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Mechanical properties of filled antimonide skutterudites

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ABSTRACT

Time-of-flight and resonant ultrasound spectroscopy techniques were employed for elastic moduli measurements on a set of various Fe_4Sb_{12}- and Co_4Sb_{12}-based skutterudites filled by mischmetal, didymium, or alkaline earths (Ca, Sr, Ba). A weak temperature influence on the longitudinal modulus C_{11} indicates weak degradation of elastic properties within the thermoelectric working temperature range. Elastic moduli for Co_4Sb_{12}-based skutterudites are only slightly higher than for Fe_4Sb_{12}-based skutterudites, and the influence of various filler atoms or filling fractions on the elastic moduli is even smaller. Ball milled and hot pressed samples (grain size ~250 nm) illustrate an obvious improvement of elastic properties in relation to those hot pressed from hand milled powders (grain size ~50 μm). Debye temperatures calculated from sound velocity measurements are comparable to the values obtained from the parameters fitted to thermal expansion, which indicate that Co_4Sb_{12}-based skutterudites having slightly higher values than Fe_4Sb_{12}-based skutterudites. Vickers hardness is increased by Co or Ni substitution and demonstrates a linear dependence on density, Young's modulus, and shear modulus.

1. Introduction

Since conventional fuel resources are limited, thermoelectric (TE) materials attracted worldwide attention as an environmental friendly technique for electric power generation or refrigeration [1]. New materials and the optimization of known compounds have steadily enhanced the efficiency of TE-materials, which is best characterized by the figure of merit $ZT = S^2T/(\rho\kappa)$ (S is the Seebeck coefficient, ρ is the resistivity and κ is the thermal conductivity). Filled skutterudites $R_xT_4Sb_{12}$ (R is a rare-earth or alkaline earth, T is a transition metal) are some of the promising TE-materials and thus were investigated broadly [2–8]. The substitution of the transition metal T in $R_yT_4Sb_{12}$ by other transition metals, for example, Co or Ni randomly substituting Fe, enhances phonon scattering i.e. reduces the thermal conductivity and consequently enhances ZT [2,8–13]. Mischmetal, Mm (50.8% Ce, 28.1% La, 16.1% Nd and 5.0% Pr) and didymium DD (4.76% Pr and 95.2% Nd), are commercially available alloys of several light rare-earth elements, cheaper than individual rare-earth metals. This fact is one of the important aspects regarding the large-scale commercial application of TE-materials.

For any application of TE-materials, mechanical properties are as important as TE properties. A long-term reliable TE device requires high elastic moduli in order to resist external bending or shaking forces, etc. without crack formation or crack propagation. Therefore, elastic properties play an important part in providing valuable information on the elasticity and mechanical stability of a solid as well as on the bonding characteristics between adjacent atomic planes, the usually anisotropic character of bonding and structural stability. To our knowledge, elastic properties have only been reported for some skutterudites i.e., sound velocity for single-crystal $CoSb_3$ [14] and polycrystalline $CoSb_3$ [15,16], $La_{0.75}Fe_3CoSb_{12}$ [15], $Ce_{0.75}Fe_3CoSb_{12}$ [15], and $LaFe_4Sb_{12}$ [16]; elastic moduli for $CoSb_3$, $La_{0.75}Fe_3CoSb_{12}$, and $CeFe_3RuSb_{12}$ [3,17–19], as well as for non-$(Fe,Co,Ni)_4Sb_{12}$ based single-crystal skutterudites [20–29] and polycrystalline $SmRu_4P_{12}$ [30]. Data from model simulations for $CoAs_3$ [31] and other skutterudites were reported as well [32–34]. Time-of-flight (TOF) or pulse-echo [35] and resonant ultrasound spectroscopy (RUS) methods [36,37] are two of the most important techniques for elastic constant measurements. The TOF method measures the sound velocity: transit time of a sound pulse through the specimen, from which the elastic constants are calculated. The disadvantage of this method is that

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for measuring various elastic constants one needs transducers differently oriented with respect to the crystal axes. It also requires a sample of macroscopic dimensions to meet the requirement that wavelengths are short compared to the dimensions of the sample. RUS uses the natural resonance of objects and is sensitive to the elastic constants and detects the true thermodynamic dissipation [37]. With modern computers, the elastic constants can be rapidly extracted from the frequency spectrum.

The present paper provides comprehensive investigations on sound velocities, elastic moduli (longitudinal modulus C_{11}, shear modulus G or C_{44}, Young's modulus E, bulk modulus B, and Poisson's ratio ν), compression, and hardness from measured data as well as the Debye temperature for selected samples from the author's previous works [8,12,13,38]. All samples were prepared by hand milling or ball milling followed by hot pressing. For ball milled samples the relative densities (Den.) are higher than 98% except for the one containing 20% secondary phases ($FeSb_2$, Sb, and Mm_2O_3, called 80%-$Mm_{0.7}Fe_4Sb_{12}$, Den. = 96.7%) and most of them exhibit a ZT > 1. Both TOF and RUS methods were employed for elastic moduli measurements.

2. Experimental procedures

Details of sample preparation and composition are given in our previous papers [8,12,13,38,39].

