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Synthesis, characterization and physical properties of the skutterudites $Yb_xFe_2Ni_2Sb_{12}$ $(0 \le x \le 0.4)$

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ABSTRACT

The skutterudites $Yb_xFe_2Ni_2Sb_{12}$ $(0 \le x \le 0.4)$ have been prepared by solid-state reaction and characterised by powder X-ray diffraction. The compounds crystallise in the cubic space group $Im\ \overline{3}$ ($a \approx 9.1$ Å) with Yb atoms partially filling the voids in the skutterudite framework. A neutron time-of-flight diffraction experiment for $Fe_2Ni_2Sb_{12}$ confirms the disorder of Fe and Ni atoms on the transition-metal site. Electrical resistivity, Seebeck coefficient and thermal conductivity measurements indicate that the thermoelectric performance of the skutterudites shows a marked dependence on the Yb content. Magnetic measurements over the temperature range $2 \le T/K \le 300$ show paramagnetic behaviour for all compounds. Decomposition studies under an oxidising atmosphere at elevated temperatures have also been carried out by thermogravimetric analysis.

1. Introduction

The ideal skutterudite structure [1] consists of an array of vertex-linked metal centred MX_6 octahedra, which results in a framework of stoichiometry MX_3 (Fig. 1). Octahedra are tilted according to the $a^+a^+a^+$ tilt system [2], generating large voids within the structure. The anion sub-lattice forms four-membered rectangular rings, which are believed to play a key role in determining the electronic properties [3]. Binary skutterudites MX_3 are known for M=Co, Rh, Ir; X=P, As, Sb. Moreover the large voids created within the framework may be occupied to varying degrees by filler atoms giving rise to filled skutterudites of general formula, $A_xM_4X_{12}$, where A may be a rare-earth, alkali metal, alkaline earth or group 13 element [4,5]. Filled skutterudites have been extensively studied as promising candidates for thermoelectric applications [6,7]. It has been suggested that such materials are manifestations of the 'phonon-glass and electron-crystal' concept (PGEC) proposed by Slack [8]. The guest atoms within the void space exhibit localised vibrational modes [9], known as rattling vibrations. These localised vibrations perturb the propagation of phonons, thereby significantly reducing the phonon contribution to the thermal conductivity. The PGEC concept postulates that this may occur without a degradation of the electrical properties of the material, which are primarily determined by the characteristics of the framework. It has been established that the properties of filled skutterudites can be tuned by varying the degree of filling of the voids with electropositive elements and through chemical substitution within the framework. The latter can also lead to charge compensation. Filled skutterudites have some of the highest thermoelectric figures of merit ($ZT = S^2T/\kappa\rho$ where S is the Seebeck coefficient, ρ the electrical resistivity and κ the thermal conductivity) at elevated temperatures, for example n-type $Ba_{0.30}Ni_{0.05}Co_{3.95}Sb_{12}$ ($ZT \approx 1.25$ at 900 K) [10] and p-type $Ce_{0.9}Fe_3CoSb_{12}$ ($ZT \approx 1.1$ at 700 K) [11].

The majority of studies of filled skutterudites have focused on the $CoSb_3$ framework [5]. By contrast, more limited investigations have been carried out for the analogous Fe/Ni phases. Replacement of cobalt by equimolar amounts of iron and nickel, yields a ternary skutterudite that is isoelectronic with the binary cobalt antimonide. $Fe_2Ni_2Sb_{12}$ exhibits lower thermoelectric performance than Co_4Sb_{12}. Rare-earth-filled $Pr_{0.1}Fe_2Ni_2Sb_{12}$ [12] and $(Pr,Nd)_{0.08}Fe_2Ni_2Sb_{12}$ [13] have been reported to exhibit n-type behaviour and a moderate thermoelectric response (e.g., $ZT \approx 0.4$ at 800 K for $(Pr,Nd)_{0.08}Fe_2Ni_2Sb_{12}$). A change to p-type behaviour may be induced by varying the Fe/Ni ratio as occurs in $(Ln)_x(Fe,Ni)_4Sb_{12}$ (Ln=Ce and/or Yb, $0 \le x \le 0.95$) [14]. Theoretical calculations on alkaline-earth-filled skutterudites $Ae(Fe,Ni)_4Sb_{12}$ (Ae=Ca, Sr, Ba) predict a high Seebeck coefficient in both n- and p- type variants [15]. However, this prediction is yet to be tested experimentally.

