Texture anisotropy of higher manganese silicide following arc-melting and hot-pressing

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ABSTRACT

In this research it is shown that thermoelectric higher manganese silicides (HMS) compounds produced by arc-melting followed by hot pressing exhibited textured behavior, due to the different number of Mn−Si bonds on the [00l] direction over the [hk0] direction, leading to ~10% *ZT* enhancement in parallel to the pressing direction compared to the transverse direction. This shows that more carful considerations are required while assuming isotropic behavior in non-cubic polycrystalline thermoelectric materials.

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1. Introduction

During the last decade, due to the increased energy demands in the world, the need for alternative sources of energy has been on the rise, motivating researchers to seek for green and renewable energy alternatives. Thermoelectricity among these has received a particular attention owing to the fact that thermoelectric devices are low cost, zero maintenance solid state conversion devices. While highly efficient IV−VI chalcogenides have been the prime compositions in commercial thermoelectric devices [1−4], their constituents are expensive (Ge), toxic (Pb) and rare (Te) [5]. Novel environmental friendly classes of thermoelectric materials such as the skutterudites, half- Heuslers and metal silicides show a high promise for replacing the chalcogenides as standard compositions in such devices [5]. The transition metal silicides in particular are very abundant, showing a high chemical, thermal and mechanical stability [6,7]. Of the transition metal silicides, the higher manganese silicide, HMS, shows the highest thermoelectric figure of merit, *ZT* ($=\alpha^2\rho^{-1}\kappa^{-1}T$, where, α- Seebeck coefficient, ρ-electrical resistivity, κ-thermal conductivity and *T*-temperature) at intermediate temperatures of up to 700 °C [6,7]. HMS consists of a group of crystallographic structures with a chemical composition of $MnSi_{1.72−1.75}$ which includes the Mn_4Si_7, $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$ and $Mn_{27}Si_{47}$ compounds.

These compositions exhibit a Nowotny chimney ladder (NCL) structure, which might be considered as a "Si-deficient" modification of the tetragonal $TiSi_2$ structure, where the manganese atoms are ordered in a tetragonal structure, whereas the silicon atoms are ordered in a chimney-like orientation in between, leading to a high crystallographic anisotropy with $a = b \ll c$ lattice parameters (Fig. 1a). In the past few years enhanced efforts were devoted to increase the *ZT* values of HMS compounds [8−21]. Some of these methods included doping or alloying of HMS with chromium [8,9], ruthenium [10], aluminum [11], germanium [12], rhenium [13,14] and iron [15,16]. Common synthesis methods included Bridgman crystal growth [14], melt spinning [17], gas atomizing [18] chemical vapor deposition [19] and an introduction of multi walled carbon nano-tubes to an HMS matrix [20]. However the vast amount this research has not managed to increase the maximal *ZT* values of HMS compounds above the 0.4−0.7 range.

Anisotropy in thermoelectric materials possesses a potential for *ZT* enhancement by synthesis of samples with a preferred orientation, exhibiting optimal transport properties. An example is the low temperature Bi_2Te_3- based thermoelectric alloys, with the anisotropic $R\bar{3}m$ crystal structure, exhibiting optimal thermoelectric properties in transverse to the crystallographic *c* axis [22].

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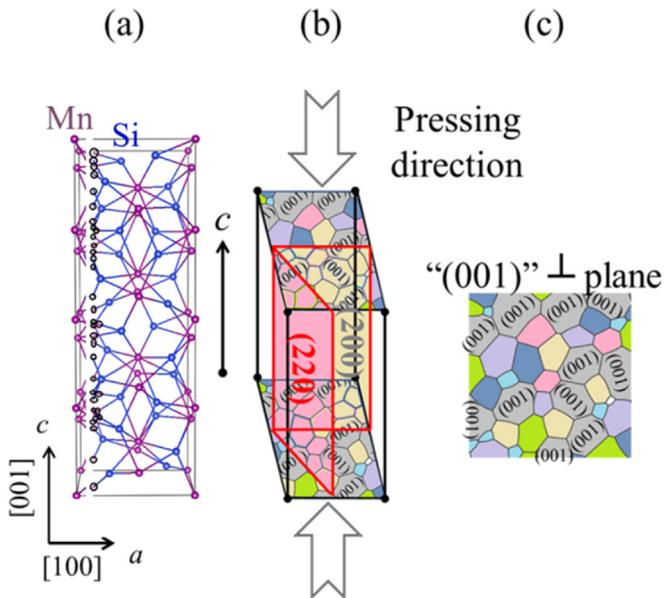
Fig. 1. (a) Schematic description of the modified tetragonal Nowotny chimney ladder crystal structure of HMS. Indicated in the black circles are bonds needed to break for a cleave along the (100) plane. (b) Schematic description of a powder metallurgy pressed pellet, exhibiting a preferred c-axis [001] orientation, in parallel to the pressing direction, as represented by a predominance of (001) oriented grains in the perpendicular plane (c).

