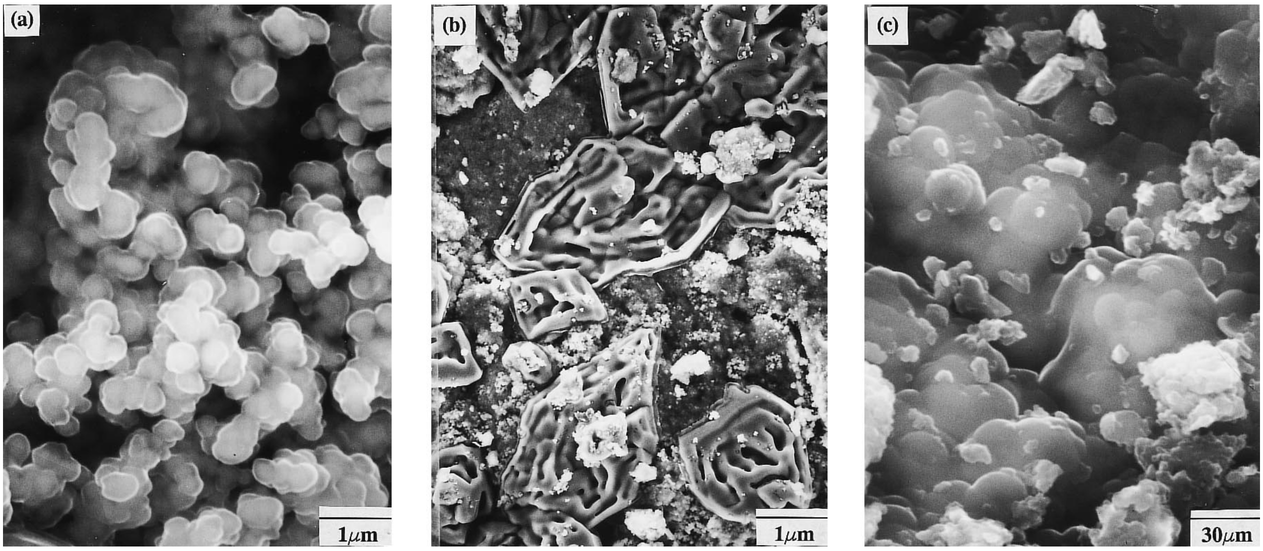

Fig. 3 Scanning electron micrographs of (a) the gel, (b) sulfur crystals deposited in the gel and (c) the sintered structure of monoclinic GeS_2

The reaction mechanism for the sol–gel processing of GeS_2, proposed by Melling,[1] consists of the following reaction steps:

$$\equiv Ge-OR + H_2S \rightleftharpoons \equiv Ge-SH + ROH \quad (5)$$

$$\equiv Ge-SH + RO-Ge\equiv \rightleftharpoons \equiv Ge-S-Ge\equiv + ROH \quad (6)$$

$$\equiv Ge-SH + HS-Ge\equiv \rightleftharpoons \equiv Ge-S-Ge\equiv + H_2S\uparrow \quad (7)$$

In reaction (7), formation of $\equiv Ge-S-Ge\equiv$ is favoured since H_2S gas is easily removed from the reaction system.

Characterization results for the gel after heat treatment indicate that the product is monoclinic GeS_2. From Table 1 it is evident that the agreement between *d*-spacings and 2θ values of the heat-treated product and the standard is excellent, showing that the product is primarily GeS_2. Its structure consists of large crystals with no evident porosity at the grain boundaries. The IR spectrum of the heat-treated product indicates that, besides consolidation in the gel during heating, reduction of GeO_2 by elemental sulfur occurred as proposed by reaction (8):

$$GeO_2 + 3S \rightleftharpoons GeS_2 + SO_2 \quad (8)$$

An absorption peak at 473 cm^{-1} in the IR spectrum of the gel was assigned to the S—S bond in elemental sulfur. This peak is shifted to higher wavenumber (483 cm^{-1}) in the heat-treated product, indicating the presence of S—S bridging in the latter. Therefore, it can be concluded that, besides conversion, during heat treatment, curing of GeS_2 molecules due to the excess of sulfur occurred producing Ge—S—S—Ge connectivities.

Semiquantitative analysis of the heat-treated gel shows that the obtained product is homogeneous, with a Ge:S atom% ratio of 1 : 2.9. This result also indicates that an excess of sulfur was introduced into the gel during synthesis.

Conclusions

The efficient preparation of GeS_2 from a gel mixture of GeO_x and GeS_x is possible by conversion of GeO_2 with sulfur simultaneously introduced into the toluene–ethoxide solution by the H_2S flow during sol–gel processing. Oxidation of H_2S by oxygen from the air in the presence of concentrated sulfuric acid (pH − 2) yields elemental sulfur and water which were transported into a toluene solution of germanium ethoxide by the H_2S gas flow and homogeneously distributed. The heat-treated product shows two types of bonds, Ge—S—Ge and Ge—S—S—Ge. Therefore, the complete consolidation of GeS_x gel and reduction of GeO_x gel with sulfur occurs upon heat treatment at 630 °C.

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