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STUDY ON THE EFFECT OF MECHANICAL ALLOYING ON PROPERTIES OF Zn–Sb ALLOY

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The effect of mechanical alloying on Zn–Sb alloy system is investigated with X-ray diffraction (XRD), laser grain size analysis and differential scanning calorimetry (DSC) respectively. The results of laser particle size analysis shows that the particle size decreases with increasing of the grinding time between 0 and 24 h. XRD and DSC results indicate that longer the grinding time of Zn–Sb is, the more content of Zn_4Sb_3 become in the product in this process.

Keywords: *mechano-chemistry, milling, phase composition, Zn–Sb*

Introduction

Zn_4Sb_3 with a complex hexagonal structure is one of the promising thermoelectric materials due to its low thermal conductivity as well as good electrical properties [1–8]. studies on the phase diagram [5, 6], physical properties [7, 8], electronic structure [9], microstructure effect [4] and processing technique [10, 11] of β-Zn_4Sb_3 have been reported. However, most studies are based on optimization of thermoelectric properties for this material and properties of powder prepared by mechanical alloying method (MA) was not reported.

Because of the large amount of induced grain boundaries, hot pressed compacts of MA thermoelectric materials show a low thermal conductivity. This directly elevates the so-called figure-of-merit. Besides, since MA occurs near room temperature, this technique can be a cost-saving process compared to the conventional vacuum melting/chill cooling/grinding process where a long processing time, high temperature and large scale facilities are required. Also MA seems to be a good alternative to make easier the preparation of this compound and reduce its cost.

The aim of our work was to study the MA process for Zn_4Sb_3. samples belonging to the homogeneity range of Zn_4Sb_3 have been prepared. The effect of grinding time on formation and stability of Zn_4Sb_3 has been studied. The powders have been characterized by Laser size analyzer, X-ray diffraction, and differential scanning calorimetry.

Experimental

Mechanical activations

Dry MA was carried out in a planetary mill (QM-ISP2, instrument plant of Nanjin University, China) operating at 500 rotations min^{-1}. High-purity antimony pieces (99.999%) and zinc shots (99.995%) were used as starting materials. The average size of the obtained powder was 20 μm for the antimony and 100 μm for the zinc, size measurements were performed by a laser size analyzer (Mastersizer2000, Malvern, Great Britain). Amounts of Sb and Zn corresponding to the nominal compositions were filled into the vial with four grinding balls. As the ball to material mass ratio (BMR) was kept at 25:1, the total mass of the material was about 10 g. In order to avoid contamination, SiN was used as vial and ball constituent.

Structural characteristics

XRD measurements have been carried out on Rigaku D/max X-ray diffractometer (Japan) using CuK_α radiation (λ=1.54 Å, voltage 40 kV, current 20 mA) with time constant 0.5 s, limit of measurement 10 impulses s^{-1}, step size 0.03 and collection time 3 s/step.

DSC measurements

Differential scanning calorimetry has been performed with a heat flow apparatus calorimeter (Labsys 1600,

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Setaram, France) which has the following characteristics: a temperature range from 293 to 1103 K, Ar.

Results and discussion

Particle Size Distribution of Zn–Sb for different grinding time

The effect of the grinding time on the particle size distribution of the activated Zn–Sb was investigated and showed in Fig. 1. The results of particle size analyses show that the particle size $d(0.5)$ of the Zn–Sb decreases from 31.28 to 8.26 μm with the increase of grinding time from 12 to 24 h. The results of particle size distribution of Zn–Sb for different grinding time indicate the number of big-particles decrease, that of small-particles increase and interval of the particle size distribution decreases with the grinding time increase.

Phase composition for different grinding time

The effect of the grinding time on the phase composition of the mechanically activated Zn–Sb was showed in Fig. 2. The results indicate that solid phase chemical reaction between Zn and Sb have 3 steps: the two metals were mixed without ZnSb in primal 6 h, some ZnSb compound were measured after grinding 6 h and Zn_4Sb_3 appear until grinding 12 h. Then the quality of Zn_4Sb_3 increase with the grinding time. And this result is consistent with that of DSC.

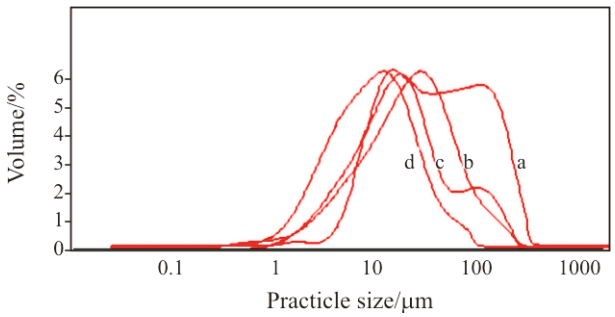

Fig. 1 Particle size distribution of Zn–Sb for different grinding time; a – 0, b – 6, c – 12 and d – 24 h

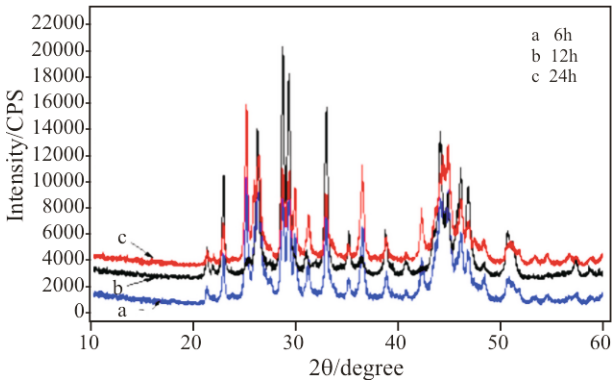

Fig. 2 Phase composition of Zn–Sb for different grinding time

Phase transition for different grinding time

The effect of the grinding time on the phase transition of the mechanically activated Zn–Sb is showed in Fig. 3. The peaks at 798 and 820 K denote the presence of ZnSb and Zn_4Sb_3 [4]. The DSC curves indicate that quantity of Zn_4Sb_3 increase with the grinding time from the peak area increase at 820 K. Considering that many defects or lattice strains are significantly imposed to material system in MA, this structural instability of Zn_4Sb_3 originating from mechanically-induced defects or strains maybe is one of the causes of peak area increase at 820 K.

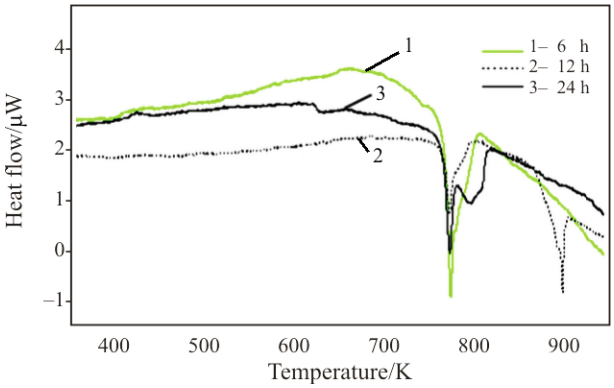

Fig. 3 DSC curve for different grinding time

Conclusions

This study shows that whatever the milling duration (until 24 h), single-phase Zn_4Sb_3 can not be prepared by MA under these conditions. The particle size decrease with increasing of the grinding time in 24 h by laser particle size analysis. The longer the grinding time is, the more the amount of Zn_4Sb_3 is prepared according to DSC and XRD results.

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