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Raman & Infrared Study of Bi Filled Co_4Sb_{12}

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Abstract. $CoSb_3$ skutterudites are established thermoelectric materials in the 500-800K temperature range. Undoped and Bi filled $CoSb_3$ samples were synthesized by induction melting-annealing process and phase confirmation done by X-Ray diffraction. The role of bismuth as a filler in $CoSb_3$ was investigated by Raman and far infrared reflectance study. It was found that bismuth strengthens Sb vibrations, and can potentially scatter Sb related acoustic phonons effectively. As a result substantial reduction in thermal conductivity may be possible with proper control of Bi filling.

Keywords: thermoelectric, induction melting, Raman, infrared, phonon
PACS: 72.20.Pa, 81.10.Fq, 78.30.Fs, 72.10 Di

INTRODUCTION

Thermoelectric materials convert thermal energy to electrical energy and vice-versa. The efficiency of this conversion depends on a dimensionless figure of merit $zT=(S^2\sigma/\kappa)T$, where S is Seebeck coefficient, σ is electrical conductivity and κ is the thermal conductivity. Good thermoelectric materials should have a high S & σ and low κ.$CoSb_3$ skutterudites are efficient thermoelectric generators having complex crystal structure, large unit cell and high carrier mobility. Large voids of radius 1.892Å are present inside the center of the Co_4Sb_{12} formula units. When these voids are filled by foreign atoms, filler atoms rattle inside the cage and scatter the heat carrying phonons. This large scattering of phonons decreases κ, thereby increasing the *z*T. The behavior of these vibration modes can be understood to some extent by Raman and Infrared spectroscopy. Here, polycrystalline $Bi_xCo_4Sb_{12}$ (x=0, 0.25, 0.5) has been synthesized and vibration modes studied by the above techniques.

EXPERIMENTAL PROCEDURE

High purity Co (99.995%), Sb (99.999%) and Bi (99.999%) were mixed in stoichiometric ratio and sealed in quartz ampoules under 10^{-4} torr vacuum. The samples were melted by induction heating at 1273 K for 15 min and then quenched in water, followed by annealing at 923 K for 144 hours. Phase identification was done by X-Ray Diffraction (Bruker D8 advance) on powdered samples. Optical measurements were done at room temperature on polished samples. Raman data was acquired using HORIBA Jobin Yvon LabRAM HR800 spectrometer with Argon 514.5 nm visible laser. Sampling was carried out by standard optical microscope using MPlan N 100X objective. Infrared measurements were carried out on Bruker IFS 66v/s Vacuum Fourier Transform Interferometer in the FIR range.

RESULTS & DISCUSSION

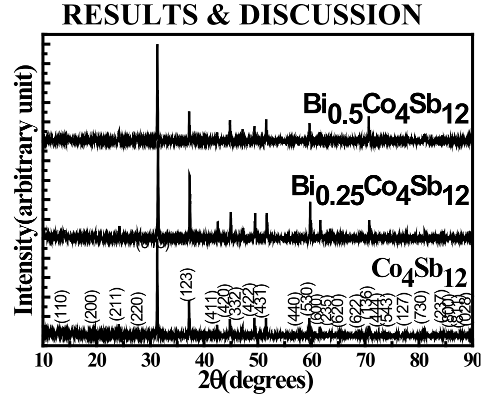

FIGURE1: XRD patterns of $Bi_xCo_4Sb_{12}$ (x=0, 0.25, 0.5)

$CoSb_3$ skutterudite phase is observed as the major phase in all samples. No secondary phases are observed in any of the samples. This indicates that Bi atom can easily be incorporated into $CoSb_3$ host lattice upto a filling limit of 0.5.

