

First synthesis of mesostructured thiogermanates

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Two mesostructured thiogermanates are prepared and characterized by powder XRD, TEM and TG-DTA.

Since the first synthesis of mesoporous M41S phases in 1992¹ numerous systems of mesoporous metal oxides have been reported.² The range of possible applications of mesoporous systems is broadened by the use of sulfides instead of oxides. Porous semiconductors are of interest owing to their special electronic and optical properties, such as luminescence. In the area of microporous sulfides promising results have already been achieved,³ but there were only a few attempts to prepare mesostructure metal sulfides.^{4–6}

In the present work we report the synthesis of different mesostructured thiogermanates dependent on pH, temperature and reaction time. We used amorphous germanium sulfide as the inorganic source and cetyltrimethylammonium bromide as the supramolecular template. The reactions were carried out under hydrothermal conditions.

There is a minimum temperature and, at lower temperatures, a minimum reaction time necessary to obtain mesostructured organic/inorganic composites (Fig. 1).

The powder diffraction pattern of the thiogermanates prepared at various pH values differ. Samples prepared at low pH (product 1) show generally one or two reflections with relatively low intensities indicating a lower crystallinity [Fig. 2(a)]. High pH values (product 2) lead to products with multiple, more intense reflections [Fig. 2(b)]. Both mesostructured thiogermanates have a lamellar structure whereas product 1 shows a higher degree of condensation between the inorganic building units.

In both cases all reflections can be indexed as $00l$ reflections whereas product 1 shows a larger d spacing (3.2 nm) for the 001 reflection than the corresponding d value of product 2 (2.8 nm).

For product 2 the TEM shows an ordered lamellar structure (Fig. 3). The distance between the layers is *ca.* 2.7 nm. In contrast product 1 is more disordered.

The results of thermochemical measurements also show significant differences between the two products. Fig. 4(a) and (b) show TG and DTA results of products 1 and 2, respectively.

The former has a more simple mechanism of decomposition with three steps of mass loss whereas the latter shows a more complex course with at least five steps.

Calculations result in a much lower molar mass of *ca.* 230 for product 1 in contrast to 600 for product 2. These results suggest a much higher content of template in product 2 which is obvious because the degree of condensation is relatively low. At high pH charge-matching interactions between the surfactant cations

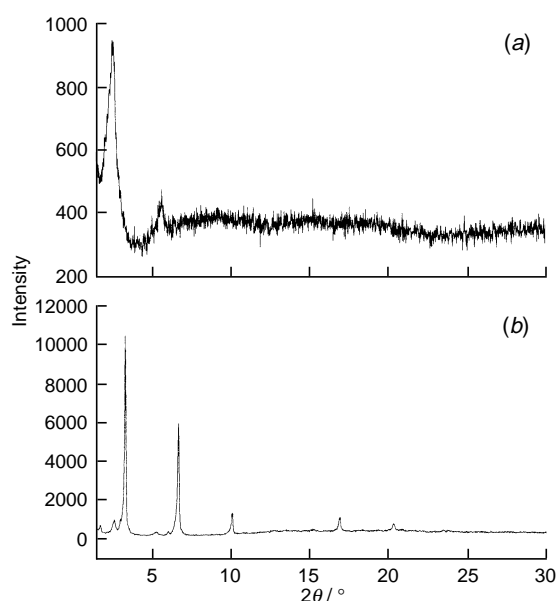


Fig 2 X-Ray powder diffraction patterns of the mesostructured products 1 (a) and 2 (b)

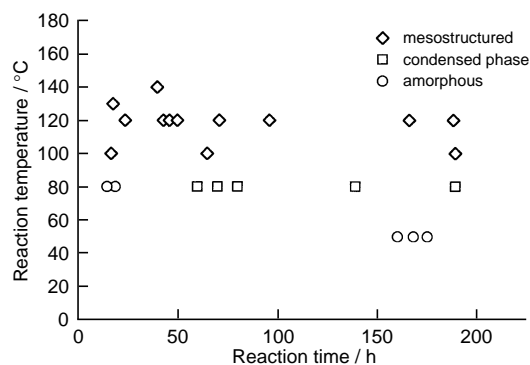


Fig. 1 Correlation between reaction time, temperature and the products obtained

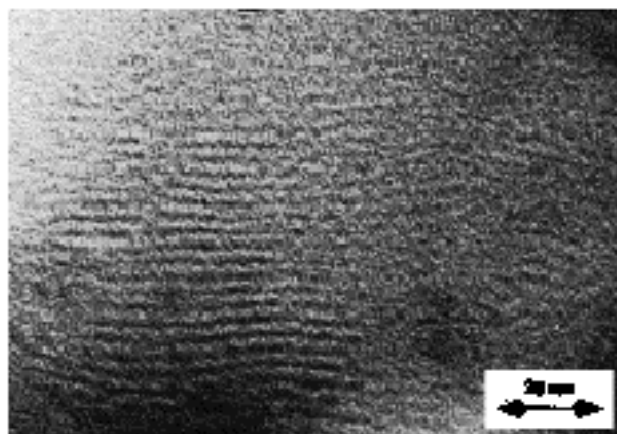


Fig 3 Transmission electron micrograph of the mesostructured product 2

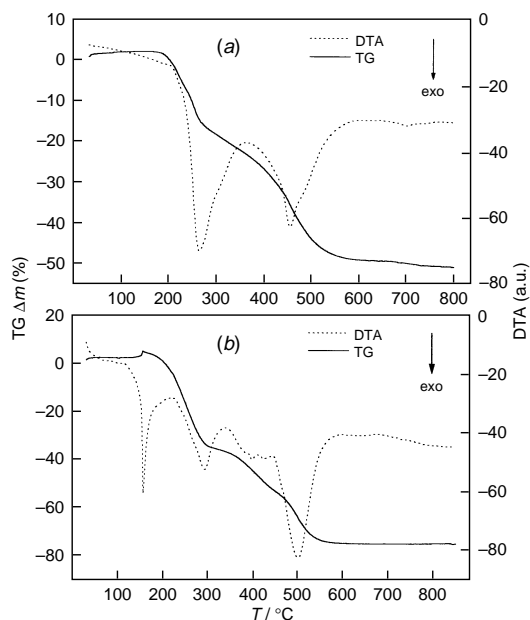


Fig. 4 TG–DTA measurements of the mesostructured products 1 (a) and 2 (b) (atmosphere: oxygen, heating rate = 5 K min⁻¹)

and the smaller thiogermanate anions lead to a more crystalline saltlike structure [Fig. 2(b)] in order to attain electrical

neutrality. At low pH additional condensation reactions take place and there is less charge per Ge_xS_y as the units get larger. Elementary analysis data give the same results.

In conclusion, we were able to mesostructure thiogermanates and demonstrated the basic correlations between reaction time, temperature, pH and the corresponding structures of the products.

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Footnote and References

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