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Li doped Mg_2Si *p*-type thermoelectric material: Theoretical and experimental study

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ABSTRACT

The aim of the study was to determine the influence of Li dopant on transport properties of Mg_2Si by using computational methods and experimental study.

The results of theoretical studies of electronic structure (Full Potential Linearized Augmented Plane Wave Method), electron density topology and bonding properties (Bader's Quantum Theory of Atoms in Molecules topological analysis of total electron density) in Li-doped Mg_2Si are presented. Detailed analysis of calculated band structures and densities of states shows that for two cases analyzed i.e.: Li substituting Si or Li located in interstitial region (4*b* Wyckoff position), the addition of lithium impurity leads to *n*-type conduction. On the other hand, if Li is located in Mg position, the samples have *p*-type conduction.

A series of samples with the nominal compositions of $Mg_{2-x}Li_xSi$, ($x = 0$–0.3) were prepared using the Pulsed Electric Current Sintering Technique (PECS) method. Structural and phase composition analyses were carried out by X-ray diffraction. The investigations of the influence of Li dopant on the transport properties i.e.: electrical conductivity, the Seebeck coefficient and the thermal conductivity were carried out. Carrier concentration was measured using the Hall method. The positive value of the Seebeck coefficient indicates that all examined samples show *p*-type conductivity, which is consistent with the theoretical predictions.

1. Introduction

Magnesium silicide Mg_2Si is one of the most promising thermoelectric materials, suitable for construction of thermoelectric generators TEG for middle range of temperatures (500–800 K). It is a non-toxic and inexpensive material in comparison to other, often used thermoelectric materials based on Te, Pb and Sb.

The fundamental parameter characterizing the functional properties of thermoelectric materials is their dimensionless thermoelectric figure of merit *ZT* [1,2].

$$ZT = \alpha^2 \sigma \lambda^{-1} T \quad (1)$$

where
- α – is the Seebeck coefficient,
- σ – is the electrical conductivity,
- λ – is the thermal conductivity,
- T – is the temperature.

The value of the *ZT* parameter correlates positively with the efficiency of the thermoelectric devices like thermoelectric generators and heat pump [3–5]. Undoped Mg_2Si does not have a high value of the *ZT* parameter ($ZT_{max} = 0.04$–0.06, $T = 750$–850 K [6–8]). However, this can be significantly enhanced by using of appropriate dopants, such as Sn, Ge, Sb and Bi, for example: $ZT_{max} = 1.2$, $T = 700$ K for $Mg_2Si_{0.6}Sn_{0.4}$ [9]; $ZT_{max} = 0.7$–0.86, $T = 823$–862 for Mg_2Si:$Bi_{0.02}$ [10–12]; $ZT_{max} = 0.56$–0.62, $T = 823$–862 K for Mg_2Si:$Sb_{0.02}$ [7,8]; $ZT_{max} = 1.4$, $T = 823$ K for $Mg_2Si_{0.53}Sn_{0.4}Ge_{0.05}Bi_{0.02}$ [13]. All of these materials are characterized by *n*-type conduction. For *p*-type materials that are currently known (impurities Ag, Ga), *ZT* parameter is usually several times lower compared to *n*-type materials ($ZT_{max} = 0.11$ for $Mg_2Si + 3\%$ Ag [14]; $ZT_{max} = 0.35$ for $Mg_2Si_{0.6}Ge_{0.4}$:Ga(0.8%) [15]). However, for the construction of thermoelectric modules, both type materials with good thermoelectric properties (high value of *ZT* parameter) are strongly desired. For this reason, the new impurities, resulting in acceptor character of conductivity in a given material are particularly sought. The aim of the study was to show the possibility of obtaining the *p*-type material by doping with lithium, introduced in a particular

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position in the Mg_2Si structure by means of theoretical calculations of the electronic structure and topological properties of electron densities verified by subsequent experimental studies.

