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# Domain structure analysis of $(AgSbTe_2)_{15}(GeTe)_{85}$ thermoelectric compounds fabricated by rapid solidification process (RSP) and spark plasma sintering (SPS)

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ABSTRACT

The domain structure of the thermoelectric compound $(AgSbTe_2)_{15}(GeTe)_{85}$ was analyzed using high resolution transmission electron microscopy. Numerous coherent domain boundaries of two different types were observed, formed by the polar phase transition from the cubic NaCl-type phase to a rhombohedral structure with an angular distortion of 0.5–1.5°. One type has twin boundaries parallel to [001] and [110] directions, the other has inversion domain boundaries parallel to [111] and [112] directions. This high density of internal interfaces could reduce lattice thermal conductivity due to phonon scattering on the interfaces, and less deleterious on electronic transport processes, because they are coherent.



## 1. Introduction

$(AgSbTe_2)_{1-x}(GeTe)_x$ thermoelectric semiconductors (called TAGS − $x$), have been recognized as thermoelectric energy conversion materials since the 1960s. Here, $x$ is the molar fraction of (GeTe), and affects the thermoelectric properties. The thermoelectric properties of TAGS alloys are closely related to lattice deformation. Pure GeTe alloys undergo allotropic transformation at 400 °C, and assume a cubic NaCl structure at higher temperatures [1,2]. Because of the stretching of the [111] axis below the transformation temperature, the alloys have a rhombohedral symmetry and can be considered to be a slightly distorted cubic B1 lattice. At room temperature, the angle between the three crystalline axes (rhombohedral angle; α) is 88.25°. When heated to higher than the transformation temperature of 400 °C, the rhombohedral angle increases to almost 90° [1].

For TAGS alloys, Ag and Sb atoms partially substitute Ge atoms, and the transformation temperature is dependent on the composition ratio of (GeTe) and $(AgSbTe_2)$ [3–5]. When GeTe alloys are cooled from the molten state to below the transformation temperature, thermal strain within the cubic NaCl lattice causes a slight shift in the position of the Ge and Te atoms. Relative atomic displacement shows up as distortion along the [111] direction in the unit lattice, and transforms the high-symmetry cubic structure into a low-symmetry rhombohedral structure [6]. The rhombohedral distortion along the [111] direction in the cubic structure can form structural modulation or twins in the (220) plane. Structural modulation or twins only occur at low temperatures and cannot be found in high-temperature cubic structures. Because electrical and thermal conductivity are influenced by the local atomic arrangement, twins occurring in low-temperature rhombohedral structures can be used as a potential scattering device.

The first crystalline study on twins in GeTe alloys was conducted by Snykers et al. [7]. They observed two types of domain structures separated by twins and inversion boundaries in GeTe alloys cooled from the molten state to below the transformation temperature, and proposed a structural model for each interface. The twin domains are dependent on heat treatment and grow smaller with increasing cooling speed. Cook et al. [8] performed transmission electron microscopy (TEM) on TAGS-85 alloys and observed antiphase domains of 400–450 nm in width at room temperature.

Twins and other defects in crystals significantly affect the thermoelectric properties of the materials. Thus, further study on the microstructure of TAGS alloys is needed to reach a better understanding of the reliability of thermoelectric materials and the limitations of their application, as well as their structural properties and electron transport. However, past research has focused more on the thermoelectric properties and mechanical properties than the alloy's microstructure. In particular, there is not a single study involving the microstructural analysis of TAGS alloys fabricated from gas atomization and spark plasma sintering (SPS).

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Against this backdrop, in this study, gas atomization and SPS were used to fabricate TAGS-85 alloys, known to have outstanding physical and mechanical properties. High-resolution transmission electron microscopy (HRTEM) was applied to analyze the twins and domain structures formed due to phase transitions involving high-temperature cubic B1 structures and low-temperature rhombohedral structures.

## 2. Experimental procedure

$(AgSbTe_2)_{15}(GeTe)_{85}$ alloys were fabricated using high purity (99.99%) granule-type Ag, Sb, Ge and Te. These were weighed to provide the required stoichiometric composition which was placed in an induction furnace and heated to approximately 800 °C and the gas-atomization process was reported in our previous paper [9,10]. As prepared alloy powder was consolidated using spark plasma sintering (SPS). The detailed SPS processing conditions were described elsewhere [9].

Specimens for TEM observation were sliced in the direction of sintering and the perpendicular direction. A dimple grinder was used to grind the specimens to 30 μm, which were processed at 4 kV and an irradiation angle of 10°. TEM observations were made using a JEM-2010, capable of HRTEM, at 200 kV.

## 3. Results and discussion

In this study, we utilized gas atomization and SPS to fabricate TAGS-85 alloys, for which only a few studies exist. Then we applied high-resolution transmission electron microscopy (HRTEM) to analyze the twins and domain structures formed due to phase transitions involving high-temperature cubic B1 structures and low-temperature rhombohedral structures. The sintered sample had a relative density of 99.8%, and no impurities or phase changes were observed in the sintering process. The results of microstructural analysis are as follows:

Fig. 1 shows the TEM image and selected area electron diffraction pattern (SAEDP) of the TAGS-85 thermoelectric compound, taken with the $[1\bar{1}0]$ zone axis. Complex domain structures accompanied by distortion and stress are observed, and the domains can be separated by two boundary types. One type consists of boundaries almost parallel to the [001] and [110] directions, shown in dotted lines. For this type, the spacing between boundaries is not consistent. The second type includes boundaries with herringbone patterns (denoted by solid lines) found on both sides of boundaries parallel to the [001] and [110] directions. The width of the domains usually falls between 50 and 100 nm, with some occasionally exceeding 150 nm. Because the width of boundaries is not perfectly parallel to electron beams, it tends to vary by a few nanometers.

