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## ADVERTISEMENT



## Thermally stable thermoelectric Zn<sub>4</sub>Sb<sub>3</sub> by zone-melting synthesis

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The thermal stability of thermoelectric  $Zn_4Sb_3$  has been investigated on samples produced by a new zone-melting technique, as well as by the conventional quench method. The multitemperature synchrotron powder diffraction data reveal that while conventionally synthesized,  $Zn_4Sb_3$  samples have almost 40% degradation in the first heating cycle at 625 K, samples prepared by zone melting only have 3% degradation. Repeated thermal cycling induces additional degradation of the quenched sample of up to 58%, compared to ~9% degradation in the zone-melted sample. Thus, zone-melting produces  $Zn_4Sb_3$  samples that are significantly more thermally stable, which make them promising for commercial implementation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2916705]

The  $\beta$  phase of the *p*-type semiconductor Zn<sub>4</sub>Sb<sub>3</sub> has excellent thermoelectric properties in the intermediate temperature range (473–673 K).<sup>1</sup> The thermoelectric figure of merit is defined as  $ZT = S^2 T / \rho \kappa$ , where S is the thermopower,  $\rho$  is the electrical resistivity,  $\kappa$  is the thermal conductivity, and T is the absolute temperature. The outstanding thermoelectric performance<sup>1,2</sup> originates from the complex crystal structure including three highly disordered interstitial Zn sites, which effectively lower the thermal conductivity while preserving the electrical conductivity.<sup>3,4</sup> Although Zn<sub>4</sub>Sb<sub>3</sub> is now known to exist in at least four crystalline phases, only the  $\beta$  phase, stable from 263 to 765 K, is a high performing thermoelectric material.<sup>1,2,5</sup> When the temperature is lowered from ambient, the crystal structure goes through two phase transitions,  $\beta \rightarrow \alpha$  and  $\alpha \rightarrow \alpha'$ , before eventually reaching an ordered triclinic  $\alpha'$ -phase at ~230 K.<sup>6</sup> In the  $\alpha'$  phase, the Zn interstitials become part of the crystalline network.<sup>7</sup>

In order to become commercially applicable, it is essential for a thermoelectric material to be stable at the operating temperature as well as during thermal cycling. Zn<sub>4</sub>Sb<sub>3</sub> was originally reported to be stable under argon up to 673 K, and up to 523 K in dynamic vacuum.<sup>1,2</sup> When held at temperatures higher than 523 K, the compound partly decomposed but the degree of decomposition was not quantitatively determined.<sup>1,2</sup> The originally reported thermal stability has been questioned by several authors who found that Zn<sub>4</sub>Sb<sub>3</sub> decomposes at temperatures below the expected stability range, forming ZnSb and elemental Zn as decomposition products.<sup>6,10</sup> These decomposition products cause a significant degradation of the thermoelectric properties and the main challenge therefore was to stabilize  $Zn_4Sb_3$  at T  $>200 \,^{\circ}\text{C.}^{6,10}$  Doping of Zn<sub>4</sub>Sb<sub>3</sub> has been suggested as a possible way to improve the stability<sup>11</sup> but although it was shown that doping can change the decomposition pattern relative to pure undoped samples, no immediate improvement of thermal stability was achieved.<sup>12</sup>

Here, we investigate the thermal stability of two completely phase-pure undoped  $Zn_4Sb_3$  samples; one prepared by the powder synthesis quench method<sup>2</sup> and one prepared