In the search for new thermoelectric materials, we have investigated filled skutterudites based on the isoelectronic ternary phase $Fe_2Ni_2Sb_{12}$. In particular, we investigate the effect on thermoelectric and magnetic properties of varying degrees of

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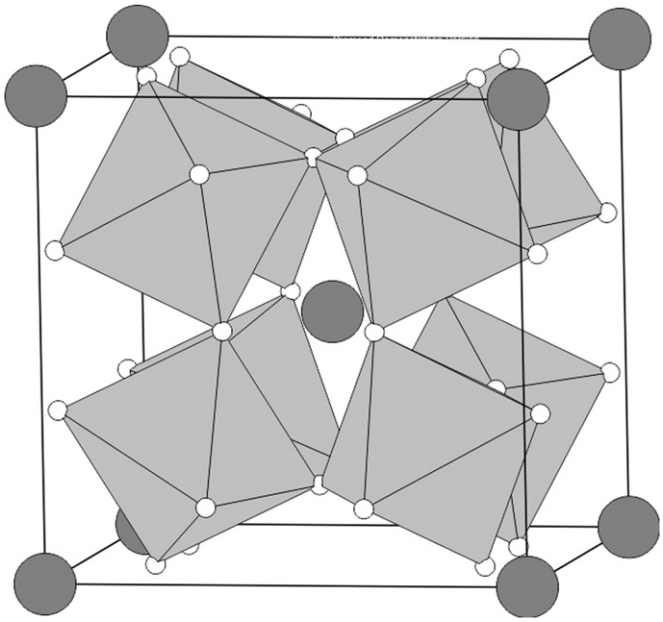

Fig. 1. The crystal structure of the filled skutterudite $Yb_xFe_2Ni_2Sb_{12}$. Key: Sb, small open circles; Yb, large shaded circles. Disordered Fe/Ni atoms reside in the centre of the shaded octahedra.

filling through preparation of the new series of quaternary phases, $Yb_xFe_2Ni_2Sb_{12}$ ($0 \le x \le 0.4$).

2. Experimental

The skutterudites $Yb_xFe_2Ni_2Sb_{12}$ ($0 \le x \le 0.4$) were prepared by mixing stoichiometric quantities of the elements Fe (Alfa, 99.9%), Ni (Aldrich, 99.99%), Sb (Aldrich, 99.999%) and Yb (Aldrich, 99.9%). The reagents were loaded into glassy carbon crucibles in an Ar-filled glove box. The crucibles were loaded into fused silica tubes under an Ar atmosphere before transferring to a vacuum line. The tubes were then evacuated ($< 10^{-4}$ Torr) and sealed. The mixtures were heated for 12 h at 1173 K, quenched in cold water and annealed at 873 K for 3 days. The tubes were opened in air and the solids finely ground before annealing in evacuated fused silica tubes at 873 K for 3 days.

The air-stable polycrystalline samples were characterised using a Bruker D8 Advance powder diffractometer, operating with germanium-monochromated Cu$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) and a LynxEye linear detector. The samples were loaded on zero-background holders and data were collected over the angular range $10 \le 2\theta/^\circ \le 120$ with a step of 0.0092° in detector position and counting times between 1.2 and 1.8 s at each step, depending on the identity of the sample. Time-of-flight (TOF) neutron diffraction data for the parent phase $Fe_2Ni_2Sb_{12}$ were collected using the HRPD diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, UK. The $Fe_2Ni_2Sb_{12}$ sample was sealed into an evacuated low-boron content silica tube and data were collected at 298 K. Initial data manipulation and reduction was carried out using the Mantid [16] software package. Neutron diffraction data from the backscattering and the 90° detector banks were summed, normalised and used simultaneously in Rietveld refinement, which was carried out using the GSAS package [17].