However due to the directional nature of the measuring apparatus for thermoelectric properties, a careful attention should be taken on characterizing the transport properties of anisotropic materials in the same direction. Single HMS crystals are known to have ~1.3 times higher Seebeck coefficient and ~5 times higher electrical resistivity in the crystallographic c-axis [001] direction, compared to the transverse a-axis [100] direction (Fig. 1a), as is summarized in Fig. 2 [7,23−26]. It was also reported that under similar conditions the thermal conductivity values are 1.5−2 lower along the c-axis compared to transverse directions [7,24]. While the differences in the resistivity or the thermal conductivity can be mainly attributed to hole mobility variations along the different crystallographic directions, a difference in the Seebeck coefficient values can be mainly attributed to anisotropy in the density of states and charge carrier concentration. Due to the fact that in single crystals, major variations of the mechanical properties are also expected along transverse crystallographic directions, and since thermoelectric

legs are subjected also to shear stresses, in the n−p couple's configuration, many of the recently reported methods for synthesis of HMS are based on powder metallurgy approaches [13,27], leading to polycrystalline samples with averaged mechanical properties. Most of the previously reported transport properties of powder metallurgy prepared HMS samples, didn't take into account any anisotropy effect of the crystal structure, while assuming isotropy due to random crystallographic oriented grains canceling each other while being distributed in the samples.

Nevertheless, it is known that some anisotropy can exist also in polycrystals in cases where specific properties, such as mechanical properties, are highly anisotropic in the constituent single crystals, leading to a textured polycrystal [28]. For example, Polycrystal plasticity and texture development of non-cubic Zr- alloys were reported to originate from a variety of active deformation modes present in each grain, non-negligible twinning activity accompanied by a substantial fraction of grain reorientation and highly directional grain interactions [29]. In the polycrystalline HCP AZ31B Mg alloy, following mechanical deformation, a high degree of plastic anisotropy was attributed to the role of non-basal dislocations and grain boundaries in accommodating a deformation along the c-axis [30]. Since plastic deformation (such as hot pressing) and cleavage of non-cubic polycrystalline materials, is often characterized by a highly anisotropic behavior of the constituent grains and by non-negligible anisotropic twinning activity affecting the grains reorientation [31], and since oriented internal stresses in HMS following arc-melting and hot pressing, can be also promoted by the reported large variations between the thermal expansion coefficients along the crystallographic c- and a-axes [32], possible preferred orientation effect on the transport properties of polycrystalline HMS following these synthesis routes, was investigated in the current research. A possible c-axis preferred orientation in parallel to the pressing direction of polycrystalline HMS is described schematically in Fig. 1b and c by a predominance of (001) oriented grains in transverse to the pressing direction.

2. Experimental procedures

2.1. Synthesis

HMS was synthesized from pure silicon (7N) and manganese (99.5%) pieces weighed at the ratio of MnSi$_{1.75}$ in an arc-melting furnace (Buhler mini arc-melting system type 'MAM-1') under an argon atmosphere upon three flipping and re-melting stages to ensure homogeneity. The samples were hand milled for obtaining powder particles size in the 63−105 μm range and hot pressed in a
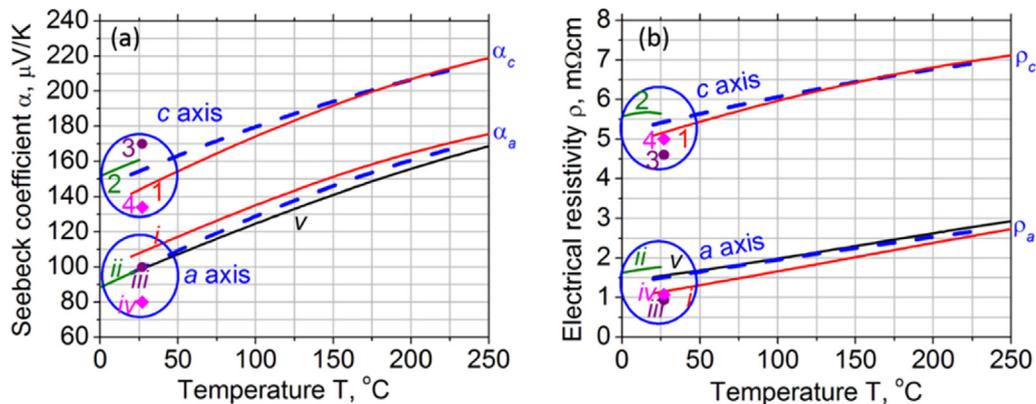
Fig. 2. Previously reported Seebeck coefficient (a) and electrical resistivity values (b) of HMS single crystals grown along the crystallographic c- (1[23], 2[24], 3[25] and 4[26]) and a- (i[23], ii[24], iii[25], iv[26] and v[7]) axes. The dashed curves are trend lines based on averaging the properties along each of the crystallographic directions.