Rapid Microwave Synthesis of Indium Filled Skutterudites:
An energy efficient route to high performance thermoelectric materials

Krishnendu Biswas, Sean Muir, and M. A. Subramanian*
Department of Chemistry, Oregon State University, Corvallis, OR 97331

*Corresponding author: mas.subramanian@oregonstate.edu

Full email addresses of all authors:

Krishnendu Biswas	krishnendu.biswas@oregonstate.edu
Sean Muir	muirs@onid.orst.edu
M. A. Subramanian	mas.subramanian@oregonstate.edu

Corresponding Author Permanent Address:

Professor Mas Subramanian
Oregon State University
Department of Chemistry
153 Gilbert Hall
Corvallis, OR 97331 U.S.A.

Tel: 1-541-737-8235

Abstract

Filled skutterudites are promising thermoelectric materials due to reduced thermal conductivity upon inserting a guest atom or 'rattler' into the $CoSb_3$ structure. By using an indium rattler dimensionless Figure of Merit (ZT) values > 1 at 650 K have been reported. The conventional synthesis of these compounds typically takes several days (~ 3 days) to obtain the final well-sintered material for property measurements. We report here a microwave-assisted synthesis method that reduces the initial calcination time from two days to two minutes. This route significantly reduces the time needed to produce materials suitable for property and device testing.

KEYWORDS: A. Intermetallic compounds, A. Inorganic compounds, B. Chemical synthesis, D. Electronic properties, D. Thermal Conductivity

1. Introduction

In our modern energy economy thermoelectric devices are increasingly important tools for converting otherwise wasted thermal energy into useful electrical energy. Filled skutterudites are known to be one of the state-of-the-art materials for high temperature applications due to their high ZT's ($ZT = S^2\sigma/\lambda$; S-Seebeck Coefficient, σ-electronic conductivity, λ-thermal conductivity) [1][2][3].

Skutterudites have a distorted ReO_3 structure with general formula AB_3 (where A = Co, Rh, Ir and B = P, As, Sb) and crystallize in a cubic Im-3 space group. Fig. 1 depicts the unit cell, which contains eight formula units (Z=8) and two void sites [4]. These voids can be filled by guest atoms, or "rattlers". Often the filled skutterudite formula is written as $X_xA_4B_{12}$ (Z=2) to indicate the guest position, X, and its filling fraction, x. The guest atoms act as both electron donors and 'rattlers' which helps to increase the power factor while reducing the lattice component of thermal conductivity. This leads to ZT values exceeding unity at high temperatures. The indium filled skutterudite with nominal composition $In_{0.2}Co_4Sb_{12}$ is reported to have a ZT ~ 1 at 650 K [5]. One general concern with commercializing skutterudite materials has been the long duration (several days) of synthesis needed, ranging from a few days to several.

For this reason we have been exploring the feasibility of microwave synthesis as a route to forming skutterudites. It is well known that inorganic materials can couple with microwave radiation and cause rapid dielectric heating of the material. The thermal energy dissipated from this process can be harnessed to drive atomic interdiffusion of reactants and product formation in a very short time. More than one review describing the use of microwaves for inorganic solid state materials synthesis exists and the reader is referred to these for a more general background [6][7]. A number of functional oxide materials have been produced with the aid of microwaves [8][9][10][11][12]. To synthesize $CaCu_3Ti_4O_{12}$ [9], $BaTiO_3$, and $PbZr_{0.52}Ti_{0.48}O_3$ [12], as well as Na_xWO_3 [13], a secondary nonreactive susceptor surrounding the reactants, was used to transfer heat and drive the reaction. In addition to oxides, a wide number of chalcogenides and intermetallic compositions, including the thermoelectric Bi_2Te_3, have been synthesized with microwaves and reactants placed in sealed ampoules [14][15][16][17]. Here we report the rapid synthesis of $In_{0.2}Co_4Sb_{12}$ utilizing microwave radiation. Using this method we have cut the calcination time required down from two days

to two minutes and the overall synthesis time including ball milling and final sintering/densification to a few hours.

