Experimental report

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Proposal: 5-21-1163 **Council:** 10/2020

Title: Variable Temperature Powder Neutron Diffraction study of Mg3Sb2 and Mg3Bi2;Defect Structure at Room Temperature and in Superionic Beta-Phase

Research area: Chemistry

This proposal is a new proposal

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Samples: Mg3Bi2
Mg3Sb2

Instrument	Requested days	Allocated days	From	To
D1B	2	1	11/10/2021	12/10/2021

Abstract:

Mg3Sb2 and Mg3Bi2 based Zintls have attracted great research interest recently as both high-performance thermoelectrics and as rechargeable magnesium-ion battery anodes. At low temperatures, their alpha-phases crystallise with the trigonal CaAl2Si2-type structure composed of Mg2+ cation layers intercalated between tightly bound [Mg2X2]2- (X=Sb,Bi) anionic layers. Deficiencies of the Mg2+ layers were often reported, potentially influencing on Mg2+ transport and sample properties. At ca. 900 and 730 °C, respectively, Mg3Sb2 and Mg3Bi2 are proposed to transform to a high-T beta-phase, with liquid-like Mg2+ within the interstices of a body-centered cubic (bcc) sub-lattice of X3- anions, which exhibit fast Mg2+ conductivity. To date, no complete structural models exist from the limited studies performed. Herein, Mg3Sb2 and Mg3Bi2 powders are synthesised in an Mg-rich environment through rapid and energy-efficient solid-state microwave approaches within minutes. We propose to conduct variable-T PND studies exploiting the superior intensity and resolution of D1B at ILL, investigating the evolution of structure, stoichiometry and defect chemistry through the alpha-beta transition.

Variable Temperature Powder Neutron Diffraction (PND) study of Mg_3Sb_2 and Mg_3Bi_2; Defect Structure at Room Temperature and in the Superionic Beta-Phase.

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1. Introduction

Isostructural Mg_3Sb_2 and Mg_3Bi_2, crystalizing in the trigonal $CaAl_2Si_2$-type layered structure (Space group *P-3ml*) as noted in our original proposal,[1] were initially studied by *Zintl* and Husemann in the 1930s.[2] Significantly, extrinsically doped n-type Mg_3Sb_2-Mg_3Bi_2 alloys have rapidly attracted interest in the last six years, becoming some of the most promising thermoelectric materials in the low-mid temperature range (*ca.* 300-700 K), equaling or surpassing the only commercial choice - Bi_2Te_3 over the past few decades.[3] Moreover, Mg_3Sb_2 and Mg_3Bi_2 have been recently proposed as potential advanced anode materials for rechargeable magnesium-ion batteries.[4] However, despite their importance, the defect crystal structures of the materials remain largely unelucidated.

The “metal to non-metal” transition of Mg_3Bi_2 has been experimentally studied since the 1990s and liquid Mg_3Bi_2 melts show low electrical conductivity but unusually high ionic mobility.[5] Intriguingly, solid Mg_3Bi_2 and Mg_3Sb_2 also undergo temperature-induced phase transitions from the room-temperature (RT) alpha phases to the high-T superionic beta phases at *ca.* 730 and 900 °C, respectively. Crystallized Bi/Sb sub-lattices superimposed on liquid-like Mg^{2+} cations were proposed.[6] Barnes *et al.* analyzed the phase transition of Mg_3Bi_2 *via in-situ* PND in 1994 and proposed a *bcc* Bi sub-lattice with a lattice parameter of 5.297(4) Å, with the same *Im-3m* structure as alpha-Ag_2Se.[7] Quasi-elastic neutron scattering experiments by Howells *et al.* in 1999 confirmed the mobile Mg^{2+} in beta-phase Mg_3Bi_2, suggesting short-distance jumping and long-distance continuous diffusion.[8] Li *et al.* quenched Mg_3Sb_2 and Mg_3Bi_2 samples into liquid nitrogen from > 1203 and 976 K, respectively; PXD revealed only trigonal α-phases with no trace of *bcc* β-phases, indicating a fast phase transition.[9] To the best of our knowledge, there is no direct experimental evidence of the α/β-phase transition of Mg_3Sb_2. The preferred sites and potential pathways of the liquid-like Mg cations remain to be revealed.The experiments in ILL proposal 5-21-1163 were performed on 11th OCT 2021.[1]