2. Material and methods

Powders of Mg (extra pure-Fisher Scientific) and Si (99.9%, Alfa Aesar, 100 mesh) and Li ingot (99.9%, Alfa Aesar) were used for the synthesis. A series of samples with nominal composition $Mg_{2-x}Li_x$-Si (x = 0, 0.05, 0.1, 0.2, 0.3) were prepared by a direct synthesis from above mentioned elements. The synthesis of pre-mixed powders was conducted in a graphite die of 10 mm diameter at a temperature of 833 K, in the PECS [16] device using Ar (99.999%) protective atmosphere. Then, each of the obtained samples was mechanically ground in an agate. Later the powders were densified in the PECS apparatus (T = 1023 K, p = 30 MPa, t = 15 min). The density was determined by hydrostatic Archimedes' method with propan-2-ol as a medium. Relative densities for undoped samples were higher than 98.5%, whereas the density of the samples doped with lithium is higher than 95%. The resulting polycrystalline samples were examined using X-ray structural analysis (X-ray Diffractometer Empyrean PANalytical, Cu Kα1, λ_1 = 1.5406 Å, Cu Kα2, λ_2 = 1.5444 Å, 2Θ angle range from 20° to 137°). On the basis of the obtained X-ray patterns and by means of the Rietveld method (FullProf package, 2013 edition), the lattice parameters of the obtained materials were determined (Fig. 3). Electrical conductivity and Seebeck coefficient was measured in steady state conditions. Thermal conductivity was determined by laser flash method (LFA MicroFlash Netzsch 457 apparatus). The carrier concentration was measured by the Hall method (B = 0.705 T, DC method, j = 25 mA/mm^2, scattering factor A = 1).

3. Computational details

The electronic structure calculations for lithium doped magnesium silicide have been carried out using WIEN2k FP-LAPW (Full Potential Linearized Augmented Plane Wave Method) package [17], within Density Functional Theory (DFT) formalism [18–23]. The calculations has been done for pure Mg_2Si crystal structure (space group 225, Fm−3m, a = 6.391 Å [24]) and for three $2 \times 2 \times 2$ superstructures in order to simulate approx. 1% of lithium doping, for various locations of Li atoms within the structure: (a) magnesium sub-lattice ($Mg_{63}LiSi_{32}$; sg no. 215, P−43m, a = 12.782 Å), (b) silicon sub-lattice ($Mg_{64}Si_{31}Li$; sg no. 221, Pm−3m, a = 12.782 Å) and (c) in interstitial region ($Mg_{64}Si_{32}Li$; sg no. 221, Pm−3m, a = 12.782 Å). The following parameters have been chosen for calculation: 3000 k-points ($14 \times 14 \times 14$ mesh within the irreducible Brillouin zone) for pure magnesium silicide and 500 k-points ($7 \times 7 \times 7$ mesh) for $2 \times 2 \times 2$ superstructures, cut-off parameter $\mathbf{Rk_{max}}$ = 7.5, GGA-PBE exchange–correlation potential [25], the values of muffin-tin radii (R_i) [a.u.]: Mg – 2.5, Si – 2.5, Li – 2.5 and the convergence criteria for SCF calculations set to $\Delta E_{SCF} \leq 10^{-5}$ Ry for total energy and $\Delta\rho_{SCF} \leq 10^{-5}$ e for electron density topology analysis. The crystal structure parameters and fractional atomic coordinates used in DFT calculations are listed in Table 1.

The calculated total SCF electron density distribution in crystal cell has been used as a basis for the calculations of the topological properties of bond critical points (within Bader's Quantum Theory of Atoms in Molecules [26] formalism). As Bader et al. [27] have shown, the analysis of the gradient vector field, derived from the scalar electron density distribution provides us with the crucial information about properties of the electron density in topologically special points (so called critical points) for which gradient of the electron density $\nabla\rho(r)$ is equal to zero and thus about bonding in given molecule or crystal and allows to uniquely partition a space into adjacent volumes and thus to define the so called topological atoms and calculate unequivocal their net charges.

