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THERMAL DECOMPOSITION OF THE BINARY COMPOUNDS GaS, GaSe AND GaTe

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ABSTRACT

The thermal decomposition in vacuum of GaS, GaSe and GaTe has been investigated. A mechanism for the dissociation of GaS is proposed.

INTRODUCTION

Among the binary gallium chalcogenides described in the literature the 1:1 compounds exhibit a pronounced two-dimensional growth character. These materials are the lemon yellow GaS, the deep red GaSe and the brown black GaTe.

Their crystal structures can be visualized as stackings of infinite layers of covalently bonded gallium chalcogen polyhedra (Fig. 1). The layers are held together by weak van der Waals forces. The polyhedra are, however, somewhat unusual in character. In the GaS (ref. 1) and GaSe (ref. 2) structures they are trigonal prisms of S_6 or Se_6 atoms surrounding doublets of gallium atoms whereas in GaTe (ref. 3) of the SiAs-type of structure (ref. 4) the polyhedra are Te_6-octahedra around a pair of gallium atoms.

In addition to a modification isostructural with GaS, GaSe exhibits several polytypes (ref. 5) representing various stackings of layers.

EXPERIMENTAL

The compounds can be prepared in many ways for instance by direct combination of the elements or by transport reactions. The products thus obtained are generally poorly crystallized and therefore another technique was chosen in the present case, *viz.* by using liquid tin as a solvent for the two elements.

It was recently reported (ref. 6) that a good crystalline yield is obtained with a starting molar ratio of 1:1:5 with tin in excess. Such mixtures of the elements were sealed under vacuum in silica tubes, which were heated to around 1000°C and then slowly cooled with a rate of 8-10°/h. The tin matrix was dissolved in concentrated hydrochloric acid which did not affect the compounds formed. It was not necessary to use very high grade purity starting elements because possible impurities seemed to prefer to be trapped in the tin matrix instead of in the crystals.

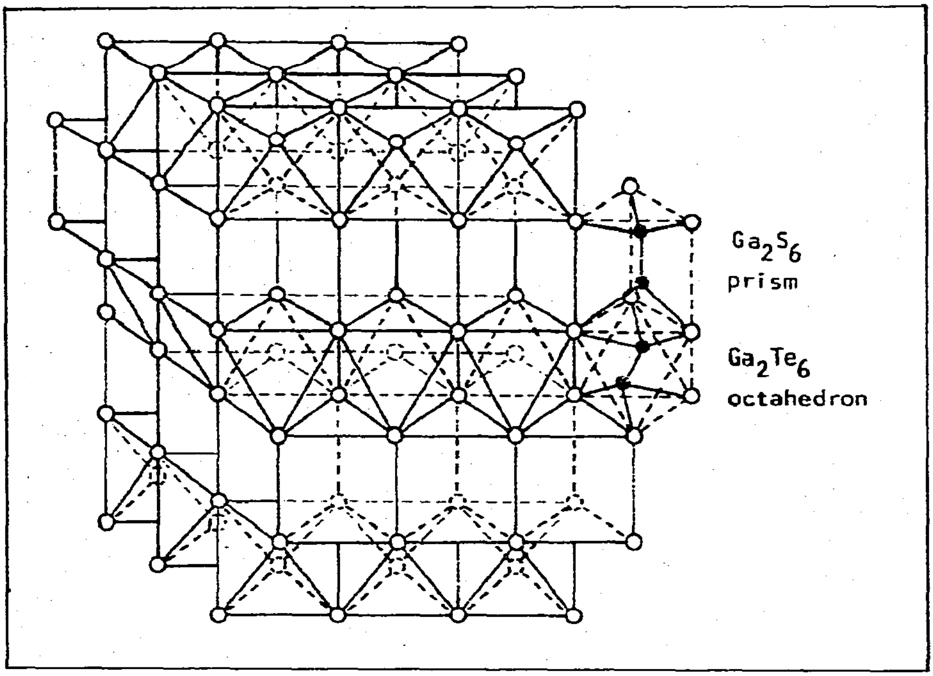

Fig. 1. A somewhat idealized picture showing the arrangement of the chalcogen atoms (open circles) in GaS, GaSe and GaTe. In the two former structures gallium pairs occur in every second trigonal prism, while in the telluride gallium pairs appear in every second octahedron.

With this preparation technique GaSe was always obtained in the modification with the smallest unit cell, i.e. the isotype of GaS.

The decomposition experiments were performed in a Mettler Thermoanalyser, model TA2. The scan speed was 10°/min under dynamic vacuum throughout the experiments. The results thus obtained for the degradation of GaS are shown in Fig. 2. In Fig. 3 the TG curves of all three compounds are presented.

RESULTS AND DISCUSSION

For all the three gallium monochalcogenides a weight loss indicating an appreciable decomposition appears at a temperature of about 800°C. If instead the onset of the decomposition is observed visually from the appearance of a "mirror-like" condensate in a colder zone of a decomposition tube temperatures 50 - 75°C less are obtained for the start of the degradation. The curves show that complete volatilization is reached at about 1000°, 950° and 1100°C for GaS, GaSe and GaTe respectively. It is noteworthy that the sulphide persists to higher temperatures than the selenide.