2. Experimental

Variable-T PND experiments were performed using the D1B diffractometer over 0.77 – 128.67° (2θ).[1] Samples were loaded to a height of *ca* 7 mm into stainless steel sample cans under Ar, which were then sealed. Data collections began at RT (293.15 K) to allow Rietveld refinement of the structure of the alpha phases. Diffraction data at intermediate temperatures were collected thereafter at 623.15 and 723.15 K. PND datasets of the β-phases were collected at 1023.15 & 1223.15 K for Mg_3Bi_2 and Mg_3Sb_2, respectively. During heating, datasets were collected every 3 min to capture reversible phase transitions.

The stainless steel sample holder inevitably contributed intense peaks to the PND patterns (refined in space group *Fm-3m*). Refinements were performed through combined Le Bail and Rietveld methods, employing GSAS via the EXPGUI interface.[10,11] Profile fitting of the stainless steel sample holder was performed by the Le-Bail method, while other relevant phases of the sample were refined through the Rietveld method. A CIF file created from the refined β-Mg_3Sb_2 structure was used for BVS calculations (*SoftBV* software) by setting Mg^{2+} as the mobile cation and Sb^{3-} as the fixed anion.[12] Refined structures and calculated iso-surfaces were plotted through the VESTA package.[13]

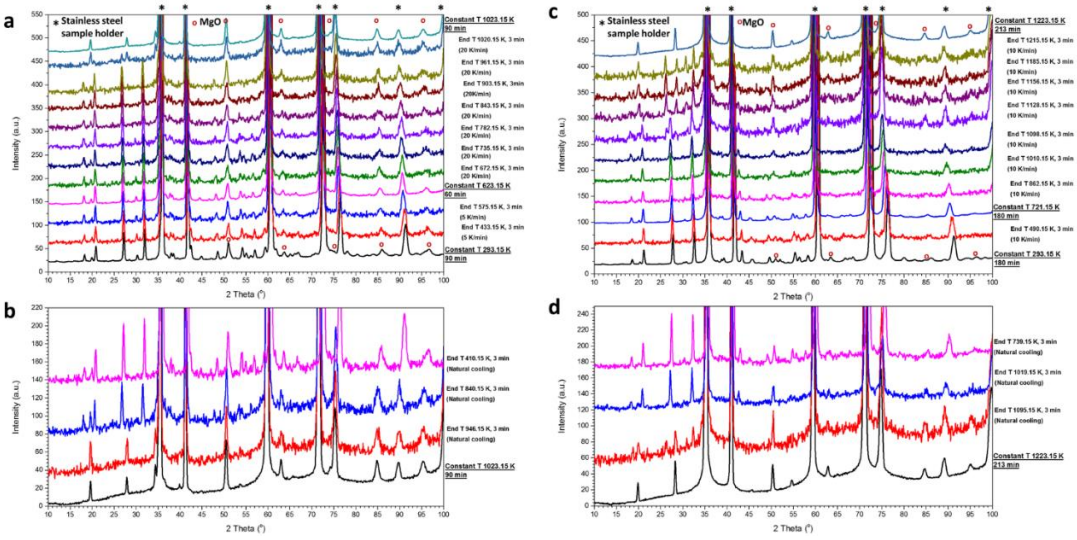

Figure 1. *In-situ* PND patterns of Mg_3Bi_2 on heating (**a**) and cooling (**b**), respectively; and Mg_3Sb_2 on heating (**c**) and cooling (**d**), respectively. The temperature, collection time and ramp rate are indicated.

