Valence Charge Density of Multi-doped Mg₂Si Thermoelectric Materials from Maximum Entropy Method Analysis

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Abstract

The valence electron topologies of Mg₂Si thermoelectric materials multi-doped with Al, Zn and Sb have been determined by the Maximum Entropy Method (MEM) using synchrotron X-ray powder diffraction data. In spite of the very low concentrations, expansion was observed in the cubic unit cells of the doped samples. Using pure Mg₂Si as a reference, charge density difference maps revealed qualitative features on the distributions of the electrons contributed by the doped atoms. The presence of excess electrons shows all doped samples are *n*-type semiconductors and they are shared among the atomic sites. We evaluated the reliability of the MEM calculated charge density by considering the effect of successively increasing the number of high angle

Bragg reflections used in the analysis on the diffraction pattern of a single doped Al-Mg₂Si sample.

Keywords: Mg₂Si; MEM; Thermoelectric.

1. Introduction

Magnesium silicide (Mg₂Si) doped with heavy elements are potentially high performance and environmental friendly thermoelectric materials. [1-4] Compared to conventional lead-based thermoelectric materials, Mg₂Si-based alloys have merit as they are non-toxic, sustainable, light and low cost. A figure of merit for the efficiency of a thermoelectric material at temperature T is given by $ZT = S^2 T \sigma / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. Therefore, a good candidate material must possess high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Previously researches have shown that p - or n -type doping enhances the efficiency of thermoelectric materials. [5-10] The electron-rich dopants can increase the carrier concentration and mobility of the conduction electrons thus enhancing the electrical conductivity. In addition, doping with heavy atoms affects lattice vibrations and helps to lower the thermal conductivity by increasing phonon-phonon scatterings. Recently, Zhao *et al.* found the thermoelectric and electrical transport properties of Mg₂Si thermoelectric materials were enhanced significantly after doping with Al, Zn and Sb. Within this class of compounds, the best ZT of 0.964 at 880 K has been achieved, a value comparable to those of PbTe-based thermoelectric materials. [11] Here, we wish to study the effect of dopants on the valence charge density using powder diffraction patterns. This investigation is relevant as the exact locations of the dopants in Mg₂Si are still ambiguous. In the case of single doping by Al or Sb, it is generally believed that since the doped

samples are *n*-type semiconductors the dopants Al should replace the Mg sites thus increasing the electron concentration. [12,13] However, there is no concrete experimental evidence to substantiate this assignment. A recent electronic structure calculation has shown that the site preference of Al at lower concentration in Mg₂Si is ambiguous. [14] This theoretical study was also not able to determine conclusively the site preference of Sb at the doping level of 1% and 3%. Finally, no experimental data is available for the Zn-doping although it is expected Zn atoms should substitute the Mg sites.

The Maximum Entropy Method (MEM) is a powerful tool for determining the most probable valence electron density distributions from X-ray diffraction measurements using a limited number of low angle Bragg reflections and without the prior knowledge of the atomic positions. [15-17] The MEM has been successfully applied to evaluate the electron density and bonding of a variety of materials including semiconductors, metals, and ionic systems. [18] For example, the MEM was used to reconstruct the charge density distribution in the perovskite structure of the manganite La_{0.67}Sr_{0.22}Mn_{1.11-x}Co_xO₃ to evaluate the effect of Co³⁺ doping in the Mn-O matrix. [19] Francis *et al.* reported the effect of Co doping on the electronic, structural, magnetic, and optical properties of ZnO bulk samples. [20] The electron density distribution of NaCoO₂ has been studied by using single-crystal X-ray diffraction data obtained at 298 K and the results show strong covalent bonding between Co and O atoms but no bonding around the Na atom. [21] Previously, a similar technique was applied to the study of thermoelectric materials. Saravanan *et al.* used the MEM and pair distribution functions to extract the electron density distribution and local structure of PbTe, pure Mg₂Si and other crystalline systems. [22-24] The electron density of the high performance thermoelectric material Zn₄Sb₃ has also been determined from synchrotron powder diffraction data. [25] In CoSb₃, Ohno *et al.* revealed three types of charge

density overlap in the phase, including a ring structure formed by four Sb atoms. [26] Recently, Kastbjerget *al.* found strong anharmonicity and large cation disorder are present in both PbTe and PbS thermoelectric materials. [27] Compared to the traditional Fourier analysis, the MEM avoids the series-termination errors on the extraction of electron density in the crystal. Therefore, with a limited diffraction data set, it may be possible to extract the valence electron density distribution of the host atoms as well as the dopant atoms in thermoelectric materials.

