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A comparison of the local structure in ball-milled and hand ground skutterudite samples using EXAFS

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ABSTRACT

Skutterudites are considered to be good thermoelectrics with high figures of merit, *ZT*. After synthesis, electrodes are created by grinding and hot pressing the resulting powder. Materials such as $NdFe_4Sb_{12}$ exhibit a significantly greater figure of merit, *ZT*, (about 43%) when it is ball milled to produce fine powders (inital powder 160 nm; after hot pressing ~330 nm). This enhancement is typically attributed to the reduced particle size, which in turn decreases the mean free path of phonons, and consequently decreases the thermal conductivity. This work aims to investigate whether there is any damage to the crystal structure in the particles formed by ball milling, which could also affect its thermal conductivity. Using a temperature dependent, Extended X-ray Absorption Fine Structure (EXAFS) analysis of a hand ground and ball milled sample of the skutterudite $Nd_yFe_4Sb_{12}$, we have determined that ball milling causes no significant damage to the local structure around any site. Consequently further improvements in *ZT* may be possible with smaller particles.

1. Introduction

Because of their unique structure and behavior, skutterudites present us with tantalizing potential applications in thermoelectrics. They take on the cubic space group $Im\bar{3}$ and the simplest compounds have the chemical formula MX_3 (where, for example, $M = Co$ and $X = Sb$). The unit cell is shown in Fig. 1 from two different perspectives, and consists of 8 individual small cubic cells, 6 of which contain a ring of X atoms and two are empty for $CoSb_3$. However, the other two sub-cubes are usually filled with a rare earth metal giving it a relatively weakly bonded "rattler" atom [1]. These are termed filled skutterudites with the chemical formula [2], $R_yM_4X_{12}$, where *R* is a rare earth metal, y is the rattler filling fraction, *M* is a transition metal including Fe, Ru and Os and *X* is a pnictogen including P, As and Sb. Here we only consider $M = Fe$, and $X = Sb$. The unit cell can also be viewed as tilted Sb-octahedra about each Fe site – Fig. 1: bottom. Note that the shortest Sb–Sb distances (2.94 and 2.99 Å) are in the ring structure which connects four Sb-octahedra.

Introducing rattler atoms in this structure leads to a significantly reduced thermal conductivity, κ, [3] although the actual mechanism [4,5] for phonon scattering is still under debate. This in turn significantly increases the material's figure of merit, *ZT*, (a measure of thermoelectric quality), where

$$ZT = \frac{TS^2\sigma_e}{\kappa}, \quad (1)$$

T is temperature, *S* is the Seebeck Coefficient, and σ_e is the electrical conductivity [6].

A further means of reducing κ is to decrease the phonon mean free path by using smaller particle sizes, produced via ball milling. Note that because electron mean free paths (which control the electrical conductivity) are already much shorter, the reduced particle size has little effect on σ_e. Such an approach has been successfully applied for the filled skutterudite $Nd_{0.86}Fe_4Sb_{12}$; after ball milling to produce small particles of order 160 nm and hot pressing which roughly doubled the size, *ZT* increased by 43% at 800 K (from 0.74 to 1.06) [7]. However, it is also possible that the ball milling process damages the local structure and bonding characteristics of the skutterudite, and in some cases can lead to amorphization [8,9] which would also affect the mean free path of the phonons. If the resulting sample were a mix of small crystallites and highly disordered/amorphous material, X-ray diffraction would see the crystallites but miss the amorphous component. In contrast, EXAFS (Extended X-ray Absorption Fine Structure) measurements

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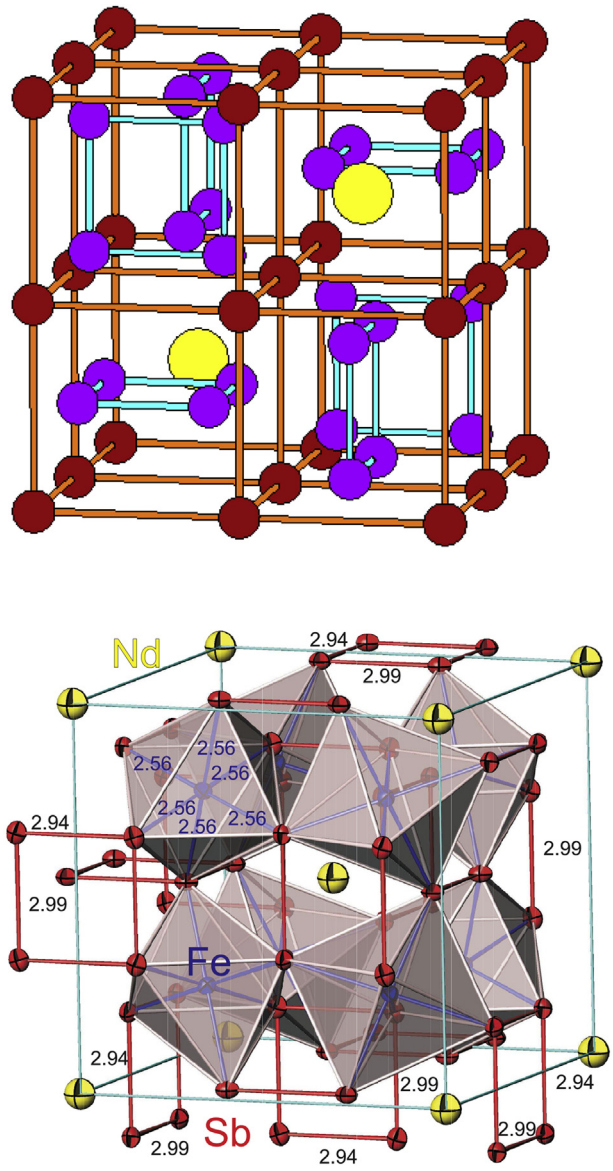