2. Experimental

High purity elemental powders of In, Co and Sb (all 99.9% purity - Alfa) were mixed in stoichiometric quantities and pressed into a pellet. The pellet was inserted in a fused silica tube (OD 11 mm, ID 9 mm, approx. 90 mm length) and sealed under a vacuum of 1x 10^{-4} torr. The fused silica tube was buried in about 110-115 grams of CuO, a strong microwave susceptor, inside of an alumina combustion boat. The alumina boat was then surrounded by high temperature fire bricks. The entire setup was placed on a rotating glass table inside of a CEM MDS-81D multi-mode microwave oven and exposed to microwave radiation (2.45 GHz) for 2 minutes at 750 W (100% power). Fig. 2 shows a schematic of the setup highlighting the various components. For comparison we synthesized the nominal composition, $In_{0.2}Co_4Sb_{12}$, with the method previously described in the literature [5]. This method involves mixing stoichiometric amounts of In, Co and Sb and calcining at 610 °C for 12 h and then 675 °C for 36 h at a rate of 1°C/min under 5% H_2 and 95% N_2 mixture atmosphere. The powders formed after 2 minutes of microwave exposure, as well as those prepared conventionally, were subsequently ball milled for three hours in acetone and sintered in N_2/H_2 flow at 675 °C for 4 h (heating rate of 5°C/min). Powder X-ray diffraction (PXRD) patterns for the microwave samples were collected with Cu K_α radiation and a graphite monochromator on a Rigaku Miniflex II from 10-120 degrees 2θ. Thermopower and resistivity were measured on a ZEM-3 (ULVAC-RIKO) from 325-625 K. Thermal diffusivity and heat capacity was measured on a NETSCZ Micro flash (LFA 457) and Metler-Toledo differential scanning calorimeter (DSC 821e), respectively, both from 325-625 K. The thermal conductivity then was calculated as, $\lambda = C_p dD$ (λ-thermal conductivity, C_p-heat capacity, d-density, and D-thermal diffusivity).

3. Results and Discussions

a) Phase formation

The XRD patterns taken immediately after microwave exposure and after the additional sintering step are shown in Figs. 3a and 3b, respectively. For comparison an XRD pattern of the conventionally prepared sample is shown in Fig. 3c. The patterns are indexed on the

basis of Im-3 cubic space group and the lattice parameter, deduced by simple least square analysis [18], is found to be a = 9.050(1)Å for the microwave prepared sample after the final sintering step. The XRD pattern following just the microwave treatment contains very minor secondary phases of $CoSb_2$ and Sb which were completely eliminated after the sintering process, Fig. 3a.

All samples after sintering have high densities (~95% of the theoretical density), suitable for both materials characterization and possible device testing. The dramatic shortening of calcination time helps to eliminate a significant hurdle in the reported synthetic process. While Co metal powder has been reported to couple with microwaves at room temperature [7], the sample batch sizes investigated here (~0.5 g) were small enough that the sample did not show significant heating after exposure to microwaves without the CuO susceptor present. The CuO surrounding the fused silica tube can be thought of as a small localized furnace with an extremely high ramp rate, much faster than what conventional furnaces are able to achieve. The temperature of the CuO after two minutes exposure was estimated to be ~650-700 °C by immediately plunging a thermocouple into the CuO bath surrounding the fused silica tube. Utilizing a preheated box furnace it should be possible to achieve similar results; however, the microwave method is still preferred as it does not require any preheating or carry the dangers associated with directly entering samples into a hot furnace zone.

b) Thermoelectric properties

The thermopower, resistivity and thermal conductivity plots of $In_{0.2}Co_4Sb_{12}$ samples synthesized by regular and microwave methods are shown in Figure 4a, b and c respectively. All physical property measurements were carried out after the sintering process. The negative thermopower observed demonstrates that electrons act as the major charge carriers, *i.e.* $In_{0.2}Co_4Sb_{12}$ is an *n*-type thermoelectric material. All thermoelectric related properties (thermopower, resistivity, and thermal conductivity) match well with those prepared with the reported method. The ZT plot shown in Figure 4d indicates that the microwave prepared samples are as good as those synthesized with the literature reported method [5].

4. Conclusions

We have successfully synthesized the skutterudite $CoSb_3$ as well as an indium-filled skutterudite with the nominal composition $In_{0.2}Co_4Sb_{12}$ using microwave energy and a strong secondary susceptor, CuO. This method significantly reduces the overall reaction time, as it

nearly eliminates the time consuming calcination step. The structural, electronic, and thermal properties of the microwave-prepared samples are similar to those of conventionally prepared samples. While $CoSb_3$ and $In_{0.2}Co_4Sb_{12}$ were chosen as a proof-of-concept for this work, it is expected that similar microwave synthesis will also work for producing other filled variants and possibly Rh or Ir based skutterudites. The reduction in calcination time (2 days reduced to 2 minutes) will result in significant energy savings, thereby making this a more energy efficient and economical route to high-performance thermoelectric materials.