3. Results and Discussion

3.1 Temperature-dependent phase transitions

Figures 1a, b show PND patterns of Mg_3Bi_2 on heating and cooling, respectively. α-Mg_3Bi_2 remained stable from 293.15-961.15 K, shifted reflections indicated lattice expansion with temperature. At 1023.15 K (750 °C), the highly symmetric diffraction peaks confirmed the stable presence of the high-T β-phase Mg_3Bi_2 with a diffuse background. The transition to β-Mg_3Bi_2 was observed between 961.15 – 1020.15 K, agreeing well Barnes ***et al.***'s study.[7] Figure 1b confirms the reversible β-α transitions upon cooling and no extra impurity phases were formed during the entire experiment. Figures 1c&d show PND patterns of Mg_3Sb_2 during heating and cooling, respectively. α-Mg_3Sb_2 remained stable from 293.15-1098.15 K. At 1223.15 K, a highly symmetric and simple diffraction pattern with a diffuse background was observed, indicating superionic β-Mg_3Sb_2. Its corresponding PND pattern closely resembles that of β-Mg_3Bi_2 (Figure 1a), suggesting an isostructural relationship, although Mg_3Sb_2 undergoes the phase transition at a temperature *ca.* 200 K higher. The results also suggested an intermediate phase between the α- and β-forms between 1156.15-1215.15 K (Figures 1c,d).High-quality data enabled systematic investigation of the T-dependent structural changes. Combined Rietveld and Le Bail methods were employed for the structure refinements. Tables 1, 2 summarize unit cell lattice parameters and occupancies of Mg(1) and Mg(2) sites for alpha-phase Mg_3Sb_2 and Mg_3Bi_2 at different temperatures. Figure 2a illustrates the corresponding crystal structure of Mg_3Sb_2 at RT. Table 1 indicates a defective Mg_3Sb_2 structure with Mg(1) vacancies at RT, equivalent to a stoichiometry of $Mg_{2.87(3)}Sb_2$; at the intermediate temperature, Mg(1) vacancies were effectively eliminated with a refined stoichiometry of $Mg_{2.94(5)}Sb_2$, which was potentially caused by extra Mg located at the grain surfaces during synthesis. Table 2 suggests Mg vacancies for Mg_3Bi_2, but the vacancies were signaled at the Mg(2) sites. The thermal expansion along the *c*-axis was slightly higher than in the *ab*-plane for both Mg_3Sb_2 and Mg_3Bi_2.

3.2 Refined crystal structures and potential Mg^{2+} cation pathways in beta phases

Figure 2b illustrates the typical crystal structure of the *bcc* sub-lattice, as refined against the PND datasets. Figure 2c shows the profile plots of combined Rietveld and Le Bail refinement against PND datasets of β-Mg_3Sb_2 and Mg_3Bi_2. The refinement results confirmed the *bcc Im-3m* structure of Bi and Sb (at the *2a* sites (0, 0, 0)) sub-lattices, leading to ***a*** = 5.3320(24) and 5.2565(15) Å, respectively. The former is a good match with Barnes ***et al.***'s PND study in 1994.[7] Interestingly, by drawing Sb-Sb bonds and projecting the beta-phase Sb sub-lattices along the [*111*] direction, we found that the beta phase resembles closely the Sb_8-packed layered frameworks. This may indicate the minor rearrangement of the distorted Sb_8 frameworks from the α-phase into uniform Sb_8 frameworks through the phase transition. We used an equivalent triclinic unit cell for β-phase Sb sub-lattices with presumed Mg positions (based on the α-structure, *i.e.* forming Mg_3Sb_2) and performed the BVS calculations, setting Mg^{2+} as the mobile cation. It should be noted that a model of Bi^{3-} is not yet available in the *SoftBV* software package; a 3- state for Bi would not be physically meaningful.

