RHOMBOHEDRAL-CUBIC PHASE TRANSITION
CHARACTERIZATION OF (Pb,Ge)Te USING HIGH-TEMPERATURE XRD

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ABSTRACT
Rhombohedral-cubic transformation in Bi2Te3 doped-Pb1-xGexTe alloys is presented. Samples of Bi2Te3 doped Pb1-xGexTe were prepared by powder metallurgy approach. These powder samples were examined by high-temperature XRD and SEM/EDS. A bulk (pressed powder) cylindrical specimen was used for dilatometry characterizations. According to the XRD examinations it seems that upon increasing the temperatures a continuous transformation occurs from the rhombohedral to the cubic phase, accompanied by the formation of a small amount of the phase Ge0.74Pb3.26Te4.

INTRODUCTION
Tellurium alloys are well known for their optical properties. Ge-Te alloys have been reported as fast switching, reversible, phase-change optical data storing media. The compound GeTe, which is also known for thermoelectric applications, is a p-type semiconductor. Additions of Bi2Te3 and PbTe to GeTe give the pseudo-binary alloys Pb1-xGexTe, doped with small amounts of Bi2Te3. The influence of these additions on the physical properties is currently under investigation.

PbTe has a cubic NaCl type structure, and GeTe attains this structure only at the elevated temperatures, but on cooling, it transforms into a slightly distorted NaCl structure, with trigonal symmetry [1]. The transition temperature, \( T_c \), is near 400 °C, and depends on the exact composition and the amount of the doping additions. Disagreement exists [1] as to whether this process is continuous or not, and therefore the possibility that this is of a first or a second order.

EXPERIMENTAL
The \( p \)-type Pb0.13Ge0.87Te + 3 mol% Bi2Te3 alloy was prepared according to the following procedure: (a) sealing the source materials (purity of 5N) at appropriate concentrations in quartz ampoule under a vacuum of 10^{-5} Torr, (b) melting the alloys in a rocking furnace at 800 °C for 1 h followed by water quenching, (c) annealing at 620 °C for 12 h, (d) attrition of the compound to a maximal particle size of 60 mesh powder, and (e) hot pressing (HP) at conditions of 520 °C/30 min/43 MPa/H2 atmosphere. Powder samples were examined by high-temperature XRD and SEM/EDS. A bulk (pressed powder) specimen, with dimensions of 20 × 5 × 5 mm3 was used for dilatometry characterizations. The dilatometer model Linseis L75 (see Figure 1) was used to determine the length change of the specimen. The specimen was heated up to 500 °C with a heating rate of 5 °C/min, in helium atmosphere. TAWIN software was used to analyze the data.
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High-resolution SEM JEOL JSM-7400F was used to examine the hot pressed specimen. High-temperature X-ray diffraction (HTXRD) examinations were done by Anton-Paar HTK-1200N hot stage attached to a Philips XRD system (Figure 2). The specimens for the HTXRD were in the form of powder filled in the sample holder.

Figure 1. Linseis L75 dilatometer.

Figure 2. Hot stage for HTXRD.
RESULTS

High-resolution SEM micrographs of the pressed powder are presented in Figure 3. The sample is mostly of a single phase, with a small amount of scattered second-phase precipitates. EDS examinations showed that these precipitates are richer in Pb than the matrix. Although the matrix composition is 42 at% Ge, 6 at% Pb, 1.5 at% Bi, and 50.5 at% Te, the precipitate composition is 24 at% Ge, 22 at% Pb, 1.6 at% Bi, and 52.4 at% Te. It is noteworthy that since the precipitates are less than 1 µm in size, the EDS error is relatively high. Yet, it is obvious that the precipitates have a higher Pb content than the matrix. Moreover, according to Figure 3 these precipitates are located at grain boundaries.

The bulk (pressed powder) sample was heated in the dilatometer up to 500 °C. The temperature dependence of the dilatation dL is presented in Figure 4. From this graph the phase transition temperature was found to be at 373 °C (the intersection of the 2 lines, according to reference [2]).
Examinations in high-temperature XRD showed gradual changes in the diffracted spectrum along the heating of the powder samples from room temperature to 500 °C. Figure 5 shows the diffractogram obtained at room temperature (RT, at the bottom of the frame), and those obtained at 200, 350, 450, and 500 °C. The upper diffractogram in the figure was obtained after cooling back to room temperature at the end of the process. As one can see, at the heating cycle a doublet peak pattern of the rhombohedral structure merges to a single peak of the cubic structure [for instance at about 42 °2θ, the (024) and (220) peaks of the rhombohedral structure merge to the (220) peak of the cubic one; see Figure 5]. This process is reversible, and was also obtained while cooling. In addition, new peaks of another phase were observed upon heating, which were found to fit the Ge_{0.74}Pb_{3.26}Te_{4} phase (PDF 03-65-7226 [3]). This phase dissolves back as the temperature reaches 500 °C, but appears again on cooling back, and retained at room temperature (see Figure 5).

Figure 6 presents the diffractograms obtained on a shorter range of 2θ, (and shorter scan time) where every scan took about 5 min. These graphs show the gradual change of the doublet pattern to a single peak, at the heating cycle (upper frame in Figure 6), and the splitting back to two peaks on cooling back to RT (lower frame).
Figure 5. Diffractogram obtained at room temperature (RT, at the bottom), through the heating cycle (at 200, 350, 450, and 500 °C), and after cooling back to RT. "#" denotes the new obtained phase peaks.

The formation of the new phase can be observed in Figure 5 (peaks denoted by "#") and 6 (appearance of the new peak at about 38 °2θ). This peak vanishes at 500 °C, and reappears on cooling back to RT. The volume fraction of the new obtained phase on the heating cycle, as can roughly be calculated from the area under the peaks in each diffractogram, was drawn against the temperature (Figure 7). It can be seen that this phase vanishes at 500 °C.

The cell parameters and the volume per atom in the structure were calculated from the peak positions in the diffractograms obtained from HTXRD. The temperature dependence of the cell parameters and of the volume per atom is presented in Figure 8. It can be seen from the graphs that there is no abrupt change of the volume per atom while moving from the rhombohedral to the cubic structure. This continuous change supports the assumption that this phase transition is indeed of a second order. This conclusion should be verified by more examinations and at different compositions.
Figure 6. Short runs while heating from RT to 500 °C (upper frame) and while cooling back to RT (lower frame).
Figure 7. The volume fraction of the new obtained phase, roughly calculated by the area under the phase peaks.

Figure 8. Cell parameters and volume per atom in the structure versus the temperature.

REFERENCES