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Figure Captions

Figure 1. The unit cell for $In_xCo_4Sb_{12}$. The indium rattler positions are located at the center, purple, and corners of the cell (corner rattler not shown). The cobalt atoms, blue, and antimony atoms, brown, form a three dimensional framework of tilted corner sharing $CoSb_6$ octahedron.

Figure 2. Schematic of the setup used for the microwave synthesis of $CoSb_3$ and $In_{0.2}Co_4Sb_{12}$ inside of fused silica ampoules (components are not drawn to scale).

Figure 3. XRD patterns of $In_{0.2}Co_4Sb_{12}$ a) sample after two minutes microwave calcination, b) microwave sample after conventional sintering, and c) prepared following the literature procedure described in ref. [5]. Impurity peaks from $CoSb_2$ and Sb are indicated as (*) in the pattern taken after two minutes of microwave calcination.

Figure 4**.** Temperature dependent a) thermopower, b) electrical resistivity, c) thermal conductivity, and d) ZT of both microwave and conventionally prepared $In_{0.2}Co_4Sb_{12}$ samples.

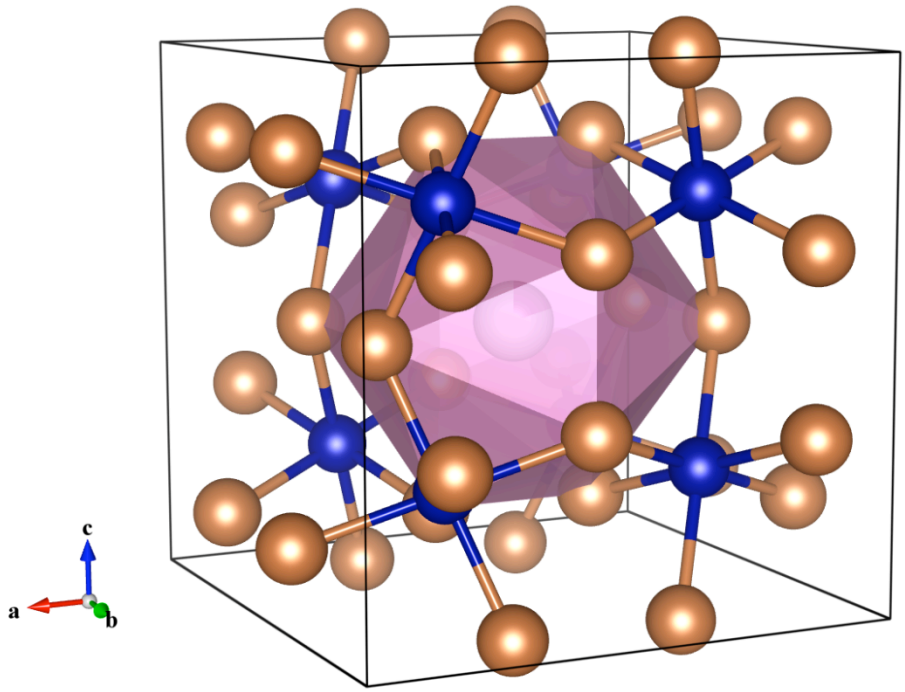

Figure 1.

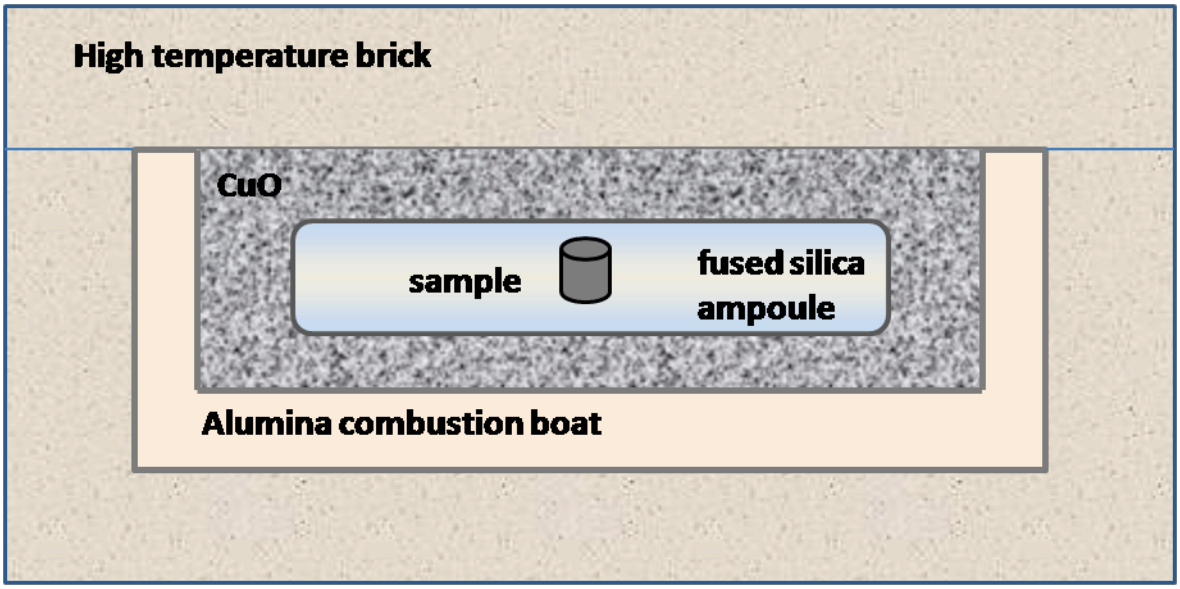
High temperature brick
CuO
sample
fused silica
ampoule
Alumina combustion boat