The objective of this paper is to characterize and better understand the effect of the electron density distribution of the dopants in Mg₂Si crystals. For this purpose, we studied Mg₂Si samples multi-doped with Al, Zn and Sb. The X-ray powder diffraction experiments were performed at the Canadian Macromolecular Crystallography Facility (CMCF) bending magnet beamline (08B1-1) and Hard X-ray MicroAnalysis (HXMA) beamline (06ID-1) of the Canadian Light Source under ambient pressure and temperature. The electron density distributions in the crystal were extracted from the analysis of X-ray diffraction patterns using the Maximum Entropy Method implemented within the *Dynomiac* code. [28]

The layout of this paper is as follows: First, details on the experimental procedure are described. The diffraction patterns of the Mg₂Si samples multi-doped with Al, Zn and Sb are compared with pure Mg₂Si. This is followed by a discussion on the trend of electron density distributions in the crystal. The paper concludes with an investigation on the dependence of the evaluated charge density with respect to the number of Bragg reflections as illustrated from the analysis of a high angle diffraction pattern of Al-doped Mg₂Si.

2. Experimental details

2.1 Synthesis and Sintering Process for Preparation of Doped Mg₂Si Samples

Polycrystalline Mg_2Si was synthesized from stoichiometric melts with $\text{Mg}:\text{Si} = 2:1$ using an electric furnace by lowering the temperature from slightly above the melting point (1378 K) of Mg_2Si . The starting materials, Mg and Si, were placed in an alumina crucible under argon-hydrogen forming gas (0.08 MPa). Three dopant impurities, antimony (Sb), aluminium (Al) and zinc (Zn), were incorporated in order to increase the electronic carrier concentrations and to promote phonon scattering. The dopants were incorporated during the synthesis process at 1378 K. The resultant polycrystalline Mg_2Si , pulverized into powder with a granule size ranging from 25 to 75 μm , was then placed into a graphite die and sintered by a plasma-activated sintering (PAS) technique using an ELENIX Ed-PAS-III-Es. The sintering was performed at 1123 K for 10 min. at a pressure of 40 MPa in an Ar atmosphere. Depending on the dopant, the sintering temperature and time were varied in order to obtain a dense material. The compositions of the samples were analysed by electron-probe microanalysis (EPMA) using a JEOL JXA-8900 instrument. The concentrations of the dopant impurities in the samples were estimated by glow discharge mass spectrometry (GDMS) using a V.G. Scientific VG-9000 spectrometer. Previous studies have demonstrated that Sb and Al doped Mg_2Si are *n*-type semiconductors and therefore the dopants should predominantly substitute in the Si and Mg, respectively. On the other hand, Zn is expected to show no significant contribution to carrier generation but influence over the phonon scattering behaviour, leading to a reduction in the thermal conductivity.

2.2 X-ray Powder Diffraction Measurements

The reference pure powder Mg_2Si with a purity of 99.5%, was purchased from Alfa Products. Powder diffraction patterns of three Mg_2Si -doped samples were measured by synchrotron X-ray at the 08B1-1 beamline of the Canadian Light Source[29], with an X-ray wavelength of $\lambda=0.68880 \text{ \AA}$. The nominal concentrations of the three dopants in the samples studied were 0~0.5

at. % of Sb, 0.5 ~ 1.0 at. % of Al, and 0.5~1.0 at. % of Zn. The nominal formulas of the compounds studied were $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ and $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$. In addition, in order to obtain diffraction data at higher scattering angles, the measurement of 1% Al-doped Mg_2Si ($\text{Mg}_{1.99}\text{Al}_{0.01}\text{Si}$) sample was performed at the HXMA beamline [30] using a shorter synchrotron X-ray wavelength of $\lambda=0.50917 \text{ \AA}$. All diffraction patterns were analyzed with the JANA 2006 software package with the lattice parameters determined by Le Bail fit. [31,32] The structure factors used in the maximum entropy analysis were extracted from Le Bail fit of the Bragg's intensities of the diffraction patterns.

