Experimental report

04/02/2016

Proposal:	**5-23-679**	**Council:**	4/2015
Title:	Crystal structure of novel thermoelectric materials based on SnSe		
Research area:	Materials		

This proposal is a new proposal

Main proposer:	**Jose Antonio ALONSO**
Experimental team:	Jose Antonio ALONSO Federico SERRANO
Local contacts:	Maria Teresa FERNANDEZ DIAZ

Samples:	Sn1-xMxSe (M= Ge, Sb, Pb) SnSe1-xBx (B= Te)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	27/11/2015	30/11/2015

Abstract:

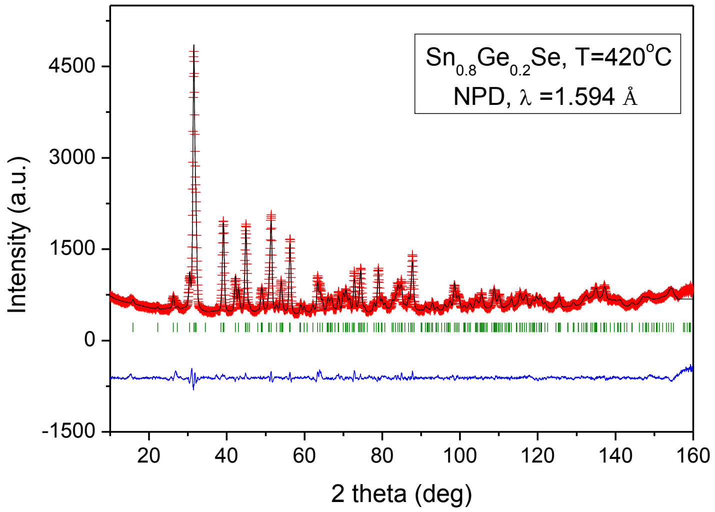
Based upon recent results on SnSe, for which appealing thermoelectric properties have been described, we have developed several novel series of doped SnSe, namely Sn1-xMxSe (M= Pb, Sb, Ge) and SnSe1-xBx (B= Te). Preliminary thermoelectric properties measurements are extremely attractive: for instance, we found for Sn0.8Sb0.2Se a negative Seebeck coefficient, in contrast with the p-type parent SnSe compound. The remaining materials present the same texture responsible for the extremely low thermal conductivities, thus anticipating high ZT values at elevated temperatures. 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.

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, 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, Ge), prepared by arc-melting. **In this experiment** we have measured the in-situ structural evolution of SnSe, $Sn_{0.8}Ge_{0.2}Se$ and $Sn_{0.8}Sb_{0.2}Se$ 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 25 °C, 200 °C, 420 °C and 580 °C.

Fig. 1 illustrates the patterns of $Sn_{0.8}Ge_{0.2}Se$ at 420 °C and 580 °C. The crystal structure can be Rietveld-refined in the orthorhombic *Pnma* space group till 420 °C. At this temperature an orthorhombic (*Pnma*) to orthorhombic (*Cmcm*) phase transition takes place. Fig. 2 shows the phase diagram displaying the thermal evolution of the unit-cell parameters of both orthorhombic phases. A dramatic rearrangement of atoms is observed along with the phase transitions, bearing a more ordered structure. Fig. 3 displays the crystal structures at room temperature, 200 °C, 420 °C and 580 °C. It is noteworthy the change in displacement ellipsoids directions with temperature, which presents its largest axis along the c direction in the *Pnma* space group, while at high temperature it is oriented along the b axis in the *Cmcm* space group. In Pnma the structure consists of trigonal pyramids $SnSn_3$ forming layers perpendicular to the [1 0 0] direction, with the thermal elipsoids oriented within the layers , whereas across the transition to Cmcm the coordination environment changes a tetragonal pyramid where the large Sn elipsoids in the basal square-plane adopt a configuration with the longest axis perpendicuar to the four closer chemical bonds, oriented along the b axis of the orthorhombic structure. Such a high thermal displacements indicate a strong rattling effect of Sn in a pentacoordinated cage, accounting for the observed decrease of the thermal conductivity and thermoelectric performance of this material.



