Experimental report

06/11/2017

Proposal: **5-24-579**

Council: 4/2016

Title: Crystal structure of novel thermoelectric materials based on SnSe

Research area: Materials

This proposal is a continuation of 5-23-679

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Samples: $Sn_{0.8}In_{0.2}Se$
$Sn_{0.8}Pb_{0.2}Se$
$SnSe_{0.8}Te_{0.2}$

Instrument	Requested days	Allocated days	From	To
D2B	3	3	02/12/2016	05/12/2016

Abstract:

Based upon recent results on SnSe, for which appealing thermoelectric properties have been described, we have developed several novel series of doped SnSe, namely $Sn_{1-x}M_xSe$ (M= Pb, Sb, Ge) and $SnSe_{1-x}B_x$ (B= Te). Preliminary thermoelectric properties measurements are extremely attractive: for instance, we found for $Sn_{0.8}Sb_{0.2}Se$ a negative Seebeck coefficient, in contrast with the ptype
parent SnSe compound. All the members of the novel series belong to the same structural type (defined
in the Pnma space group). We aim to analyze the effect on the crystal structure of the diverse chemical dopings, in connection with their thermoelectric properties and to investigate their evolution across the phase transitions at about 820 K from the low-temperature structure (GeSe-type) to the high-temperature Cmcm structure, for which the highest ZT values have been measured. In the precedent experiment we studied Sb and Ge doping; in this continuation we aim to study Pb and In doping. Unreported change of sign of Seebeck is observed for Pb-doped samples, related to the structural phase transition.

Thermoelectric materials can convert temperature gradients, prominently those generated by waste heat with thermoelectric generators, into useful electrical power, as they present the advantage of converting temperature differences into electrical potential difference[1,2]. Recently, a new material has drawn the attention of the thermoelectric scientific community, since the description of a record-high ZT value of 2.6 at 923 K was described in single crystalline SnSe p-type semiconductor[3], associated with a phase transition from GeSe-type (space group *Pnma*) to Thalium-Iodide-type (s.g. *Cmcm*) The reported properties for single crystal materials have not been reproduced in polycrystalline specimens[4], where ZT values reach 0.5 at 820 K.

Encouraged by these reports we have prepared through a simple and straightforward preparation procedure highly textured SnSe samples with a record Seebeck coefficient and an extremely low thermal conductivity.[5] A test NPD study was essential to investigate the structural details of SnSe and other derivatives as $Sn_{1-x}R_xSe$ (R= Ge, Sb), this bulk study being by far much less sensitive to the preferred orientation effects.

In order to improve thermoelectric figure of merit, we have been working on several novel series of doped SnSe, namely $Sn_{1-x}R_xSe$ (R= Sb, Pb, In), prepared by arc-melting. In this experiment we have measured the in-situ structural evolution of the $Sn_{0.8}Sb_{0.2}Se$, $Sn_{0.8}Pb_{0.2}Se$ and $Sn_{0.9}In_{0.1}Se$, systems in the thermal range of maximum thermoelectric efficiency. Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. The high intensity mode ($\Delta d/d \approx 5 \cdot 10^{-4}$) was selected, with a neutron wavelength λ= 1.594 Å within the angular 2θ range from 8° to 156°. About 2 g of the sample was contained in a cylindrical vanadium holder (dia. 8 mm), and the counting time was 2 h. The measurements were carried out in air at 298, 473, 693 and 853 K.