2.3 Maximum Entropy Method (MEM)

The Maximum Entropy Method, based on the information theory,[15] can be used to determine the electron density distribution from the analysis of the structure factors obtained from a powder diffraction pattern. In this work, the charge density distributions were analysed using the Dysnomia software package. [28] In the MEM analysis, the unit cell was partitioned into $128 \times 128 \times 128$ pixels. The initial charge density used a uniform distribution. The total scattering factor ($F(000)$) was scaled to the nominal concentration of the dopants. Thus, the $F(000)/a^3$ are $152 \text{ e/\AA}^3$ for pure Mg_2Si , $153.1 \text{ e/\AA}^3$ for $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, $153.46 \text{ e/\AA}^3$ for $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$, $153.12 \text{ e/\AA}^3$ for $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, and $152.04 \text{ e/\AA}^3$ for $\text{Mg}_{1.99}\text{Al}_{0.01}\text{Si}$. The three-dimensional (3D) and two-dimensional (2D) visualization charge densities were plotted using the VESTA program. [33-36]

2.4 Electronic Structure Calculations

First principles electronic calculations were performed using density functional theory (DFT) within the Perdew-Burke Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP) code. [37-40] For all calculations, the projector-augmented wave (PAW) [41,42] potentials were used with the following valence configurations: $3s^23p^1$ for Al, $3d^{10}4s^2$ for Zn, $5s^25p^3$ for Sb, $3s^23p^0$ for Mg and $3s^23p^2$ for Si.

For Al, Zn, and Sb substitutions, two models with different substitution sites were considered. Two models with 0.6 at % of each dopant (Al, Zn, and Sb) doped Mg_2Si were constructed from a $3 \times 3 \times 3$ supercell of the pure crystal. In the first, Zn atoms were put on the Mg sites with Si sites substituted by Al and Sb (*i.e.* $(Mg_{214}Zn_2)(Si_{104}Al_2Sb_2)$). In the second model, some Mg atoms were replaced by Al and Zn with Si sites substituted by Sb (*i.e.* $(Mg_{212}Zn_2Al_2)(Si_{106}Sb_2)$). A $2 \times 2 \times 2$ k -point mesh was used for the calculation of the projected density of states (pdos) on the supercells.

3. Results and Discussion

High-resolution synchrotron angle dispersive X-ray diffraction patterns of pure Mg_2Si and doped Mg_2Si samples were measured under ambient conditions (Fig. 1(a) and (b)). The lattice parameters were determined from full profile Le Bail to the diffraction patterns using angular data with range from 5° to 40° . The X-ray diffraction patterns of pure Mg_2Si can be indexed readily to the cubic anti-fluorite (CaF_2) structure with space group $Fm-3m$. In increasing diffraction angle, the Miller indices (hkl) of the Bragg peaks were assigned to (111), (200), (220), (311), (222), (400), (331), (420), (422), (511), (440), (531) and (600) reflections. The diffraction patterns of all the multi-doped Mg_2Si samples share the same profile as pure Mg_2Si except the

positions of the Bragg peaks shifted noticeably to lower angles. (See Fig. 1(a)) This observation indicates that even with small dopant concentrations (0.5%~1.0%) the cubic lattice of Mg_2Si was expanded. This is clearly seen in the expanded region 9° - 12° of the (111) peak. (See Fig. 1 (b)) The cubic cell parameter of pure Mg_2Si $a = 6.2843(9) \text{ \AA}$ is increased to between $6.3571(9) \text{ \AA}$ and $6.3634(9) \text{ \AA}$ by the substitutions of the dopants Zn, Al, and Sb, respectively. This trend can be rationalized from the fact that the atomic size of Zn is larger than Mg, and Sb is larger than Si. A more detailed examination of the lattice constants of the doped Mg_2Si samples shows, for instance, compared with $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, the lattice constant of $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ is larger, possibly due to the higher doping concentration of Zn. In comparison, the lattice parameter of $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ is similar to $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, suggesting that Al has little effect on the size of the crystal lattice, probably due to the similar atomic sizes of Al and Mg atoms.

Fig. 1(a) Angle dispersive X-ray diffraction patterns of pure Mg_2Si and doped Mg_2Si measured at ambient conditions; (b) The expanded diffraction patterns between 9° to 12° of the (111) peak.