The time-of-flight sound pulse measurements were performed on cylinders (height = 10 mm, diameter = 10 mm) with a frequency of 10 MHz. The absolute values of the elastic moduli were derived from the measured sound velocity using equations [35,40]:

$$C_{11} = \rho_d \nu_L^2 \tag{1}$$

$$C_{44} = G = \rho_d \nu_T^2 \tag{2}$$

$$E = \rho_d \frac{3\nu_T^2\nu_L^2 - 4\nu_T^4}{\nu_L^2 - \nu_T^2} \tag{3}$$

where ρ_d is the material density measured by Archimedes' method in distilled water, ν_L and ν_T are the longitudinal and transverse sound velocities, respectively, measured with the TOF method. Poisson's ratio and bulk modulus were calculated from the equations:

$$\nu = \frac{E}{2G} - 1 \tag{4}$$

$$B = \frac{E}{3(1-2\nu)} \tag{5}$$

Resonant ultrasound spectroscopy was used to determine elastic properties via eigenfrequencies of samples and the knowledge of sample mass and dimensions. The RUS theory [36,37] establishes the relation between kinetic energy and elastic energy and hence makes it possible to carry out a least squares fit by minimizing the sum of the squared differences between the measured and the calculated eigenfrequencies to derive the elastic properties. The measurements were performed in two different types of RUS instruments. For RUS measurements at the University of Cambridge for $Ba_{0.075}Sr_{0.025}Yb_{0.1}Co_4Sb_{12}$ and $Mm_{0.7}Fe_3CoSb_{12}$ (RUS1, see Table 1), spectra were collected in the frequency range from 200 kHz to 1.1 MHz on parallelepiped-shaped samples, which were mounted corner-to-corner, face-to-face, and edge-to-edge between transducers in order to obtain all resonant eigenmodes. For each sample 25 peaks resulting from excited resonant eigenmodes and corresponding overtones were fitted via a Lagrangian minimization routine gaining elastic constants C, where shear modulus and bulk modulus are calculated for an isotropic system:

$$G = C_{44} \tag{6}$$

$$B = C_{11} - \frac{4}{3}C_{44} \tag{7}$$

Then Young's modulus was calculated from equation:

$$E = \frac{9BG}{3B+G} \tag{8}$$

Poisson's ratio was calculated from Eq. (4).

For RUS measurements at the University of Vienna (RUS2, see Table 1), the cylindrical samples were mounted edge-to-edge between the two piezo-transducers and were excited via a network analyser in the frequency range from 100 kHz to 500 kHz. As the average symmetry of all samples is isotropic, the Young's modulus and Poisson's ratio were the fitting variables. Then the bulk modulus was calculated using Eq. (5) and the shear modulus was calculated from Eq. (4).

For an isotropic material, C_{11} is calculated from the equation:

$$C_{11} = 3B - \frac{6B\nu}{1+\nu} \tag{9}$$

C_{44} = G (Eq. (2)), and ν_L and ν_T are calculated with Eqs. (1) and (2) from C_{11} and C_{44} respectively.

The errors of above measurements (TOF and RUS) are within 0.5%.

The Vickers hardness (HV) was measured under a load of 1 N sustained for 10 s in a MHT microhardness tester, mounted on a Carl Zeiss Axioplan optical microscope.

The engineering stress–strain deformation was carried out at room temperature at a crosshead speed of 0.5 mm/min on a Shimadzu AG50 universal testing machine with a Messphysik ME46NG video-extensometer and a compression cage for uniaxial compression. The marks for the extensometer were fixed on the stamps of the compression cage. The samples had a height of 5.85 mm and a cross section of 3.85 mm times 3.94 mm.

3. Results and discussion

3.1. Sound velocities and elastic moduli

Two basic types of waves exist in a solid: longitudinal and transversal (shear) waves. Both types depend on the elastic stiffness constant C_{ij} via Eqs. (1) and (2). The results of TOF and RUS measurements are listed in Table 1. For the samples investigated throughout the present work, temperature dependent longitudinal sound velocity ν_L and longitudinal modulus C_{11} are illustrated in Fig. 1. Although TOF and RUS measurements use different techniques and evaluation methods, room temperature values of ν_L and C_{11} for $Mm_{0.7}Fe_3CoSb_{12}$ are almost identical. All ball milled samples show a higher C_{11} than hand milled skutterudite samples demonstrating the strong influence of densification achieved by hot pressing ball milled nano powders. It can be seen from Table 1 that the relative density for ball milled samples is higher than 98% (except for "80%-$Mm_{0.7}Fe_4Sb_{12}$" with 96.7%) while for hand milled samples the highest density reached is 96.2%. The dependence of the elastic moduli on density is also reported in literature, e.g., for iron [41,42] and ceramics [43,44]. With similar density, ball milled n-type $Ba_{0.075}Sr_{0.025}Yb_{0.1}Co_4Sb_{12}$ and $(BaYb)_{0.03}Co_4Sb_{12}$ in our work and $CoSb_3$ (literature, see Table 1) have slightly higher C_{11} than p-type ball milled skutterudites. The hand milled $Ca_{0.07}Ba_{0.23}Co_{3.95}Ni_{0.05}Sb_{12}$ shows even larger values C_{11} and C_{44} than some of the ball milled Fe_4Sb_{12}-based skutterudites (Fig. 1b and Table 1). The reason might be that the small amount of Ni substituting Co strengthens the mechanical behaviour as reported in [45].

For the group of ball milled Fe_4Sb_{12}-based skutterudites (Fig. 1), the values of ν_L and C_{11} are slightly different from each other due to various compositions and densities. The same situation arises