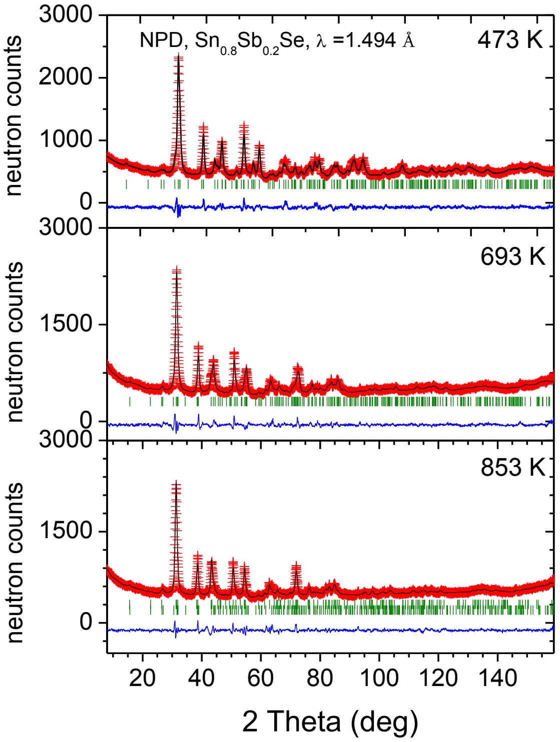


Fig. 1 illustrates the patterns of $Sn_{0.8}Sb_{0.2}Se$ at 473, 693 and 853 K. The crystal structure can be Rietveld-refined in the orthorhombic *Pnma* space group till 693 K. At higher temperature an orthorhombic (*Pnma*) to orthorhombic (*Cmcm*) phase transition takes place. The phase transition temperature is expected at 800 K for pristine SnSe, but for the Sb-doped sample a slight amount (20%) of *Pnma* phase is still detected at 853 K.

***Figure 1**. Rietveld refinement NPD profile for $Sn_{0.8}Sb_{0.2}Se$ at 473 K (top panel), 693 K (mid panel) and 853 K (bot panel). Observed (red crosses), calculated (black line), and difference (blue line).*

Fig. 2 shows the DSC analysis of pristine SnSe and $Sn_{0.8}Sb_{0.2}Se$, where a shift towards higher phase-transition temperature is observed. Fig. 3 displays unit-cell parameters of both orthorhombic phases and their thermal evolution, constituting the phase diagram of $Sn_{0.8}Sb_{0.2}Se$.

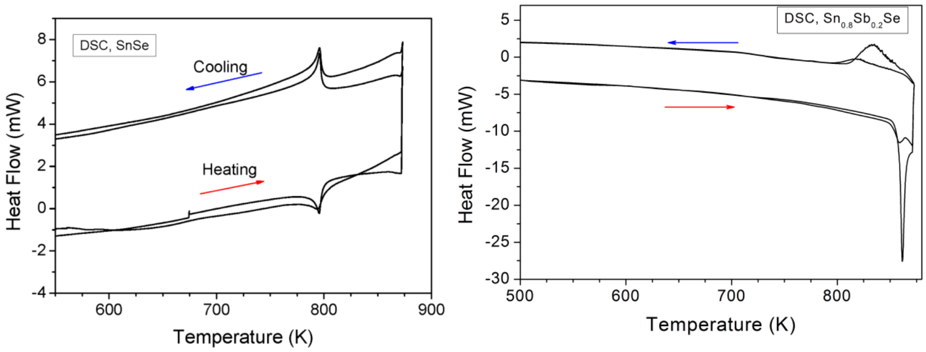
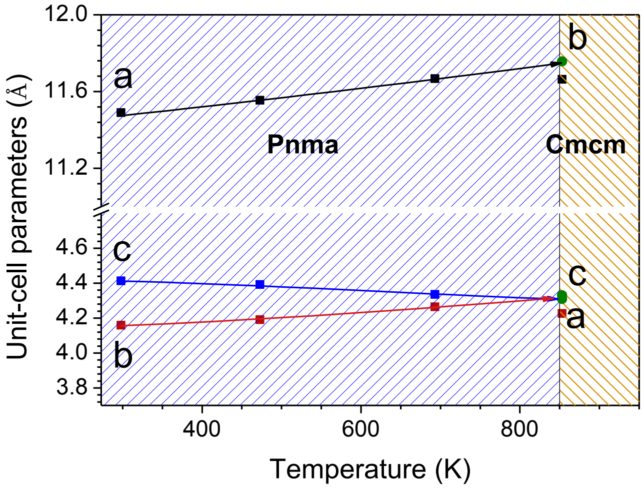


***Figure 2**. DSC curves for SnSe and $Sn_{0.8}Sb_{0.2}Se$, collected in two consecutive heating and cooling cycles.*

***Fig. 3** Thermal evolution of structural parameters. Green symbols represent structural parameters of the high-temperature Cmcm phase.*



Finally, Fig. 4 illustrates the NPD patterns of $Sn_{0.8}In_{0.2}Se$ at room temperature and $Sn_{0.8}Pb_{0.2}Se$ at 693 K. Both samples can be Rietveld-refined in the orthorhombic *Pnma* space group at room temperature; however, for the Pb sample, data at 693 K is already defined in the *Cmcm* orthorhombic space group, as the temperature phase transition in this SnSe derivative is lowered.