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by a new zone-melting technique.<sup>13</sup> A large batch of  $Zn_4Sb_3$ was prepared from stoichiometric ratios of 99.99% Zn shots and 99.5% antimony powder in a quartz ampoule. The vacuum sealed ampoule was horizontally placed in a furnace and heated with a 400 K/h ramp to 973 K under continuous rotation for 2 h before quenching in ice water. This resulted in a polycrystalline, rod shaped sample. Part of the quench synthesized product was used as a feeding rod in the subsequent zone-melting process. The feeding rod was placed on top of a nonstoichiometric rod (Zn<sub>52</sub>Sb<sub>48</sub>) in a quartz ampoule. Below the nonstoichiometric rod, a small piece of feeding rod was placed as support. The zone melting was performed in an induction furnace in a 100 psi He atmosphere, choosing the interface between the lower feeding rod, and the nonstoichiometric rod as the starting point. After establishing a stable melt zone, the ampoule was moved through the heating zone under continuous rotation  $(\sim 8 \text{ rpm})$  with a speed of approximately 1 mm/h.

Multitemperature, high-resolution powder diffraction data were recorded using the large Debye-Scherrer camera at beam line BL02B2, SPring8, Japan.<sup>14</sup> To ensure a homogeneous grain size, an ethyl alcohol floating technique was applied before transferring the sample to a 0.2 mm capillary. The data were measured at  $\lambda = 0.42236(1)$  Å with the wavelength determined from refinement on a CeO<sub>2</sub> standard, and the exposure time was set to 5 min. Data sets were recorded at 300, 400, 500, 505, 510, 515, 520, 525, 530, 535, 540, 575, and 625 K. After the first heating, the sample was cycled between 300 and 625 K three times to investigate the long term stability. All the data were Rietveld refined using the program FULLPROF.<sup>15</sup> Data above  $2\theta = 40^{\circ}$  were found to be very weak for all samples and they were omitted in the refinements. A pseudo-Voigt function with seven parameters (three Gaussian, two Lorentzian, and two asymmetry) was found to give a good description of the peak shapes; the background was fitted using linear interpolation between approximately 60 points. Selected crystallographic details are listed in Table I for data sets recorded at 300 K before and after heating. Full details of the multitemperature refinements are given in the supporting information (Tables S1-S4) for both zone-melted and quenched sample.

Iversen *et al.* have shown that the zone-melting technique leads to samples with  $ZT \sim 1.3$  at 673 K, which is

TABLE I. Crystallographic details and refinement residuals for the zone melted (ZM) and the quenched (Q) samples. Start refers to refinement of the dataset recorded before heating and after refers to refinement of the dataset recorded at 300 K after three heating cycles.

	ZM start	Q start	ZM after	Q after
T (K)	300	300	300	300
$T_{\text{expt}}$ (min)	5	5	5	5
No. of data points	7513	7507	7506	7507
No. of reflections	4682	4863	4613	4682
No. of parameters	88	90	99	116
$R_F(\%)$	2.05	1.34	3.19	2.83
$R_{\rm Bragg}$ (%)	2.12	1.84	4.09	2.71
$R_p$ (%)	2.72	2.39	4.82	4.06
$R_{wp}^{'}(\%)$	3.72	3.15	6.59	6.16
$\chi^2$	4.11	2.91	14.10	12.50
a=b (Å)	12.2182(1)	12.2257(1)	12.2338(1)	12.2383(2)
<i>c</i> (Å)	12.4106(1)	12.4162(1)	12.4271(1)	12.4256(2)
X	0.220(4)	0.241(4)	0.053(3)	0.218(4)
Y	0.019(4)	0.023(4)	0.010(4)	0.0001(0)
Biso Sb1	1.11(2)	1.26(2)	1.13(3)	1.01(5)
Biso Sb2	1.27(3)	1.25(3)	1.13(3)	0.94(6)
Biso Zn	2.19(5)	2.11(5)	2.26(6)	2.11(11)
Occupancy Sb1	1	1	1	1
Occupancy Sb2	1	1	1	1
Occupancy Zn1	0.921(5)	0.905(3)	0.954(4)	0.944(7)
Occupancy Zn2	0.063(2)	0.052(1)	0.059(3)	0.065(4)
Occupancy Zn3	0.055(4)	0.047(2)	0.022(2)	0.034(5)
Occupancy Zn4	0.052(1)	0.032(1)	0.045(2)	0.045(4)
Volume (Å <sup>3</sup> )	1604.5(3)	1607.2(3)	1610.7(1)	1611.7(4)
wt % ZnSb	0	0	4.8(2)	4.0(2)
wt % ZnO	0	0	2.5(4)	21.1(4)
wt % Sb	0	0	1.57(8)	32.3(2)

