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Dependence of thermoelectric behaviour on severe plastic deformation parameters: A case study on p-type skutterudite $DD_{0.60}Fe_3CoSb_{12}$

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Abstract

High-pressure torsion (HPT), a severe plastic deformation technique, can effectively improve the thermoelectric performance of skutterudites, resulting in ZT values higher than for ball-milled and hot-pressed (BMHP) samples. In this paper the influence of the HPT parameters, i.e. the number of revolutions (equivalent to the applied strain), the processing temperature and the hydrostatic pressure on the microstructural and thermoelectric properties of the skutterudite $DD_{0.60}Fe_3CoSb_{12}$ are evaluated and compared with the BMHP samples before HPT processing. Whilst the three parameters have specific effects on (i) the crystallite size, (ii) the density of lattice defects and (ii) the density of cracks, a suitable combination thereof allows for an increase of the figure of merit by at least 20%.

Keywords: Skutterudite; Severe plastic deformation; High pressure torsion; Nanostructures

1. Introduction

Thermoelectric materials are able to directly convert thermal energy into electrical energy and reversibly electrical energy into thermal energy. The potential of a material for thermoelectric applications is determined by the dimensionless figure of merit:

$$ZT = S^2T/(\rho\lambda) \quad (1)$$

where S is the Seebeck coefficient or thermopower ($S \sim \Delta V/\Delta T$), T the temperature, ρ the electrical resistivity and $\lambda = \lambda_e + \lambda_{ph}$ the total thermal conductivity, consisting of the electronic part λ_e and the phonon part λ_{ph}. The power factor, $pf = S^2\sigma$ (with σ as the electrical conductivity $= 1/\rho$) depends on the carrier concentration (n) and passes through a maximum for small gap semiconductors with $n \approx 2.5 \times 10^{19}$ cm^{-3}. The electronic part of the thermal conductivity is linked to the electrical resistivity via the Wiedemann–Franz law:

$$\lambda_e \sim L_0T/\rho \quad (2)$$

with the Lorentz number $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}. As it is not possible to decrease λ_e without decreasing the power factor, the only way to increase ZT is by decreasing λ_{ph}, the lattice part of the thermal conductivity.

It is possible to decrease λ_{ph} by enhancing the scattering of the heat carrying phonons via various mechanisms: scattering on phonons (N) including Umklapp processes (U), scattering on lattice defects and impurities (D), on grain boundaries (B) and on electrons (E) [1]. In the Debye approximation of the thermal conductivity [2–4],

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$$\lambda_{ph} = \frac{k_B}{2\pi^2 v_s}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{\tau_C}{(e^x-1)^2} dx + \frac{I_2}{I_1} \quad (3)$$

with the sound velocity, v_s, expressed as

$$v_s = \frac{k_B \theta_D}{\hbar (6\pi^2 N)^{\frac{1}{3}}} \quad (4)$$

and

$$x = \frac{\hbar\omega}{k_B T} \quad (5)$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, θ_D is the Debye temperature and ω is the phonon frequency; these scattering mechanisms are taken care of via relaxation times τ_i, which can be summarized according to Matthiessen's rule yielding a total relaxation time τ_c:

$$\tau_c^{-1} = \tau_N^{-1} + \tau_D^{-1} + \tau_B^{-1} + \tau_E^{-1} + \tau_U^{-1} \quad (6)$$

Generally $I_2 = 0$ for $\tau_N \gg \tau_U$ (for details see Ref. [5]).

Besides Umklapp processes (τ_U^{-1}) and scattering on electrons (τ_E^{-1}), one way of decreasing λ_{ph} is by reducing the grain size d according to $\tau_B^{-1} = v_s/d$. Another possibility is to scatter phonons on lattice defects and dislocations because τ_D^{-1} includes the contribution of the dislocation core $\tau_{core}^{-1} \propto N_D r^4 \omega^3 / v_c^2$ with N_D as dislocation density and the surrounding strain field $\tau_{str}^{-1} \propto N_D \gamma^2 b\omega/2\pi$ with the Burgers vector b of the dislocation.

Another route for higher ZT values is an enhancement of the Seebeck coefficient without in parallel enhancing the electrical resistivity i.e. via a decoupling of ρ and S.

