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Spinodal decomposition in $(Ca_xBa_{1-x})_yFe_4Sb_{12}$

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Abstract

The thermoelectric and structural properties of a double filled skutterudite solid solution $(Ca_xBa_{1-x})_yFe_4Sb_{12}$ were investigated. Using X-ray powder and X-ray micro analyses (EPMA) an immiscibility gap was established with a critical point at $x \approx 0.45$ and a critical temperature that depends on the filling level ($T_C = 590 \pm 5$ °C at $y = 0.8$ and $T_C = 610 \pm 5$ °C at $y = 0.9$). The thermoelectric properties were measured for samples prepared in four different states: (i) a single phase solid solution $(Ca_xBa_{1-x})_yFe_4Sb_{12}$; (ii) a two phase microcrystalline mixture of $Ca_yFe_4Sb_{12}$ and $Ba_yFe_4Sb_{12}$; (iii) a single phase structure obtained after annealing of the latter sample at 600 °C for 200 h; (iv) a spinodally demixed sample after annealing at 400 °C for 672 h. The thermoelectric properties of the phase mixture (ii) are compatible with data reported for the microcrystalline end members ($Ca_yFe_4Sb_{12}$ and $Ba_yFe_4Sb_{12}$), whilst the single phase (i and iii) and spinodally decomposed (iv) samples show increased thermopower and decreased thermal conductivity, similarly to those observed for nano-structured $Ca_yFe_4Sb_{12}$ and $Ba_yFe_4Sb_{12}$.

Keywords: Spinodal decomposition; Annealing; Thermal conductivity; Intermetallics; Skutterudites

1. Introduction

Skutterudites crystallize as structures of $LaFe_4P_{12}$ type, a filled variant of the $CoAs_3$ prototype (space group $Im\overline{3}$). In the general formula $E_yT_4X_{12}$ T is a transition element of group VIII in the 8c position (¼, ¼, ¼), X is a pnicogen atom in sites 24e (P, As, Sb) and electropositive E atoms fill the icosahedral void 2a (0, 0, 0) [1–4]. Skutterudites are among the most promising thermoelectric (TE) materials, characterised by a high $ZT = S^2T/\rho\lambda$, i.e. the dimensionless figure of merit, used to determine the thermoelectric quality of a material, where S is the Seebeck coefficient, T is the temperature, ρ is the electrical resistivity and λ is the thermal conductivity, the latter being the sum of two contributions, λ_e due to electronic transport and the lattice thermal conductivity λ_{ph} due to phononic heat transport ($\lambda = \lambda_e + \lambda_{ph}$). For optimal thermoelectric efficiency a high average ZT_a in the experimentally used temperature range is required.

Reducing the lattice thermal conductivity is an important issue in achieving high ZT values. Studies report that alkaline earth or/and rare earth filler elements, particularly in the form of double or multifillers, are efficient in reducing the lattice thermal conductivity λ_{ph} [5–9] due to enhanced scattering of phonons on the rattling atoms in the icosahedral voids, raising the ZT values above those of single filled ones [10–15]. Additional nanostructuring may enhance the scattering of heat carrying phonons and thus further lower the thermal conductivity of thermoelectric materials [16–24]. In previous works we showed that (i) ball milling can produce materials with crystallite sizes of 100–200 nm, that (ii) severe plastic deformation by high pressure torsion can reduce the grain size even more

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(to about 50 nm) and in this way reduce the lattice thermal conductivity and increase the thermopower, and the ZT values [25–29] remain enhanced even if the electrical resistivity is elevated.

Another route to produce materials with an ultrafine microstructure involves so-called spinodal decomposition, as shown for the thermoelectric systems $Pb_{1-x}Sn_xTe$–PbS [30] and $Ge_x(Sn_yPb_{1-y})_{1-x}Te$ [31] achieving a significant decrease in lattice thermal conductivity.

The current investigation tries for the first time to exploit binodal/spinodal decomposition in thermoelectric double filled skutterudites $(Ca_xBa_{1-x})_yFe_4Sb_{12}$. The influence of heat treatment on the physical properties of $(Ca_xBa_{1-x})_yFe_4Sb_{12}$ was investigated and compared with that for the pure end members $Ca_yFe_4Sb_{12}$ and $Ba_yFe_4Sb_{12}$.