Fig. 1. The filled skutterudite structure. The top figure emphasizes the ring and rattler locations for this case, red is a transition metal, blue is a pnictogen, and yellow is a rare earth metal. The lower figure features octahedra of Sb around the Fe atoms and shows how they are tilted. The shortest Sb–Sb distances (2.94 and 2.99 Å) are between four octahedra and form the ring structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are sensitive to all atoms in the sample and if there were a significant fraction of disordered material, the amplitudes of the EXAFS peaks at low T would be smaller than expected. In this paper we will use temperature dependent EXAFS measurements to compare the disorder and bond strengths in $Nd_yFe_4Sb_{12}$ for all three sites (Nd, Fe and Sb), between a hand ground (HG) and a ball milled (BM) sample.

2. Experimental details

The sample materials were prepared via a master alloy, using an annealing-reaction-melting technique followed by hand grinding or ball milling and hot pressing as described in detail in Ref. [7] The rare earth used was the less expensive metal, Didymium - a mixture of ~95% Nd and 5% Pr. The BM sample was ground in a rotating drum containing hard metallic spheres to obtain particles initially ~166 nm in size. In both cases the resulting powders were hot pressed (56 MPA uniaxial pressure, T = 700 °C, Ar gas, for 30 min) which increased the particle size to ~330 nm. This is the same material for which the improved ZT = 1.1 was reported [7].

There are several different particle size designations and different means of estimating them. In the hot pressed samples, individual grains can be observed in SEM pictures - but within each grain there are small crystallites - small pieces of single crystal that scatter X-rays coherently. During hot pressing some nanoparticles grow together making somewhat larger crystallites. Also for powders some individual particles may contain multiple crystallites. A recent paper [10] discusses these various size measurements and some general details are included in the supplement along with SEM images for these samples.

The grain size is less well known and was determined from broken surfaces in the SEM images – see supplement. These sizes were 0.1–0.4 μm for the ball-milled and 1–4.5 μm for the hand ground samples.

For the EXAFS samples, the hot pressed material was re-ground and passed through a sieve. These powders were brushed onto scotch tape which was then folded over to make a double layer; the resulting particle size was ≤5 μm. Several of these double layers were stacked on the sample holder to obtain the desired step height in the absorption data for a given edge. X-ray absorption data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 4-1 for both Fe and Sb K edges and beamline 7-3 for the Nd L_{III} edge. Both beamlines used Si 220 monochromator crystals, detuned to 50% to minimize harmonics.

3. Step subtractions

Most of the data reduction followed standard procedures and was carried out using the RSXAP package [11]. However, for these samples there is a slight interference from other edges and these edge steps had to be removed in the data processing. First, Nd came in the form of Didymium and therefore had a slight concentration (~5%) of Pr. Since the Nd data were collected at the L_{III} edge at 6.21 keV, the Pr L_{II} edge at 6.44 keV was visible. To remove this, a function $f(E) = s(E) + \sum_n g_n(E)$ was fitted to the Pr L_{II} edge from a separate energy space data file focusing on this edge. This consisted of a step function, $s(E)$, and a set of Gaussians, $g_n(E)$ where,

$$s(E) = \frac{A}{\pi}\left(\arctan\left(\frac{E - E_0}{\Delta}\right) + \frac{\pi}{2}\right) \tag{2}$$

$$g_n(E) = A_n\sqrt{\frac{1}{2\pi\sigma_n^2}}e^{-\frac{\left(E-E_{0_n}\right)^2}{2\sigma_n^2}}, \tag{3}$$

where E is energy, A is the amplitude of the step function, Δ is the width of the step, E_0 is the edge position for Pr, A_n are the amplitudes of the Gaussians, σ_n^2 are the "variances" or widths of each Gaussian and E_{0_n} are the position of the Gaussian peaks. $f(E)$, in our case using three Gaussians, is then normalized to 1.0, and multiplied by the relative step height, a, of the Pr L_{II} step to the Nd L_{III} edge, which was ~0.05. It was then subtracted from the normalized energy space data of Nd which were then renormalized. Since ball milling made use of manganese steel, a tiny Mn K edge at 6.54 keV was visible for one BM sample only. This was removed in the same manner as before but with only a step function fitted to the Mn edge visible in the Nd data near 6540 eV.

For the Fe K edge (7.112 keV) data a more complicated correction was needed to subtract the Nd L_I edge (7.126 keV) absorption, since