comparable to the highest values reported for samples prepared by the conventional quench method.<sup>13</sup> Figure 1 shows powder synchrotron x-ray diffraction patterns recorded at 300 K on the two samples. Refinement against the structural model of Snyder *et al.*<sup>3</sup> reveals that both samples are completely phase pure. Even with an intense third generation synchrotron source, which routinely allows the detection of crystalline phases down to a 0.3% level,<sup>16</sup> no impurity peaks are observed. The structural data for the two samples are comparable to each other and to the values given by Snyder *et al.*<sup>3</sup> The lattice constants are a=12.2257(1) and 12.2182(1) Å, and c=12.4162(1) and 12.4106(1) Å for quenched and zone-melted sample, respectively, compared to a=12.2282(3) Å and c=12.4067(4) Å reported by Snyder et al.<sup>3</sup> from single crystal data. When comparing the structural parameters, it is seen that the zonemelted sample has a significantly higher Zn content than the quench sample (see supporting material) but further analysis is needed to fully understand the atomic scale differences between the samples.

Figure 1 shows the synchrotron powder patterns at 300 K after three heating cycles up to 625 K (i.e., the thermal history is  $300 \rightarrow 625 \rightarrow 300 \rightarrow 625 \rightarrow 300 \rightarrow 625 \rightarrow 300 \text{ K}$ ). The difference in the thermal behavior of the two samples is striking. The sample synthesized by the conventional quench method has a large number of additional high-intensity peaks generated from decomposition phases, identified by Rietveld refinement as ZnSb, ZnO, and elemental Sb (details are given in Table I). In contrast, the zone-melted



FIG. 1. Powder patterns of  $Zn_4Sb_3$  prepared by zone melting (a) and by quench synthesis (b) recorded at 300 K before heating and after three heating cycles. The vertical lines correspond to the position of Bragg peaks of (from the top)  $Zn_4Sb_3$ , ZnSb, ZnO, and Sb.

sample only exhibits small additional impurity peaks and it is clear that the thermal degradation is much more limited for this sample. Figure 2(a) plots the weight fraction of  $Zn_4Sb_3$ , determined by Rietveld refinement, in the first heating cycle (300-625 K) of the two samples. It is quite surprising to observe that the quenched sample starts to decompose even below 500 K. At 500 K, the sample has already lost  $\sim$ 4 wt. % of the initial Zn<sub>4</sub>Sb<sub>3</sub> phase, and decomposition phases ZnSb, ZnO, and Sb are observed. Further heating accelerates the degradation of Zn<sub>4</sub>Sb<sub>3</sub> and at 625 K, only  ${\sim}60$  wt. % of the original  $Zn_4Sb_3$  phase is left. Simultaneously, the amount of elemental Sb linearly increases and reaches almost 20 wt. % at 625 K [Fig. 2(b)]. A large quantity of ZnO forms between 575 and 625 K, where it increases from  $\sim 1$  wt. % at 575 K to  $\sim 10$  wt. % at 625 K, which corroborates the idea of Zn disappearing from the structure and transforming into ZnO during heating in air.<sup>12</sup> Recent tracer diffusion studies have shown that Zn is highly mobile with properties approaching ionic conductors such as AgI.<sup>17</sup> The extreme mobility of Zn in Zn<sub>4</sub>Sb<sub>3</sub> may also be the origin of the extreme sensitivity of the thermoelectric properties to the sample compaction method.<sup>18</sup>

