

Optimization of Ball-Milling Process for Preparation of Si-Ge Nanostructured Thermoelectric Materials

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Here we report on technical details of preparation of Si-Ge-based nanostructured thermoelectric materials by a mechanical alloying method. It has been shown that for a milling speed of 350 rpm a single Si-Ge phase is formed after milling time less than 6 h.

Keywords: Mechanical Alloying, Thermoelectricity, Si-Ge, Nanostructure.

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1. INTRODUCTION

It has been recognized recently that the bulk nanostructuring approach provides a route for the reliable improvement in the performance of thermoelectric materials (see for recent review Ref. [1]). A marked increase in the figure-of-merit ZT has been reported for materials with nanoscaled grain size. The increase of ZT is mainly attributed to a reduction in thermal conductivity due to the enhanced phonon scattering at the grain boundaries.

Method of mechanical alloying is particularly suitable for the preparation of a large quantity of nanostructured thermoelectric materials with superior, as compared to single- or polycrystalline analogues, thermoelectric properties. For example, considerable progress has recently been made in improving thermoelectric properties of p -type as well as n -type Si-Ge materials [2,3]. However, reported in the papers technical details of the ball-milling process are often cursory [3]. Here we report on the evolution of structural properties of n -type Si-Ge thermoelectric materials during ball-milling.

2. EXPERIMENTAL DETAILS

The materials were prepared from powders of high-purity (better than 99.999%) Si, Ge, and P by a Fritsch planetary mill using stainless steel vial and balls at milling speed up to 350 rpm and milling time up to 18 h. Crystal structure of the Si-Ge powdered samples was checked by a Rigaku Ultima x-ray diffractometer (XRD) whereas microstructure and chemical composition were identified by transmission and scanning electron microscopy (TEM and SEM, respectively).

3. EXPERIMENTAL RESULTS

In order to track evolution of the crystal structure of the studied alloys, and determine optimal parameters of the milling, we varied milling speed and milling time. The milling speed varied from 250 to 350

rpm whereas milling time varied from 1 to 18 h.

XRD examination revealed that in the case of milling speed 250 rpm the solid solution of Si-Ge is formed after milling time 12 h. However, chemical characterization of the sample by an Energy Dispersive X-ray Spectroscopy (EDX) showed that the sample is contaminated by a sizable (around 1 at.%) amount of Fe which is a consequence of the use of stainless steel vial and balls. In order to eliminate Fe contamination, a high milling speed was used in further experiments.

Results of the x-ray diffraction measurements revealed that for a milling speed of 350 rpm a single phase Si-Ge was formed after milling time less than 6 h (Fig. 1). The mean size of crystallites estimated from the XRD data by a Williamson – Hall method was found to be of about 10 nm and decreases with the increase in the milling time.

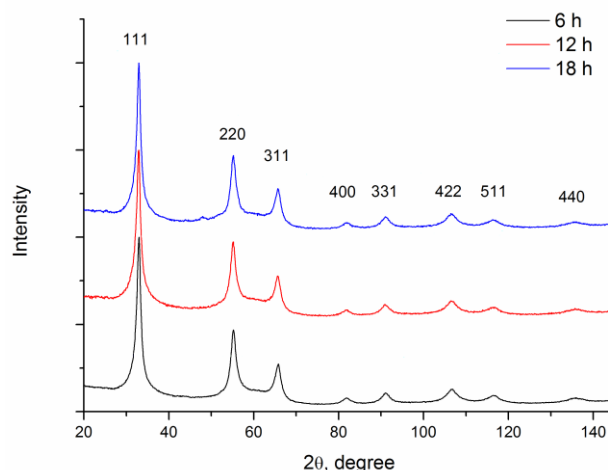


Fig. 1 – X-ray diffraction patterns of $\text{Si}_{30}\text{Ge}_{20}\text{P}_2$, prepared by mechanical alloying at a milling speed 350 rpm

Powdered Si-Ge sample prepared by mechanical alloying at a speed of 350 rpm for milling time 6 h was further characterized by the TEM and SEM

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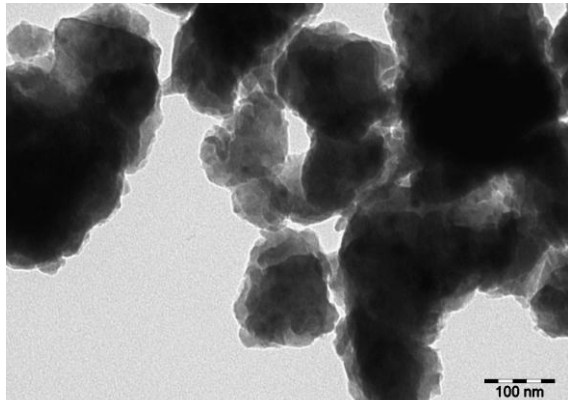


Fig. 2 – Transmission electron microscopy images of $\text{Si}_{10}\text{Ge}_{20}\text{P}_2$ mechanically alloyed at a milling speed 350 rpm for 6 h

techniques. It was seen from TEM pictures that the crystallites in the as-prepared powder agglomerate in larger particles with an average size below 200 nm (Fig. 2). All these results are in a good agreement with those published by Wang et al. [3].

4. SUMMARY

It has been shown that Si-Ge nanostructured materials with the mean crystallite size of about 10 nm can be prepared by mechanical alloying of the raw ingredients for 6 h at a milling speed of 350 rpm.

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