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Mechanochemical syntheses of antimony selenide, tin selenides and two tin antimony selenides

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Abstract

Sb_2Se_3, SnSe, $SnSe_2$, $SnSb_2Se_4$, and $Sn_2Sb_6Se_{11}$ were prepared from powdered elements in a planetary ball mill. The progress of the reactions was investigated in situ by difference thermoanalysis and ex situ by X-ray analyses. $SnSb_2Se_4$, and $Sn_2Sb_6Se_{11}$ are probably both positioned in the homogeneity region of the only ternary compound of the system Sn–Sb–Se.

Keywords: Antimony selenide; Tin selenide; Tin antimony selenide; Mechanochemistry

1. Introduction

The possibility to prepare congruently the melting compounds of the systems Sn–Se, Sb–Se, and Sn–Sb–Se by mechanical alloying was investigated. Only one ternary compound $Sn_2Sb_6Se_{11}$ was found in the latter system by Wobst [1], but Smith [2] reported X-ray data of $SnSb_2Se_4$ therefore mixtures with both stoichiometries were investigated.

2. Experimental

Mixtures with the composition Sb_2Se_3, SnSe, and $SnSe_2$, as well as Sn–Sb–Se mixtures in the molar ratio of 1:2:4 and 2:6:11 were prepared from powdered elements (Sn 99.999%, Strem Chemicals, Sb 99.999%, ABCR, Se 99.999%, Heraeus) and treated in a planetary ball mill (Pulverisette 7; Fritsch; rotational speed 400 rpm; tungsten carbide bowls, volume 12 ml; tungsten carbide milling balls, diameter 12 mm; argon atmosphere). Crystalline and amorphous selenium were used in the synthesis of Sb_2Se_3, tin of different grain size in the preparation of tin selenides (112–180 μm; SnSe, $SnSe_2$) and <36 μm (ternary educt mixtures, $SnSe_2$).

The thermal analyses were performed with a DTA device [3] in the range 25–650 °C with a heating rate of 10 K/min (Ni/NiCr thermocouples, silicon as reference material). The system was calibrated with the melting points of Ga, In, Pb, Sb, and Ag. The standard deviation of the onset temperatures was ±3 K. The samples with a mass of 0.15–0.17 g were sealed in evacuated silica ampoules (length: 55 mm, diameter: 4.0 mm, wall thickness: 0.5 mm). X-ray measurements were carried out with the aid of a transmission powder diffractometer STADI P (Stoe) (Cu Kα1 radiation, 154.051 pm, germanium single crystal monochromator, linear position sensitive detector).

Samples of the reaction mixtures were taken after milling periods of 1, 2, 5, 10 min, and then in 10 min intervals up to 1 h for the binary mixtures and in

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intervals of 1, 2, 5, 15, 25, 40, and 60 min for the ternary mixtures.

3. Results

3.1. Binary mixtures

The diffractograms showed that the reaction between Sb and Se needed intense milling, thus only after 3 h, the reaction was completed. Amorphous Se decreases the reaction time to 40 min. Complete reaction was observed after 20 min in the preparation of SnSe and after 30 min of $SnSe_2$. The DTA curves showed an exothermic reaction at 237.6 °C in the case of Sn + Se and at 244.7 °C of Sn + 2Se. Tin powder with a smaller grain size used in the synthesis of $SnSe_2$ shortens the milling period by 10 min.

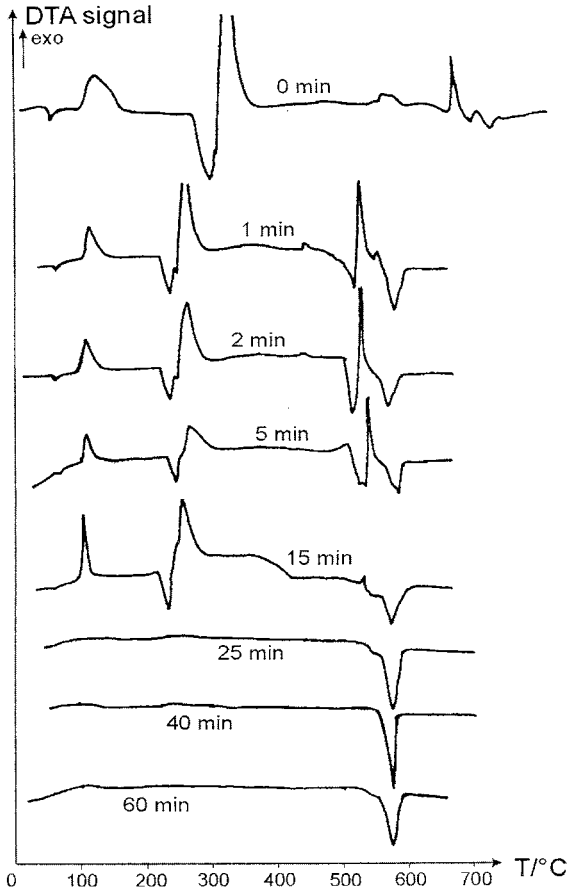

Fig. 1. DTA-curves of $SnSb_2Se_4$ after increasing milling times.

3.2. Ternary mixtures

The two investigated compositions have very similar DTA curves (Fig. 1). Recrystallisation of Se at 104.1 °C is followed by a double peak at 219.1 °C due to melting of Se and Sn. This induces a strong exothermic reaction at approximately 241.7 °C. The next effect broad endothermic effect which indicates partial melting of the mixtures starts at 428.9 °C induces again an exothermic effect with an average value of 528.4 °C with completion of the reaction. After milling periods in the range 25–40 min, the DTA curves show only one effect with a small shoulder at 560.5 °C in "$SnSb_2Se_4$" and at 561.3 °C in"$Sn_2Sb_6Se_{11}$". Both temperatures correspond to melting of the conventionally prepared compounds. The X-ray reflection patterns of both mixtures agree with that of $Sn_2Sb_6Se_{11}$after these milling periods. Because the two ternary compositions have nearly identical DTA curves and diffractograms, it may be concluded that both samples are positioned within the homogeneity region.

4. Summary

The results confirm that binary and ternary tin selenides can be prepared by mechanical alloying. The reactions can be accelerated by using amorphous Se or element powders with small grain sizes.

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