The intensities of the Bragg reflections of pure and doped Mg_2Si were determined from Le Bail fit to the diffraction profiles. The background was represented by a 15 terms Legendre polynomial function. The lineshape of the Bragg peaks was assumed to be a pseudo-Voigt function, a combination of Gaussian and Lorentzian profile functions. Fig. 2 (a)-(d) shows the measured and refined profiles of pure and doped Mg_2Si samples, respectively. The measured data (crosses) and calculated diffraction profiles (continuous solid line) are in reasonable agreement with each other. In addition, the vertical lines below the diffraction pattern indicate the calculated positions of Bragg peaks. The calculated structure factors (F_{cal}), the observed structure factors (F_{obs}), and the standard derivation ($\sigma(F_{\text{obs}})$) are summarized in Table 1. The small standard derivation errors (0.5~3) in $\sigma(F_{\text{obs}})$ indicate the goodness of the fitted intensities.

Fig. 2Le Bail fit to the experimental X-ray diffraction patterns for (a) pure Mg_2Si ; (b) $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$; (c) $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$; and (d) $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$.

Table 1 The structure factor of pure & doped Mg₂Si obtained from diffraction data.

Pure Mg ₂ Si				Mg _{1.99} Al _{0.005} Zn _{0.005} Si _{0.995} Sb _{0.005}			
<i>h k l</i>	F _{obs}	F _{cal}	σ (F _{obs})	<i>h k l</i>	F _{obs}	F _{cal}	σ (F _{obs})
1 1 1	45.61	44.07	0.71	1 1 1	47.17	46.60	0.91
0 0 2	-31.15	-31.51	0.84	0 0 2	-26.05	-25.90	0.86
2 0 2	100.00	100.08	1.23	2 0 2	100.00	97.78	1.54
1 1 3	33.97	35.51	0.70	1 1 3	33.00	32.93	0.95
2 2 2	-26.81	-26.40	0.90	2 2 2	-23.39	-23.22	0.57
0 0 4	87.36	87.49	1.71	0 0 4	82.94	80.94	2.33
3 1 3	30.76	31.48	0.90	3 1 3	31.17	29.96	1.30
2 0 4	-21.82	-20.91	0.97	2 0 4	-18.40	-18.09	0.58
2 2 4	75.60	74.42	1.16	2 2 4	72.62	70.10	1.49
3 3 3	27.17	27.26	0.83	3 3 3	27.33	26.61	1.41
1 1 5	27.17	27.45	0.83	1 1 5	27.33	25.79	1.41
4 0 4	68.14	65.73	1.64	4 0 4	66.94	61.73	2.40
3 1 5	24.68	24.48	0.52	3 1 5	24.39	22.93	1.37
0 0 6	-13.43	-13.43	0.27	0 0 6	-10.54	-10.63	1.18
4 2 4	-13.43	-13.49	0.27	4 2 4	-10.54	-10.81	1.18

Mg _{1.995} Zn _{0.005} Si _{0.995} Sb _{0.005}			
<i>h k l</i>	F _{obs}	F _{cal}	σ (F _{obs})
1 1 1	47.67	46.72	1.09
0 0 2	-28.16	-27.68	1.13
2 0 2	100.00	98.33	1.66
1 1 3	34.64	32.81	1.22
2 2 2	-23.64	-23.16	0.95
0 0 4	89.51	84.99	2.99
3 1 3	31.83	29.64	1.73
2 0 4	-18.82	-18.46	0.61
2 2 4	74.72	71.38	1.87
3 3 3	28.06	27.64	0.98
1 1 5	28.06	26.97	0.98
4 0 4	65.40	61.09	3.27
3 1 5	25.36	22.82	1.88
0 0 6	-11.36	-11.26	1.13
4 2 4	-11.36	-11.37	1.13

Mg _{1.99} Zn _{0.01} Si _{0.995} Sb _{0.005}			
<i>h k l</i>	F _{obs}	F _{cal}	σ (F _{obs})
1 1 1	47.60	46.69	0.88
0 0 2	-29.02	-28.59	0.81
2 0 2	100.00	100.08	1.40
1 1 3	36.67	35.10	0.89
2 2 2	-24.64	-23.90	0.91
0 0 4	90.71	88.22	2.18
3 1 3	31.36	30.01	0.98
2 0 4	-19.86	-19.25	0.57
2 2 4	74.47	73.19	1.42
3 3 3	28.57	27.92	1.23
1 1 5	28.57	27.03	1.23
4 0 4	64.88	63.22	2.16
3 1 5	25.49	23.76	1.16
0 0 6	-11.52	-11.56	1.12
4 2 4	-11.52	-11.63	1.12