Figure 2.

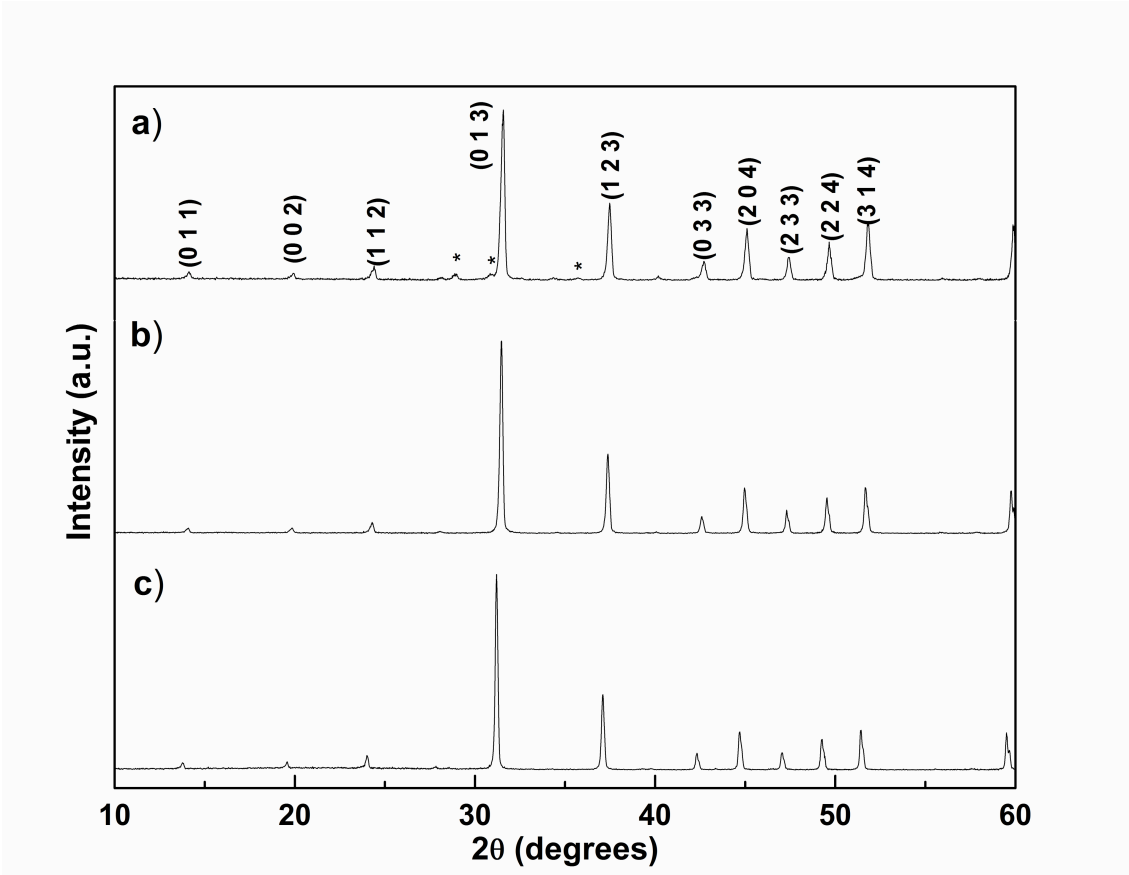
a)
b)
c)
(0 1 1)
(0 0 2)
(1 1 2)
(0 1 3)
(1 2 3)
(0 3 3)
(2 0 4)
(2 3 3)
(2 2 4)
(3 1 4)
*
Intensity (a.u.)
10
20
30
40
50
60
2θ (degrees)

Figure 3.