The Mott's formula,

$$S \approx \frac{1}{N}\frac{dN}{dE}\bigg|_{E_F} \quad (7)$$

shows that the Seebeck coefficient primarily depends on the energy derivative of the density N of the carrier states at the Fermi level E_F. Hicks and Dresselhaus [6], Dresselhaus et al. [7,8,10], Dresselhaus and Heremans [9] and Minnich et al. [11] have shown that the Seebeck coefficient S can be increased when the grain sizes reach a few tens of nanometers (favourable <10 nm) because in that case the parabolic shape of the simple density of states (DOS)–E curve splits up to spike-like structures for nano-wires or quantum dots.

Heremans et al. [12] recently found a new route ("engineered impurity-induced band-structure distortion") to enhance S: doping by proper elements can form resonant impurity states at E_F which may favourably change the electronic density of states.

"Bottom-up methods" like hand milling (HM), ball milling (BM) combined with hot pressing (HP) are reasonable ways to prepare materials with a crystallite size of the order of several hundred nm and crystal imperfections (e.g. dislocation densities of $\sim 10^{12}$ m^{-2}). With these methods nanostructured multifilled p- and n-type skutterudites have reached remarkably high ZT values, e.g. $ZT = 1.2$ at 700 K (p-type) [13,14] or $ZT > 1.4$ (n-type) [15,16] at 800 K.

Severe plastic deformation (SPD) (and high pressure torsion (HPT) as one of its major representatives) is a "top-down process", which achieves materials with ultrafine grains (UFGs) in the sub-micrometer or nanometer range [17–19]. With this method an extremely large plastic strain under a significantly high hydrostatic pressure is imposed on a sample without any essential change of the sample's geometry, which leads to (i) ultra-fine-grained structures (crystallite sizes of the order of 100 nm and less) and (ii) an enhanced formation of lattice defects – vacancies and particularly dislocations (for details see Refs. [20–26]).

In the field of thermoelectrics, hitherto only a few studies reported the impact of SPD on the thermoelectric behaviour of Heusler alloys [27]; however, more applications are found for Bi–Te alloys (Ref. [26] and references therein). Recently Zhang et al. [28], and Rogl et al. [25,29–31] investigated HPT processed skutterudites, and Yan et al. [32] the clathrate $Ba_8Cu_{3.5}Ge_{41}In_{1.5}$. Zhang et al. [28] devoted their work to the change of the thermal conductivity, crystallite size and magnetic properties after HPT processing. Rogl et al. concentrated on the change of the structural, physical and mechanical properties of p- and n-type skutterudites after HPT processing, focusing mainly on (i) the changes of the processed samples after various annealing times [25], (ii) the sample's position in the processed disc [25,26], (iii) starting conditions (HM or BM samples) [31], (iv) the changes of crystallite size and dislocation density after HPT and annealing processes [25,29], as well as (v) TEM analysed defects of a processed n-type skutterudite [30]. They found that lattice defects and grain boundaries reduce the lattice thermal conductivity substantially via phonon scattering and thus enhance ZT at least by 20% [25,26,29,30] but also observed the influence of HPT processing parameters.

Therefore in this paper we will systematically evaluate the influences of various HPT processing parameters on the thermoelectric behaviour of the skutterudite $DD_{0.60}Fe_3CoSb_{12}$. The parameters studied were: the number of revolutions (NR), representing different plastic strains, the processing temperature (PT) and the processing pressure (PP). For these investigations we chose $DD_{0.60}Fe_3CoSb_{12}$ not only because it has already a high ZT before HPT processing ($ZT \sim 1.1$ at 800 K), but also because it was investigated in previous studies [25,26], and these results will be compared with the new data.

2. Experimental

The p-type skutterudites with the nominal composition $DD_{0.60}Fe_3CoSb_{12}$ (DD stands for the natural double filler didymium from Treibacher Industrie AG, Austria, containing 4.76 mass% Pr and 95.24% Nd, Fe, Co and Sb from Alfa Aesar) were prepared via a reaction-melting technique followed by ball-milling in a Fritsch Pulverisette high