Studies of host and dopant ion distributions in Mg_2Si-based thermoelectric materials employing electron channeling

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Structure determination and refinement by application of electron microscopy-based spectroscopic techniques has been widely exploited since the 1960's. In this aspect, electron spectroscopy methods –such as energy dispersive X-ray spectroscopy (EDS), or Electron Energy Loss Spectroscopy (EELS)– are utilised, under strong channeling conditions, where the yield of element characteristic X-ray emission is modified, dependent upon the kind of atoms in the crystal lattice [1]. These channeling effects are powerful in determining atomic site locations in crystals and techniques such as ALCHEMI (Atom Location by CHanneling Enhanced Microanalysis) have been developed and widely applied since then.

Our group has particularly focused applications of electron channeling in materials for renewable technologies and energy harvesting, such as magnesium silicide (Mg_2Si) thermoelectrics (TE) and their alloys with Sn or Ge. Their advantages are their inexpensive production costs, abundancy, atoxic nature of raw materials and increased figure of merit *ZT* [2]. Synthesis of mixed nanocrystalline Mg_2Si, often doped with Bi ions has been exploited, with a scope to improve its TE properties. However, the exact location of alloy ions (Si, Sn, Ge) or dopants is still a controversial issue [3]; application, therefore, of electron channeling is highly desirable in order to accurately determine and refine the structural characteristics.

Bi-doped $Mg_2Si_{1-x}Sn_x$ (x=0, 0.4 and 0.6) materials were prepared by solid state reaction combined with ball milling and followed by hot press sintering. Electron channeling experiments were carried out in a JEOL 2100 transmission electron microscope (TEM) with a LaB_6 electron source, operating at 200 kV. The TEM is fitted with an EDS detector (EDAX Apollo XLT TEM-SDD). The probe size during analysis was set at 40 nm and the beam semi-convergence angle was 1.5 mrad.

Mg_2Si compounds crystallize in the high symmetry CaF_2 structure (Fm$\underline{3}$m (#225) space group), where Si/Sn occupy the (0,0,0) octahedral positions (C sites) and Mg occupy the two sets of tetrahedral positions (¼,¼,¼) and (¼,¼,¾), i.e. T sites at the unit cell. The octahedral site (½,½,½) at the centre of the unit cell (N site) is, by default, empty. The projected structure along the [$\overline{1}$ 10] direction is depicted at Fig. 1. There, ions located in each of the three different sites (C, T and N) can be distinguished along the (111) planes. Therefore, the channeling experiments have been performed using the {111} rows of reflections, as shown in the convergent beam electron diffraction (CBED) pattern of Fig. 2. In the series of the planar channeling experiments performed, we collect the EDS spectra after small tilting increments of the sample along the {111} row of reflections, so the incident electron beam forms small angles with the {111}-types of planes.

The variations of the normalized X-ray emission for each one of the elements in Bi-doped $Mg_2Si_{0.6}Sn_{0.4}$, as we tilt from $\overline{555}$ to 555 reflections, are depicted at Fig. 3. In general, the X-ray intensities profiles are symmetrical, in accordance with the $Mg_2Si_{0.6}Sn_{0.4}$structure.

Furthermore, we note that the Mg normalized counts are always distinct and complementary with the Si, Sn and Bi ones, which confirms that Mg ions predominately occupy the tetrahedral T sites, where the other three ions occupy octahedral ones (C and N). Variations in the X-ray intensities' profiles, as well as the specific site locations for the octahedral positions will be analyzed and discussed.

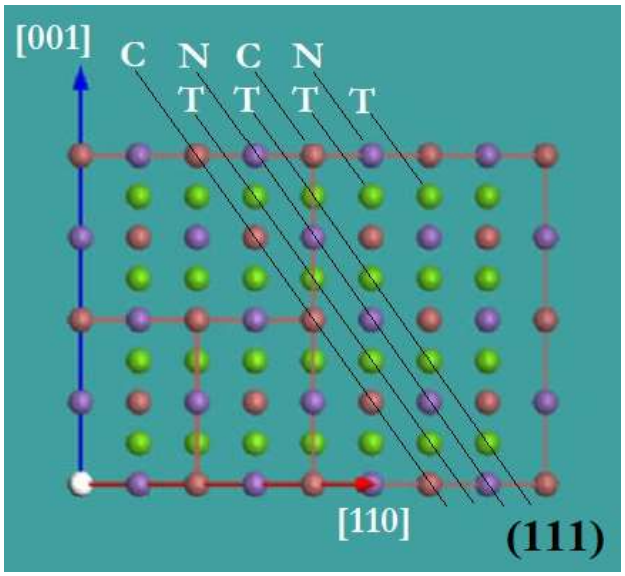

Fig. 1: *Structure of the Mg_2Si-based compounds along [$\bar{1}$10]. Green, red and purple spheres represent T (Mg), C (Si or Sn) and N sites, respectively.*

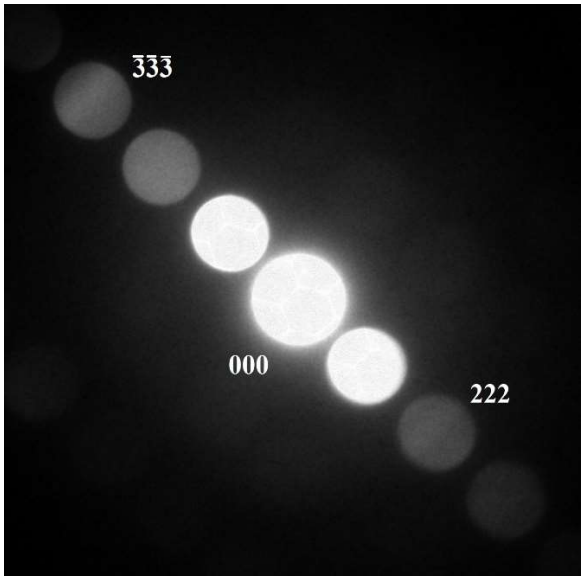

Fig. 2: *CBED pattern from a $Mg_2Si_{0.6}Sn_{0.4}$ particle, illustrating the diffraction conditions' set up for channeling.*

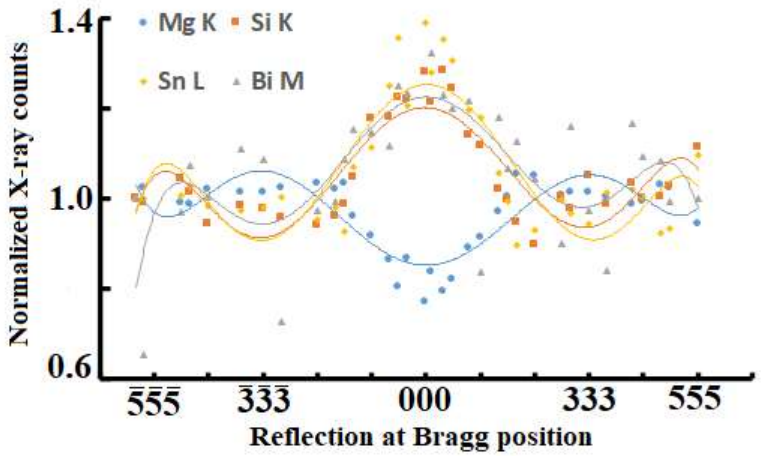

Fig. 3: *Normalized X-ray counts for all elements of the area analyzed at the $Mg_2Si_{0.6}Sn_{0.4}$ particle.*

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