Table 1. Lattice parameters and Mg site occupancy factors (SOF) at different temperatures.

Collection temperature and time of the PND dataset	293.15 K 180 min	721.15 K 180 min	*ca.* 1068.15 – 1098.15 K 3 min
Lattice parameter *a* / Å	4.5691(5)	4.6082(10)	4.6575(17)
Lattice parameter *c*/ Å	7.2426(16)	7.3233(33)	7.4315(57)
Cell volume / Å^3	130.942(30)	134.678(60)	139.609(112)
SOF Mg(1)	0.87(3)	0.94(5)	1.0 [b]
SOF Mg(2)	1.0 [a]	1.0 [a]	1.0 [b]
$a/a_{293.15\ K}$	1.0	1.008555	1.019351
$c/c_{293.15\ K}$	1.0	1.011154	1.026092

Table 2. Lattice parameters and Mg site occupancy factors (SOF) at different temperatures.

Collection temperature and time of the PND dataset	293.15 K 90 min	623.15 K 60 min	*ca.* 901.15 – 961.15 K 3 min
Lattice parameter *a* / Å	4.6594(5)	4.6926(6)	4.7294(32)
Lattice parameter *c* / Å	7.4040(17)	7.4633(17)	7.5336(82)
Cell volume / Å^3	139.207(31)	142.327(33)	145.931(249)
SOF Mg(1)	1.0 [a]	1.0 [a]	1.0 [b]
SOF Mg(2)	0.914(46)	0.965(35)	1.0 [b]
$a/a_{293.15\ K}$	1.0	1.007117	1.012021
$c/c_{293.15\ K}$	1.0	1.008120	1.017501

a. Refinement led to a value higher than unity, thus this value was fixed at 1.0.
b. Refinement was not attempted due to the short PND collection duration of 3 min.

Figure 2d shows BVS-calculated potentials for Mg^{2+} diffusion within Sb sub-lattices. A total of 12 locations with a minimum potential of 0.0 eV for Mg^{2+} were identified in a single unit cell. Only an activation energy of < 0.284 eV is required for Mg^{2+} cations to diffuse through saddle points from the neighboring minimum-potential sites, with a diffusion distance of 2.63 Å. Figure 2e shows the corresponding unit-cell structure with favoured Mg^{2+} pathways in this superionic phase. The 3D pathways are isotropic and a large fraction of vacant Mg sites exist in the triclinic Sb sub-lattices, considering the stoichiometry of Mg_3Sb_2.