The charge densities of the samples were determined from the structure factors extracted from the X-ray diffraction patterns using the MEM. Since only low angle diffraction data are available, the charge distributions are more representative to that of the valence electrons. For pure Mg_2Si , convergence in the MEM refinement was reached when the Lagrange parameter (λ)=0.001 and reliability indices $R_{\text{MEM}}=1.58\%$ and $wR_{\text{MEM}}=2.08\%$ were achieved (where R_{MEM} is the unweighted index and wR_{MEM} is the weighted index). For the doped Mg_2Si samples, similar analyses with comparable accuracy were obtained. The 3D MEM charge density surface contour plot for pure Mg_2Si showed the correct positions of charge density in Mg and Si sites (Fig.3). In the unit cell, the silicon atoms occupied the 4a Wyckoff position (0 0 0) face-centred sites, while the magnesium atoms occupied the 8c (1/4 1/4 1/4) tetrahedral sites. This description is consistent with the face-centered cubic crystal structure of pure Mg_2Si with an $Fm-3m$ space group. The atomic positions, charge density distribution and the atomic size for Si and Mg are clearly displayed in the 3D density plot. Furthermore, visualization of the charge density shows the ionic nature of the chemical bonding indicating the electron charges distribution are visually very similar at the Si and Mg sites as the size of the charge clouds were comparable between the Mg and Si atoms. The results obtained here are similar to those previously reported. [22]

Fig. 3 3D charge density of pure Mg_2Si in the unit cell (The value of the contour surface is $0.5 \text{ e}/\text{\AA}^3$.)

To reveal the distribution of the excess electrons donated by the dopants, three-dimensional (3D) and two-dimensional (2D) electron density difference ($\Delta\rho$) maps in which the electron density of pure Mg_2Si was subtracted from the doped samples were calculated. The 3D electron distribution differences are shown in Fig. 4 (a) and (b). In Fig. 4 (a) and (b), positive and negative differences were plotted with surface contours of $\pm 0.5 \text{ e}/\text{\AA}^3$, respectively. It is surprising that both positive and negative density difference were found in the atomic core regions. It might suggest there may be core polarization. However, as will be discussed below, this explanation is untenable as the inherent errors in the analysis are very large in the atomic core region.

A strategy to analyze the MEM results is to fix the unit cells of the doped Mg_2Si samples to that of pure Mg_2Si . In this case, for the doped Mg_2Si samples, the only difference is the number of electrons added in the unit cell. As mentioned above, we always found spurious positive and negative electron density ($-0.5 \sim 0 \text{ e}/\text{\AA}^3$) inside the core region of Mg atoms. This observation is

unrealistic as we have only used X-ray diffraction data up to d -spacing of 1 Å, therefore, it is not expected that reliable density with $r < 1$ Å can be obtained. We therefore ignored the core electron density and only analyzed the positive electron density difference. In Fig. 5, the electron density difference maps of the doped samples projected in the (100) and (110) planes of the unit cell are compared by using the experimental unit cells for the analysis of the MEM for the doped samples. The (100) plane contains only the Si atoms and the (110) plane contains both Si and Mg atoms. The results show the obvious trend that all the doped samples gained electrons in the crystal with the addition of the dopants (Sb, Al and Zn). The most important observation is that, even though doped atoms are expected to locate at specific atom sites, the extra electrons are not localized in specific spatial regions, but both Mg and Si sites gain electrons. This observation will be explained later with the DFT-calculated density of states.

Examination of the MEM derived electron densities of the doped Mg_2Si samples shows the charge accumulation on the Si sites increased in the order of $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Al}0.5\%\text{Zn}0.5\%$) $<$ $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Zn}0.5\%$) $<$ $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Zn}1.0\%$). (See Fig. 5 (a) and (b)) Comparing the charge density difference maps containing only the Si atoms in the (100) plane (Fig. 5 (a)), we found that $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ and $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ are similar, indicating that the increase of Zn concentration does not affect the charge distribution, so it is likely that Zn does not occupy the Si sites. The charge density difference of $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ is different from those of $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ and $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$. Since the only difference in chemistry is the addition of the Al atom in $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$, we may conclude Al occupies the Si sites. An additional evidence is that the charge density on the Si sites in $\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ is lower than the other two compounds