The zone-melted sample displays a very different behavior with essentially no weight loss up to 520 K [Fig. 2(a)]. Between 520 and 525 K, there is a small weight loss of ~3 wt. % Zn<sub>4</sub>Sb<sub>3</sub>, simultaneous with the formation of ZnO and elemental Sb. This is consistent with Zn leaving the sample and forming ZnO in an atmosphere of air. Thus, Zn<sub>4</sub>Sb<sub>3</sub> appears to have a subtle phase transition at ~523 K. In contrast to the quenched sample, further heating to 625 K does not induce additional decomposition of the zone-melted sample and at 625 K, there is still ~97 wt. % of the original phase left. Thus, for the zone-melted sample slight decomposition is an isolated event at ~523 K.

Figure 2(c) shows the weight fraction of the remaining  $Zn_4Sb_3$  phase determined at 300 K after each of the three



FIG. 2. (Color online) (a) Weight fraction of Zn<sub>4</sub>Sb<sub>3</sub> as a function of temperature in the first heating cycle. (b) Weight fraction of impurity phases ZnSb, ZnO, and Sb as a function of temperature in the first heating cycle. (c) Weight fraction of Zn<sub>4</sub>Sb<sub>3</sub> as a function of heating cycles. (d) Weight fraction of impurity phases ZnSb, ZnO, and Sb as a function of heating cycles. Zn<sub>4</sub>Sb<sub>3</sub> prepared by quench synthesis has open circles and the zone melting sample has open squares. Blue, black, and red squares correspond to ZnSb, ZnO, and Sb in the zone-melted sample, and blue, black, and red circles correspond to ZnSb. ZnO, and Sb in the quenched sample, respectively.

heating cycles. Clearly, the sample produced by quench synthesis has a serious stability problem. After the first heating cycle, only  $\sim 60$  wt. % remains and repeated heating causes further degradation leaving only  $\sim$ 42 wt. % of the original Zn<sub>4</sub>Sb<sub>3</sub> phase after three cycles. The zone-melted sample is much more stable than the quenched sample, also during thermal cycling [Fig. 2(d)]. Although each heating/cooling cycle induces a small decomposition of about 3% at 523 K, more than 91 wt. % of the target phase is still remaining after three cycles. Iversen et al. observed that zone-melted samples reach constant thermoelectric properties after repeated thermal cycling.<sup>13</sup> This suggests that if cycling was continued, the zone-melted phase would have reached a stable plateau of degradation. The limited degradation of the zone-melted sample is an enormous improvement in stability compared to samples prepared by the quench method. The present experiments were performed on powders and it is conceivable that compacted samples would be more stable during thermal cycling. However, it is unlikely that this would improve stability properties of the quenched sample enough to meet commercial requirements.

In summary, the thermal stability of two Zn<sub>4</sub>Sb<sub>3</sub> samples, prepared by different synthesis methods, was investigated by multitemperature synchrotron powder diffraction. ZnSb, ZnO, and elemental Sb have been identified as decomposition products, and the degree of decomposition was quantified by Rietveld refinement. The stability of Zn<sub>4</sub>Sb<sub>3</sub> is enormously improved by the zone-melting synthesis technique. Thermal cycling leaves only  $\sim$ 42 wt. % of the original phase in case of the quenched sample compared with  $\sim$ 91 wt. % in the zone-melted sample. The high temperature decomposition of Zn<sub>4</sub>Sb<sub>3</sub> is found to be extremely complex and challenging studies remain to understand its detailed behavior. We conclude that Zn<sub>4</sub>Sb<sub>3</sub> prepared by zone melting is significantly more stable than Zn<sub>4</sub>Sb<sub>3</sub> synthesized by the conventional quench method and indeed, zone-melted Zn<sub>4</sub>Sb<sub>3</sub> appears to be a promising candidate for commercial implementation in thermoelectric generators operating at intermediate temperatures.

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