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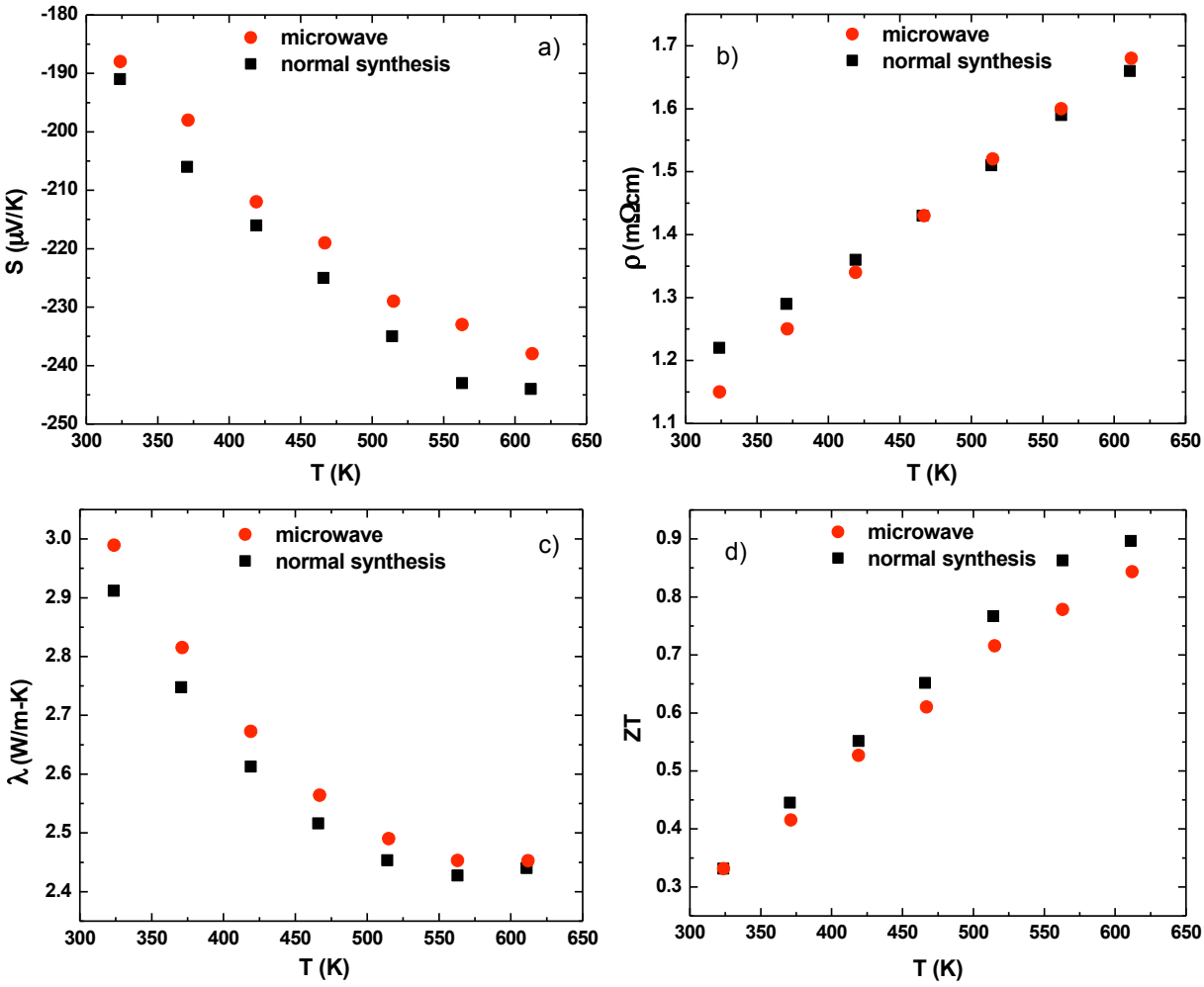
a)
microwave
normal synthesis
S (μV/K)
T (K)
b)
microwave
normal synthesis
ρ (mΩcm)
T (K)
c)
microwave
normal synthesis
λ (W/m-K)
T (K)
d)
microwave
normal synthesis
ZT
T (K)

Figure 4.