In $CoSb_3$ unit cell, out of four formula units, one formula unit is empty and other three consist of

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TABLE 1. Phonon frequencies of $CoSb_3$ (Raman& Infrared)

Raman Shift (cm^{-1}) $CoSb_3$	Theoretical (cm^{-1})[1]	Modes	FTIR (cm^{-1}) $CoSb_3$	Theoretical (cm^{-1})[3]	Modes
80.3	83.3	F_g	119	120	F_u
106.8	109.8	F_g	245	247	F_u
148.2	150.5	A_g	256	257	F_u
159.8	156.7	F_g	278	275	F_u
180.3	178.2	E_g			

four membered Sb rings in the centre. Hence, possible interactions are Co-Co, Sb-Sb or Co-Sb. The eight sensitive Raman modes for $CoSb_3$ skutterudite are $2A_g+2E_g+4F_g$[1].The experimental data and theoretically calculated Raman shifts for $CoSb_3$ are given in Table(1). In Bi filled samples all the Raman peaks shift up a little as shown in fig 2. For $Bi_{0.25}Co_4Sb_{12}$ and $Bi_{0.5}Co_4Sb_{12}$ the first F_g mode is observed at 83.13 cm^{-1} and 82.02 cm^{-1} which is slightly shifted towards the higher frequency than that of unfilled Co_4Sb_{12}.Similar result has been reported for rare earth filled skutterudites[2] where the filler atom has been shown to weaken some of the Sb vibrations as well as strengthen other Sb vibrations. The strengthening corresponds to up shift in Raman peaks while weakening to down shift. Up shift in Raman peaks in Bi filled Co_4Sb_{12} indicates that Bi filler may strengthen the Sb vibration modes.

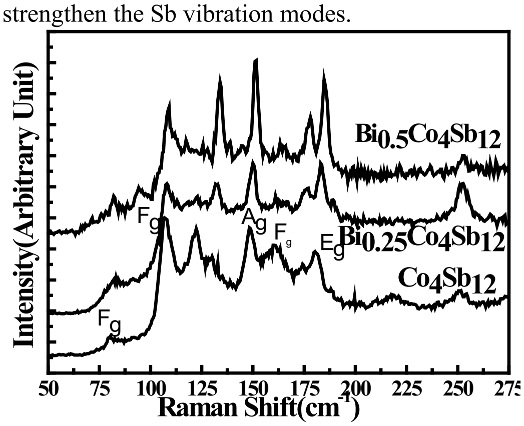

FIGURE 2. Raman spectra of $Bi_xCo_4Sb_{12}$ (x=0, 0.25, 0.5)

FTIR spectrum for all the samples is shown in figure (3).$CoSb_3$ showed poor reflectance as compared to the Bi filled samples. However, the peaks at 118.6, 245, 256 & 278 cm^{-1} were identified as belonging to the F_u zone centre vibrations of the $CoSb_3$ crystal. Comparison with available literature data is given in Table (1).In addition to these, samples $Bi_{0.25}Co_4Sb_{12}$ and $Bi_{0.5}Co_4Sb_{12}$ showed peaks at 137,186 and 415cm^{-1}.These could possibly be due to Bi since it is a heavy element and is thus expected to give low frequency phonon vibration modes. Large κ reduction by scattering of Sb related phonons (50-175cm^{-1}) has been predicted [3].Since Bi vibrations fall in the above range, Bi can scatter phonons effectively.

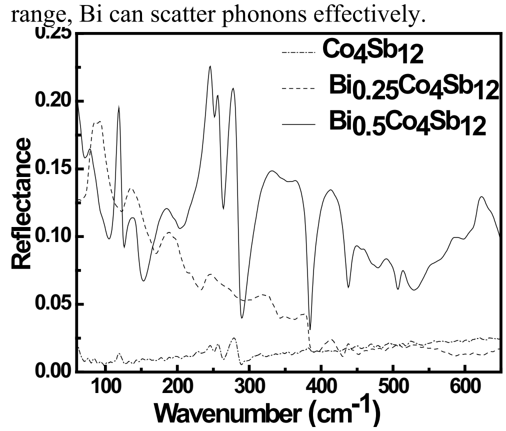

FIGURE 3 FTIR spectra of $Bi_xCo_4Sb_{12}$ (x=0, 0.25, 0.5)

CONCLUSIONS

Bi filled $CoSb_3$ skutterudites were prepared by induction heating process. Bi atom was found to be incorporated into the lattice for both the filling fractions of bismuth. Bi vibration modes were found to lie near Sb related phonon modes, thereby indicating it as effective scattering centre. The observed Raman shift confirmed that Bi vibration modes could strengthen the Sb vibrations. To investigate the role of Bi further as a filler atom, detailed theoretical study needs to be undertaken.

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