Thermoelectric measurements were performed on hot-pressed pellets of $Yb_xFe_2Ni_2Sb_{12}$ (823 K, 60 MPa, 30 mins, N_2 atmosphere). The densities of the resulting pellets correspond to *ca.* 95% of the crystallographic density. Rectangular blocks with approximate dimensions of $2 \times 2 \times 10$ mm were cut from the pellets. Electrical resistivity measurements were performed using the four-probe DC method. Owing to the low resistance of the samples, measurements were made using a constant current power supply and a nanovoltmeter. Four 50 μm silver wires were attached to the block using colloidal silver paint and connections were made to a TT*i* QL564P power supply and a Keithley 2182 nanovoltmeter. The sample stick was mounted in an Oxford Instruments CF1200 cryostat connected to an ITC502 temperature controller and data were collected over the temperature range $80 \le T/\mathrm{K} \le 360$ in 20 K steps. Seebeck coefficient measurements were performed over the temperature range $100 \le T/\mathrm{K} \le 350$ in 5 K steps. The samples were mounted on a stick designed and built in-house, which includes a small heater located close to one end of the sample, thus allowing a temperature gradient to be applied to the sample. Two 50 μm copper wires were attached to the ends of the sample, and connections were made to a Keithley 2182 nanovoltmeter. Two Au:0.07%Fe *vs.* chromel thermocouples were placed in contact with the sample at the hot and cold ends, and connected to an ITC503 temperature controller (Oxford Instruments). The sample stick was placed in an Oxford Instruments CF1200 cryostat connected to an ITC502 temperature controller. The Seebeck coefficient, at a given temperature, was determined by sweeping a temperature gradient, ΔT, of up to 5 K and measuring the corresponding thermal voltage, ΔV [18]. The Seebeck coefficient was determined by extracting the gradient from a plot of ΔV *vs.* ΔT by least-squares fitting of the straight line. Thermal diffusivity measurements were carried out over the temperature range $373 \le T/\mathrm{K} \le 623$ in steps of 50 K using an Anter Flashline 3000 instrument. Measurements were made on 2 mm thick, 13 mm diameter pellets of *ca.* 95% of theoretical density. This instrument determines both the thermal diffusivity (α) and the heat capacity (C_p) of the sample, and the thermal conductivity (κ) is calculated from the relationship: $\kappa = \alpha C_p \rho$, where ρ is the sample density. For the determination of the heat capacity, side-by-side testing of a reference material, PyroceramTM 9606, of known heat capacity, was carried out. The procedure used for the determination of the heat capacity is described in detail in Refs. [19,20].

Magnetic measurements were performed using a SQUID magnetometer (Quantum Design, MPMS XL). Data were collected over the temperature range $2 \le T/\mathrm{K} \le 300$ both after cooling in zero applied field (ZFC) and after cooling in the measuring field (FC) of 1000 G. The thermal stability of the samples at elevated temperatures was investigated with a DuPont 951 thermogravimetric analyser. The samples (*ca.* 30 mg each) were loaded into silica crucibles and heated at a rate of 2 K min^{-1} up to 1073 K under a 60 mL min^{-1} flow of air.

3. Results and discussion

Rietveld refinements for $Fe_2Ni_2Sb_{12}$ were carried out using TOF powder neutron diffraction data. The initial structural model was that proposed by Kjekshus and Rakke [21]. Analysis of neutron diffraction data indicates that this material crystallises in the cubic space group $Im\overline{3}$ No superstructure reflections were observed in the neutron diffraction data, consistent with complete disorder of the transition-metal cations over the octahedral sites. This is in accord with previous observations on the Ce-filled skutterudites $Ce_\delta Fe_{4-x}Ni_xSb_{12}$ ($0.06 \le \delta = (4-2x)/3 \le 0.72$) [22]. Details of the neutron refinement are presented as Supplementary Information.

Rietveld refinements for $Yb_xFe_2Ni_2Sb_{12}$ were performed using powder X-ray diffraction data. A representative refinement for $Yb_{0.4}Fe_2Ni_2Sb_{12}$ is shown in Fig. 2. All other profiles can be found in the Supplementary Information. Table 1 summarises the refined parameters from the Rietveld analysis for $Yb_xFe_2Ni_2Sb_{12}$.