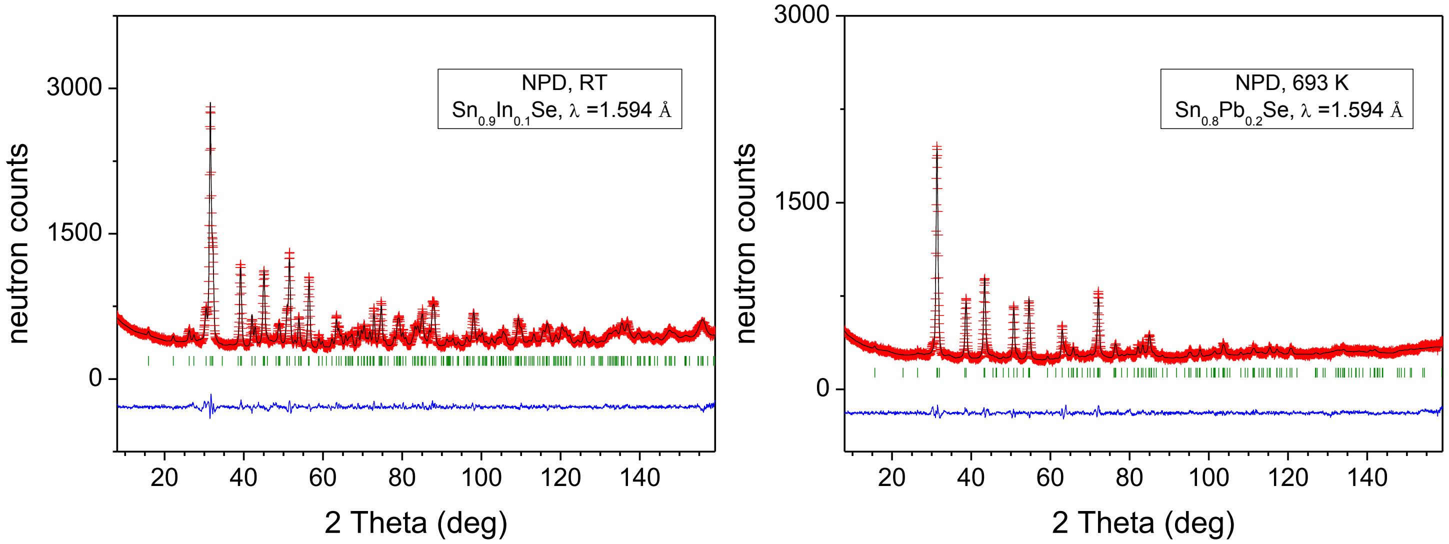


Figure 4. *Observed (crosses), calculated (full line) and difference (at the bottom) NPD profiles for* $Sn_{0.9}In_{0.1}Se$ *at room temperature and* $Sn_{0.8}Pb_{0.2}Se$ *at 693 K. The vertical markers correspond to the allowed Bragg reflections.*

References

1. M. Martín-González, O. Caballero-Calero, P. Díaz-Chao, Renewable and Sustainable Energy Reviews **24** 288–305 (2013).
2. G. J. Snyder, E. S. Toberer, *Nature Materials* **7**, 105 - 114 (2008)
3. L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* **508**, 373 (2014).
4. S. Sassi, C. Candolfi, J.-B. Vaney, V. Ohorodniichuk, P. Masschelein1, A. Dauscher, B. Lenoir, *Appl. Phys. Lett.* **104**, 212105 (2014)
5. F. Serrano-Sánchez, M. Gharsallah, N. M. Nemes, F. J. Mompean, J. L. Martínez, J. A. Alonso, *Appl. Phys. Lett.* **106**, 000000 (2015) DOI: 10.1063/1.4913260