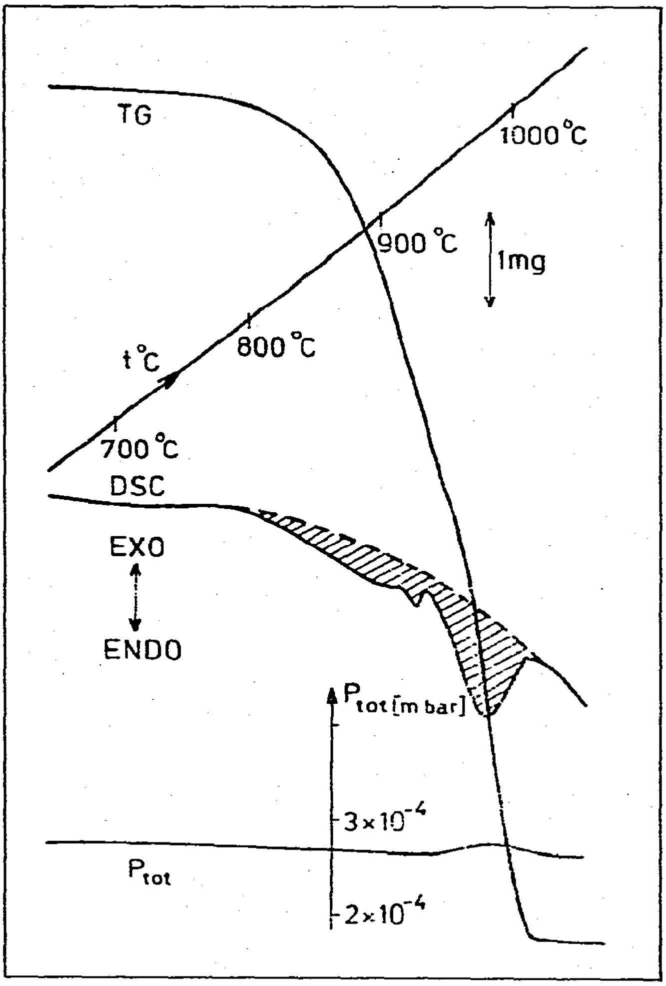

Fig. 2. The decomposition of GaS under vacuum. Starting weight 9.48 mg.

The GaS curve differs markedly from the continuous behaviour of those of the two other compounds by showing a distinct "knee" (Figs. 2 and 3) at about 975°C. The effect appearing in this region is further demonstrated by the presence of an endothermic peak in the DSC curve (Fig. 2). The degradation of GaS obviously follows another route than the simple volatilization process likely to be present for GaSe and GaTe. Under the experimental conditions given in Fig. 2 the decomposition of GaS could proceed according to the reaction

$$3\ GaS\ (s)\ =\ Ga_2S\ (g)\ +\ GaS_2\ (s)$$

which is in accordance with the gravimetric observations.

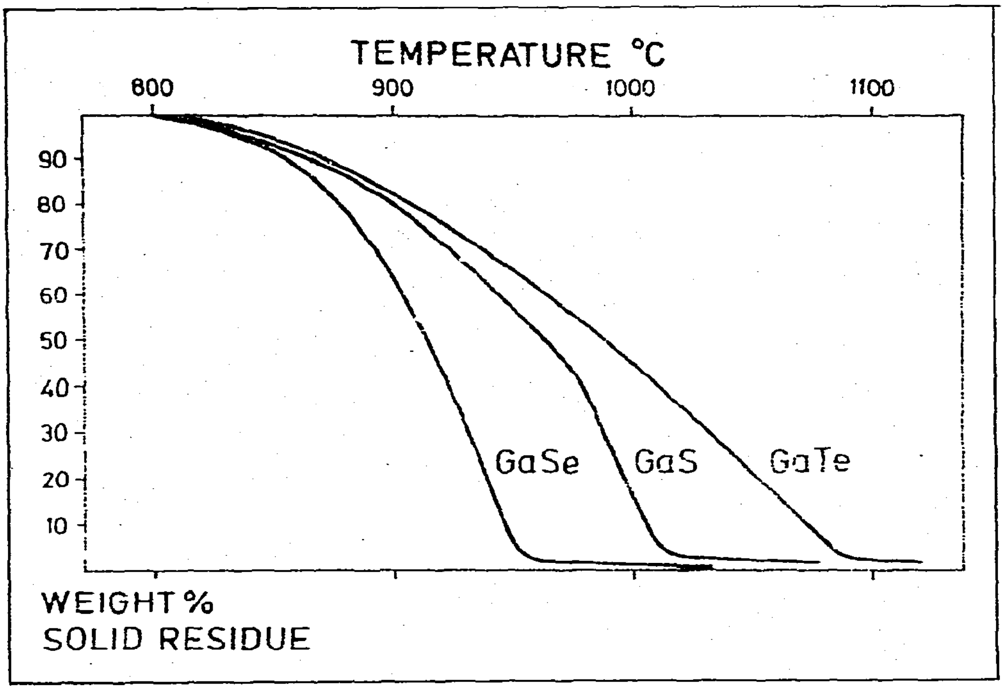

Fig. 3. A summary of the TG curves obtained from GaS, GaSe and GaTe.

It is noteworthy that the decomposition of the binary IV-V compounds SiP, SiAs, GeP, and GeAs (ref. 7), which all have layer-like structures similar to those of the gallium chalcogenides, takes place in ways very different from those observed in the present study.

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