2. Experimental details

Samples with the general formula $Ca_yFe_4Sb_{12}$, $Ba_yFe_4Sb_{12}$ and solid solution $Ca_{0.46}Ba_{0.46}Fe_4Sb_{12}$ (sample B) were prepared from a master Fe_4Sb_{12} alloy via a melting reaction technique from stoichiometric amounts of high purity elements (iron wire with a minimal purity of 99.5 mass% and bulk antimony with a minimal purity of 99.95 mass% from Alfa Aesar, Germany) by mixing, sealing in evacuated quartz tubes, melting at 960 °C and air quenching. Then stoichiometric amounts of Ca/Ba (both with a purity of 99.99 mass% from Alfa Aesar, Germany) were added, the samples were sealed under vacuum in quartz tubes, heated for 4 days at 600 °C, melted at 960 °C and air quenched. The bulk materials obtained were ground to fine powders in an argon filled glovebox (O_2 and H_2O below 5 ppm) in a tungsten carbide/Co mortar and filtered through a microstrainer to obtain particles of <20 μm. Alternatively double filled $(Ca_xBa_{1-x})_yFe_4Sb_{12}$ samples were prepared by mechanical mixing of $Ca_{0.91}Fe_4Sb_{12}$ and $Ba_{0.83}Fe_4Sb_{12}$ (samples A1 and A2) and of $Ca_{0.84}Fe_4Sb_{12}$ and $Ba_{0.93}Fe_4Sb_{12}$ (sample A3). The mixtures were loaded in a 10 mm diameter graphite die inside the glovebox and hot pressed (HP) under Ar employing a uniaxial FCT hot press system (HP W 200/250-2200-200-KS) at 600 °C and 56 MPa for 2 h. The cylindrical specimens obtained (1 cm diameter × 8 mm high) were cut into several pieces, sealed in evacuated quartz tubes and subjected to heat treatment as described in Table 1. The bulk of sample B was treated in the same way as described for samples A1, A2 and A3.

X-ray powder diffraction data were collected with Cu $K_{\alpha 1}$ radiation and a Huber Guinier image plate recording system using pure Ge (99.9999%) as an internal standard ($a_{Ge} = 0.5657906$ nm). X-ray spectra were used to calculate the lattice parameters, using the programs STRUKTUR [32] and FULLPROF [33] for quantitative refinement. The chemical composition was analysed by electron probe microanalysis, using energy dispersive X-ray spectroscopy (EPMA EDX) with Inca Penta FETx3 Zeiss Supra55VP equipment. SEM pictures of the fracture surface were taken with the same equipment. EPMA was employed to extract the ratio among the filler atoms (at a precision of about 10%) and these ratios were then used for quantitative Rietveld refinement, where the total filling level (i.e. the occupancy of the sum of the various filler atoms in site 2a) was determined at an accuracy of 1% from the overall electron density in the 2a position. Element mapping was employed for the decomposed sample to study the exact distributions of Ca and Ba. X-ray data and lattice parameters were collected for samples A1, A2 and A3 before and right after each heat treatment.

For transmission electron microscopy (TEM) investigations disc-shaped specimens were prepared by spark erosion followed by mechanical grinding. The discs were subsequently mechanically dimpled on one side to a final thickness of about 30 μm and thinned to perforation using a Leica RES101 ion mill. Ion milling was carried out from the top and bottom simultaneously at an inclination angle of 15°. Both guns were operating at a voltage of 3 kV and a current of 1 mA. During the milling procedure (about 12 h) the sample was rotated at 1 rpm. The TEM study was carried out using a Philips CM200 microscope operating at an acceleration voltage of 200 kV.

Thermodynamic boundary curves for the spinodal ($\partial^2G/\partial x^2 = 0$) and the binodal ($\partial^2G/\partial x^2 > 0$) regions were calculated assuming a simple regular solution for the Gibbs free energy G, exploiting Eqs. (1)–(3).

$$T_C = \frac{\alpha}{2R} \tag{1}$$

and

$$T = \frac{2\alpha}{R}x_1(1 - x_1) \tag{2}$$

for the spinodal decomposition, and

$$T = 2T_C\frac{1 - 2x_1}{\ln\left(\frac{1 - x_1}{x_1}\right)} \tag{3}$$

for the binodal curve, with $x_2 = 1 - x_1$, the mole fractions, R is the gas constant $R = 8.3144621\ \mathrm{J\,K^{-1}\,mol^{-1}}$, T is the temperature in K, T_C is the temperature in K of the critical point for decomposition, and α is the regular solution parameter characterising the interaction of Ca and Ba atoms in solution [34].

Cahn [35] (and references therein) calculated the amount of supercooling necessary for spinodal decomposition of an alloy at the top of the miscibility gap. In order to estimate the degree of suppression of the spinodal critical temperature due to coherency strain the critical point for a material of the critical composition can be approximated by:

$$\left(\frac{\partial^2 f'}{\partial c^2}\right) = 4k(T - T_C)N \tag{4}$$

The spinodal is at $T = T_C$, and instability sets in at

$$T_C - T = \frac{\eta^2 E}{2(1 - v)kN} \tag{5}$$