The boundaries with herringbone patterns are almost parallel to the [111] and [112] directions, and are symmetrical along the boundaries parallel to the [001] and [110] directions. The boundaries with herringbone patterns in the elliptical areas 1 and 2, denoted by white dotted lines, have different bearings. The boundaries between these areas, unlike the boundaries parallel to the [110] direction, have an irregular boundary contrast. The formation of the domain structure and distortion of the crystal alleviate the thermal strain caused by the phase transition from the high-temperature cubic NaCl to the low-temperature rhombohedral structure. This is similar to the introduction of surface roughness and twins to minimize stress and alleviate macro-level distortion of boundaries during martensitic transformation.

The SAEDP shows reflection due to the distorted cubic NaCl structure, and the separation of diffraction spots in the high-order reflections (e.g., 440 or 400) can be clearly observed. However, the boundary

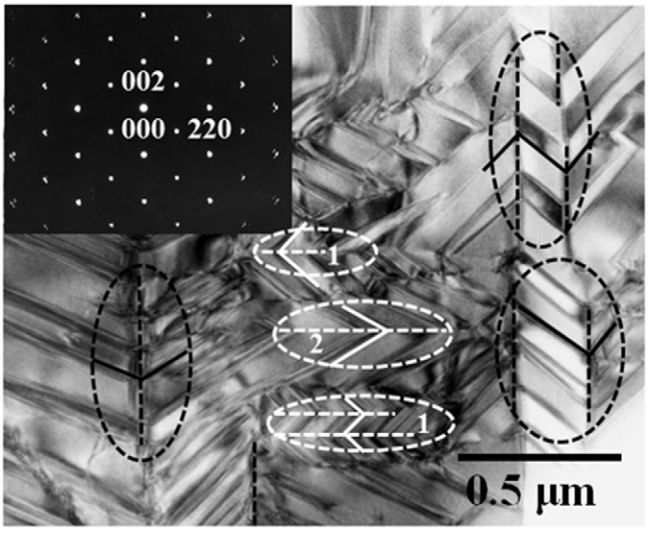


**Fig. 1.** TEM image and SAED pattern showing the complex domain structure in TAGS-85, taken along the $[1\bar{1}0]$ zone axis. Domains are divided by two different types of boundary, indicated by solid and dotted lines. The boundaries with herringbone pattern are symmetrical on both sides of the boundaries, parallel to the [001] and [110] directions.

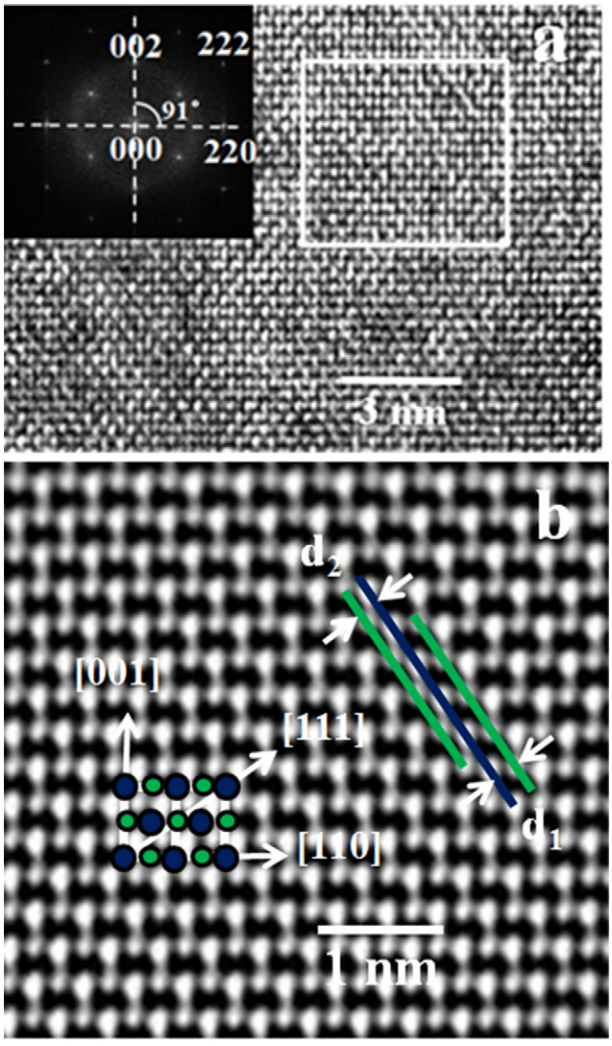


**Fig. 2.** (a) HRTEM image and FFT pattern taken with $[1\bar{1}0]$ zone axis, (b) Filtering image of white square region in (a); The atomic arrangement of a polar rhombohedral structure corresponding to the HRTEM image is inserted in (b). The staggering of the (111) plane perpendicular to the polarization axis is clearly apparent in (b), as marked by $d_1$and $d_2$.