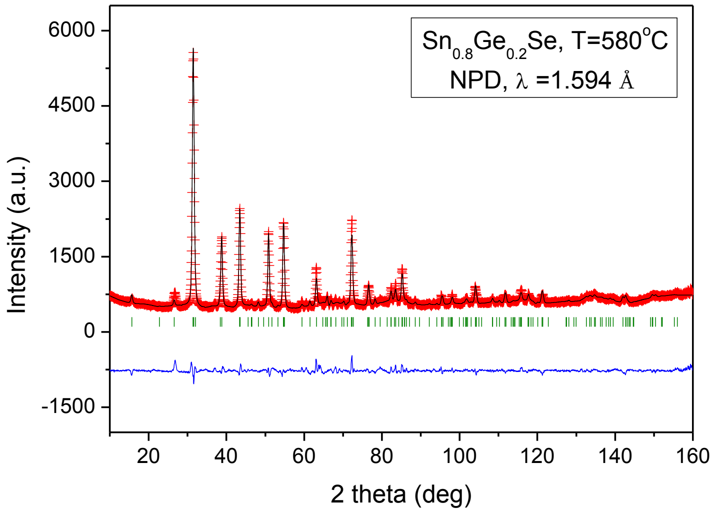


Fig. 1. *Observed (crosses), calculated (full line) and difference (at the bottom) NPD profiles for* $Sn_{0.8}Ge_{0.2}Se$ *at 420 °C and 580 °C, just below and above the phase transition. The vertical markers correspond to the allowed Bragg reflections.*

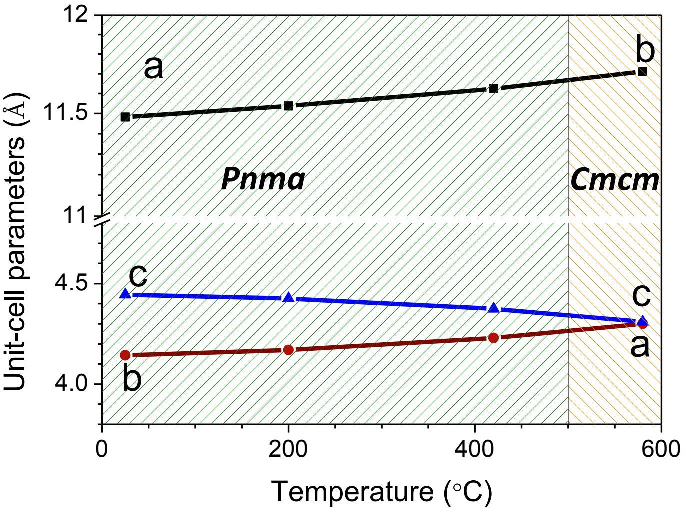


Fig. 2 *Phase diagram showing the thermal evolution of the unit-cell parameters.*

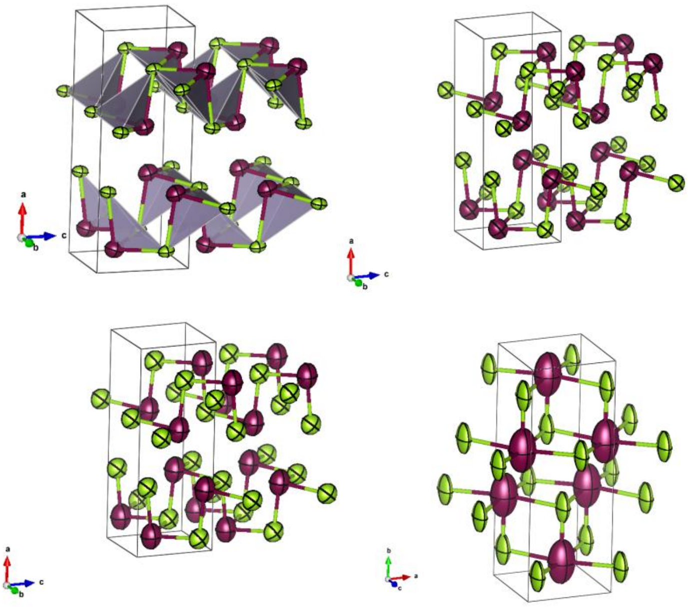


Fig. 3. *Crystal structures of the orthorhombic phases at at 25 °C, 200 °C, 420 °C and 580 °C.*

References

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