($\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ and $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$), since Al has one less electron than Si. If the Zn atoms indeed are situated at the Mg sites, as suggested above one would expect when the concentration of Zn is increased from 0.5% to 1.0%, there will be more electrons at those sites. This description is indeed confirmed by the difference in electron topology around the Mg sites showing an increase of electron density from 0.5% to 1.0% Zn. Finally, unlike Si sites, the electron distribution around the Mg sites is not spherical, but exhibits additional features. The apparent difference can be explained by the fact the valence electrons of Mg are in sp^3 hybridized orbitals since the atoms are in tetrahedral sites. However, in the (100) plane showing the Si atoms, there is no projection of the electron density of the Si-Mg bond on this plane. In comparison, the (110) plane cuts into the Mg-Si orbitals and revealing the directional sp^3 -like orbital density feature. Therefore, from the MEM charge density analysis, we can conclude that the Zn dopants should occupy the Mg sites. The increase in electron density suggests both Al and Sb occupy the Si sites. This assignment is at odds with the *n*-type semiconductor property of the synthesized samples, which indicate Al dopants substitute for Mg and the extra electrons are in the valence band. However, a recent theoretical calculation suggested that the conclusion on the Al substitution site in Mg_2Si is still ambiguous, in particular at low Al concentration. [14] The present results provide a new perspective on the possible locations of the dopants in the crystal: Al and Sb substituted the Si sites but only Zn occupied the Mg sites.

Fig. 4 3D electron density difference ($\Delta\rho$) of doped Mg_2Si samples ($\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ (Sb0.5%Al0.5%Zn0.5%), $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ (Sb0.5%Zn0.5%), and $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ (Sb0.5%Zn1.0%)) relative to pure Mg_2Si with isosurface contour values of (a) $0.5 \text{ e}/\text{\AA}^3$ and (b) $-0.5 \text{ e}/\text{\AA}^3$.

Fig. 5 2D electron density difference ($\Delta\rho$) of doped Mg_2Si samples ($\text{Mg}_{1.99}\text{Al}_{0.005}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Al}0.5\%\text{Zn}0.5\%$), $\text{Mg}_{1.995}\text{Zn}_{0.005}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Zn}0.5\%$), and $\text{Mg}_{1.99}\text{Zn}_{0.01}\text{Si}_{0.995}\text{Sb}_{0.005}$ ($\text{Sb}0.5\%\text{Zn}1.0\%$)) relative to pure Mg_2Si in (a) (100) and (b) (110) planes. The contour levels are shown in the side bars.

Since the exact locations of the dopants are not uncertain, we performed theoretical DFT calculations on two different multi-doped Mg_2Si models in order to clarify the situation. In the first model, we assumed that the Zn atoms substituted the Mg sites, and Al and Sb resided at the Si sites. (*i.e.* $(\text{Mg}_{214}\text{Zn}_2)(\text{Si}_{104}\text{Al}_2\text{Sb}_2)$). In the second model, some Mg atoms were replaced with Al and Zn and some Si atoms replaced by Sb (*i.e.* $(\text{Mg}_{212}\text{Zn}_2\text{Al}_2)(\text{Si}_{106}\text{Sb}_2)$). In Fig. 6 (a) and (b), we observed no localized mid gap band and the electrons are delocalized over the entire crystal structure. It should be noted that both structural models resulted in an *n*-type semiconductor. (Fig. 6 (a)) The first model shows below and at the Fermi level the dominant contributions are from Si, Mg and Al atoms with very small participation of Zn and Sb atoms. In Fig. 6 (b), the density of

states is projected into individual atomic orbitals. The p -type atomic orbitals of both Mg and Si atoms contribute to the density of states near the Fermi level and supporting the suggestion that both Mg and Si are sp^3 hybridized.

The calculated projected densities of states (pdos) of the second multi-doped $(\text{Mg}_{212}\text{Zn}_2\text{Al}_2)(\text{Si}_{106}\text{Sb}_2)$ model are shown in Fig. 7 (a) and (b). The only difference of this model with the previous one is that Al atoms now substituted the Mg sites instead of Si. If this was the case, there will be more free electrons available with this substitution. Comparing to the $(\text{Mg}_{214}\text{Zn}_2)(\text{Si}_{104}\text{Al}_2\text{Sb}_2)$ model, the Fermi level indeed shifts to a higher energy as more free electrons should contribute to the conduction band. The same observation is made that the calculated projected orbital densities of states for all atoms show that, although the dopants replace the Mg and Si sites, the dopant electrons are spread over the entire crystal and not localized in specific regions.