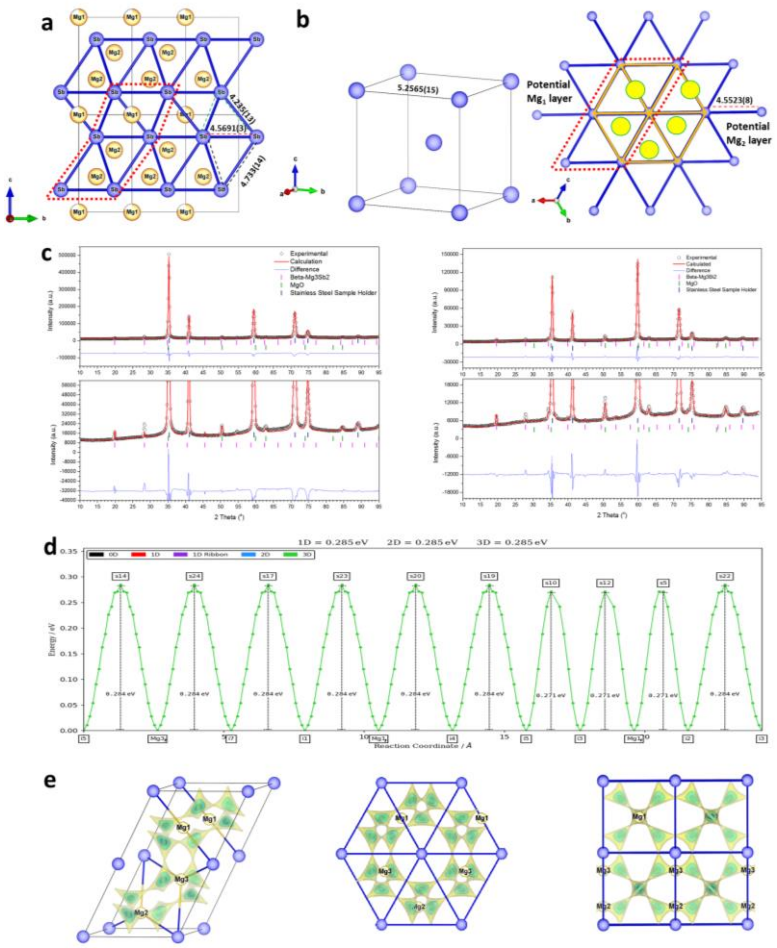

Figure 2. (a) Crystal structure of α-Mg_3Sb_2; **(b)** typical *bcc* crystal structure of β-Mg_3Sb_2; **(c)** profile plots for β-Mg_3Sb_2 and Mg_3Bi_2; **(d)** BVS-calculated potentials for Mg^{2+} diffusion within the crystal structure in (e); and **(e)** the corresponding structural plots and iso-surfaces for the Mg^{2+} potentials. A cubic unit cell is highlighted by orange lines in (b). Yellow circles in (b) illustrate the potential accommodation of Mg atoms based on (a). In (e), black iso-surfaces indicate minimum Mg^{2+} potential locations (0 eV); cyan iso-surfaces are at + 0.2 eV and yellow iso-surfaces are + 0.24 eV. Bond distances in Å.

4. Conclusions

In summary, the *in-situ* variable-T PND experiments have enabled the detailed scrutiny of defect structures in isostructural α-Mg_3Sb_2 and Mg_3Bi_2 from RT to intermediate Ts. The reversible alpha-beta phase transitions of Mg_3Sb_2 and Mg_3Bi_2 were elucidated successfully; both superionic β-phases were confirmed with *bcc Im-3m* structured Sb/Bi sub-lattices. The BVS calculations identified the favored Mg sites and diffusion pathways for Mg cations in the equivalent triclinic sub-lattices, suggesting short-distance jumps and long-distance continuous diffusion. An intermediate phase (with a pattern resembling β-Mg_3Sb_2 with some extra diffraction peaks) was suggested near the alpha-beta phase transition at *ca.* 1156.15 – 1215.15 K. The outcomes of this experiment contribute to a fundamental understanding of the structure-dynamics relationships in Mg_3Sb_2 and Mg_3Bi_2 solids.

References

1. Fan Z., *et al.* Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.5-21-1163.
2. Zintl E., *et al.* Physical Chemistry **21B** 138-155 (1933).
3. Mao J., *et al. Science* **365**, 495-498 (2019).
4. Tan Y.H., *et al. ACS Nano* **12**(6), 5856-5865 (2018).
5. Guo C., *et al. Journal of Physics: Condensed Matter* **8**, 10823 (1996).
6. Zhang J., *et al. npj Computational Materials* **5**, 1-17 (2019).
7. Barnes A.C.,*et al. Journal of Physics: Condensed Matter* **6**(32) L467 (1994).
8. Howells W.S., *et al. Physica B: Condensed Matter* **266** 97-99 (1999).
9. Li A., *et al. Research* 1934848 (2020).
10. Toby B.H. *Journal of applied crystallography* **34** 210-213 (2001).
11. Le Bail A. *Powder Diffraction* **20** 316-326 (2005).
12. Wong L.L. *et al. Chemistry of Materials* **33** 625-641 (2021).
13. Momma K., *et al. Journal of applied crystallography* **44** 1272-1276 (2011).