4. Results and discussion

4.1. Electronic structure calculations

Detailed analysis of electronic structure calculated for Li-doped magnesium silicide shows (Fig. 1) that when lithium replaces silicon or locates in interstitial region, the overall structure exhibit n-type conduction. If, on the other hand, lithium is located in Mg sub-lattice, the resulting structure will exhibit p-type conduction.

This difference in conductivity type can be easily explained by comparison of respective defect equations written down for each of three analyzed structures. In the case of $Mg_{2-y}Li_ySi$, the defect equation reads:

$$(2-y)\mathrm{Mg} + y\mathrm{Li} + \mathrm{Si} = (2-y)\mathrm{Mg}^x_{\mathrm{Mg}} + y\mathrm{Li}'_{\mathrm{Mg}} + \left(1-\frac{y}{4}\right)\mathrm{Si}^x_{\mathrm{Si}} + \frac{y}{4}V^{\cdots\cdot}_{\mathrm{Si}} + \frac{y}{4}\mathrm{Si}$$

One can easily see, that replacement of magnesium by lithium results in a formation of positively charged vacancies in silicon sub-lattice and removal of silicon excess in a form of separate phase (the latter was confirmed by XRD data – not included in this work due to paper size limits). Similar equations can be formulated for lithium located in silicon sub-lattice and in interstitial region:

$$\mathrm{Mg_2Si_{(1-y)}Li_y} : 2\mathrm{Mg} + (1-y)\mathrm{Si} + y\mathrm{Li} = \left(2-\frac{3}{2}y\right)\mathrm{Mg}^x_{\mathrm{Mg}} + (1-y)\mathrm{Si}^x_{\mathrm{Si}} + y\mathrm{Li}^{\cdots}_{\mathrm{Si}} + \frac{3}{2}yV''_{\mathrm{Mg}} + \frac{3}{2}y\mathrm{Mg}$$

$$\mathrm{Mg_2SiLi_y} : 2\mathrm{Mg} + \mathrm{Si} + y\mathrm{Li} = \left(2-\frac{y}{2}\right)\mathrm{Mg}^x_{\mathrm{Mg}} + \mathrm{Si}^x_{\mathrm{Si}} + y\mathrm{Li}^{\cdot}_i + \frac{y}{2}V''_{\mathrm{Mg}} + \frac{y}{2}\mathrm{Mg}$$

In both cases the process of magnesium silicide doping with lithium would result in a formation of negatively charged vacancies in magnesium sub-lattice and appearance of separate MgO phase formed from excess of magnesium.

4.2. Electron density topology

The total electron density distribution data obtained from FP-LAPW SCF calculations has been used as a basis for Bader's QTAiM topological analysis and the calculated net charges as well as volumes of topological atoms are presented in Table 2 (lithium and respective atoms bonded with lithium are in bold). Presented results indicate that substitution of magnesium by lithium leads to the smallest structure deviation – net charges and topological volumes calculated for silicon and magnesium atoms are very similar to those in pure magnesium silicide with root mean square error (r.m.s.e.) equal to 0.03 and 4.49 for net charge and volume, respectively. In the case of the structure with lithium located in a void the changes are also small, but here the environment of two atoms is influenced by lithium insertion, namely Si_2 and Mg_4 (r.m.s.e. equal to 0.05 and 4.68 for net charge and volume, respectively). The strongest structure deviation, as a result of Li doping, is in case of superstructure where lithium replaces silicon – here not only a charge of magnesium atom bonded with lithium, but also the volume of topological atom are strongly influenced (net charge equal to 1.032 vs 1.463 in pure Mg_2Si and volume equal to 90.7 vs 55.4 in Mg_2Si resulting in overall r.m.s.e. equal to 0.13 and 10.93