To conclude, the electronic structures of two theoretical structural models, *i.e.* with Al substituting either the Mg or Si sites, cannot differentiate the preferences of the dopant. Nevertheless the theoretical results do not contradict the observed electron density difference discussed above, indirectly showing the present assignments of the substitution sites are plausible.

Fig. 6 Projected density of states (pdos) of $\text{Mg}_{214}\text{Zn}_2\text{Si}_{104}\text{Al}_2\text{Sb}_2$ model (a) into atomic composition; (b) into atomic orbitals.

Fig. 7 Projected density of states (pdos) of $\text{Mg}_{212}\text{Zn}_2\text{Al}_2\text{Si}_{106}\text{Sb}_2$ model (a) into atomic composition; (b) into atomic orbitals.

The maximum entropy method (MEM) is a powerful technique to determine the electron density distribution if only a limited set of diffraction data is available. However, it does have limitations. First, the quality of the experimental data is an important factor, this is particularly important for the intensities extracted from powder patterns. Second, the calculated electron density is dependent on the numbers of Bragg reflections considered in the MEM analysis (*i.e.* errors introduced by the limited maximum scattering angle). We investigated this effect on a 1% Al-doped Mg₂Si sample (Mg_{1.99}Al_{0.01}Si) using synchrotron radiation measured with a shorter wavelength ($\lambda=0.50917$ Å), in which higher angle Bragg reflections were collected. From 5° to 52°, a total of 55 non-overlapping reflections can be indexed and their intensities extracted (Fig. 8). To study the errors introduced to the computed charge density due to the restricted number of reflections included in the calculations, MEM charge density maps were constructed with 15, 20, 30, 45 and 55 Bragg reflections. Deviations of the charge density were examined from the difference with the full data set (*i.e.* 55 reflections). As shown in Fig. 9, the major discrepancy is concentrated at the atomic sites with a radial spread of *ca.* ~1 Å. This is not surprising as the high angle structure factors are more sensitive to the core electrons. In the worst possible case (*i.e.* using 15 Bragg reflections) the largest difference in the electron density is at most $14 \text{ e}/\text{\AA}^3$ with the electron cloud extended about the atom center of about 1 Å. Since the positive electron density differences are located away from the atomic sites in the density maps of the doped samples, we believe the results are qualitatively correct. Although the errors of electron density in the core regions become smaller as an increasing number of Bragg reflections are introduced, we conclude that it is difficult to obtain highly accurate measurements of the electron density distribution for the doped samples with small doping concentrations by using the MEM.

Fig. 8 Refined X-ray diffraction pattern for 1% Al-doped Mg_2Si ($\text{Mg}_{1.99}\text{Al}_{0.01}\text{Si}$).

Fig. 9 3D electron density difference of 1% Al-doped Mg_2Si ($\text{Mg}_{1.99}\text{Al}_{0.01}\text{Si}$) (a) between 15 and 55 reflection peaks used; (b) between 20 and 55 reflection peaks used; (c) between 30 and 55 reflection peaks used; and (d) between 45 and 55 reflection peaks used. (Yellow: positive charge density; Green: negative charge density)

4. Conclusions

High resolution powder diffraction patterns of pure and multi-doped Mg_2Si have been measured by synchrotron X-ray. Analyses show the addition of the dopants expanded the unit cells from pure Mg_2Si . It is gratifying that even using a limited set of low angle Bragg reflections the charge density distribution of pure Mg_2Si can be reconstructed using the Maximum Entropy Method (MEM). Analysis also revealed subtle differences in the valence electron topologies between doped and pure samples. It is found that the electrons contributed by the dopants populated the conduction band and are not localized on the dopant sites. This observation is supported by results of theoretical DFT calculations on two different doping models showing that these electrons occupied the conduction bands and are delocalized. In contrast to the electron density difference profile in (100) plane showing only the Si atoms, in the (110) plane, the electrons distribution around Mg sites is found to have additional features. These features can be explained by electrons on the Mg polarized along the Mg-Si bond direction in the (110) plane but have no projection in the (100) plane. Studies on the charge density difference maps strongly suggest that the Zn dopant should occupy the Mg sites whilst Al and Sb occupied the Si sites. Comparisons of MEM charge densities calculated with systematic increase in the number of high angle Bragg reflections included in the analysis on Al-doped Mg_2Si indicate that the electron density maps for the multi-doped samples are denominated by the valence electrons and should be qualitatively correct.

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