Synthesis and Characterization of the Divalent Samarium Zintl-phases SmMg_2Bi_2 and SmMg_2Sb_2

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Abstract: Single crystals of LnMg_2Bi_2 ($\text{Ln} = \text{Yb}, \text{Eu}, \text{Sm}$) and SmMg_2Sb_2 were synthesized using Mg-Bi metal and Mg-Sb metal fluxes, respectively. The crystal structures are of the CaAl_2Si_2 type with space group $P3m1$ (#164, $Z = 1$): SmMg_2Bi_2 ($a = 4.7745(1)\text{\AA}$, $c = 7.8490(2)\text{\AA}$), EuMg_2Bi_2 ($a = 4.7702(1)\text{\AA}$, $c = 7.8457(2)\text{\AA}$), YbMg_2Bi_2 ($a = 4.7317(2)\text{\AA}$, $c = 7.6524(3)\text{\AA}$), and SmMg_2Sb_2 ($a = 4.6861(1)\text{\AA}$, $c = 7.7192(2)\text{\AA}$). Heat capacity, electrical transport, and magnetization of all bismuth containing phases were measured. The materials behave as “poor metals” with resistivity between 2 and 10 m Ω -cm. Temperature independent Van Vleck paramagnetism is observed in SmMg_2Bi_2 indicative of divalent samarium (Sm^{2+}) ions.

Introduction

Zintl phases are a class of materials with a variety of properties, more specifically rare-earth Zintl-phases combine interesting magnetic and electronic properties. Exploration of the available elemental constituents and stoichiometry of these materials is an ongoing endeavor employing various synthesis techniques.^{1,2} One such class of materials is the CaAl_2Si_2 structure type (also referred to as the $\text{Ce}_2\text{O}_2\text{S}$ type) which is a layered structure accommodating various elements. The structure and properties of these materials can be understood by the Zintl concept, with $\text{Al}_2\text{Si}_2^{2-}$ layers separated by Ca^{2+} monolayers (Figure 1a).³ Site preferences within the $\text{Al}_2\text{Si}_2^{2-}$ layer depend on the relative electronegativity of the elements⁴, while the Ca^{2+} layer charge balances the material⁵⁻⁷.

The CaAl_2Si_2 structure type is host to a class of materials which can be developed for their thermoelectric properties; specifically the AMg_2Pn_2 , AZn_2Pn_2 , and ACd_2Pn_2 series of compounds where $\text{A} = \text{Ca}, \text{Sr}, \text{Eu}, \text{Yb}$; and $\text{Pn} = \text{pnictides: P, As, Sb, Bi}$. Thermoelectric figures of merit (ZT) are given for $\text{YbCd}_{2-x}\text{Zn}_x\text{Sb}_2$ $ZT = 1.2$ at 700K,⁸ EuZn_2Sb_2 $ZT = 0.9$ at 700K,⁹ and YbMg_2Bi_2 $ZT = 0.4$ at 600K.⁷ The tunability of these materials¹⁰ is exemplified by the $\text{YbCd}_{2-x}\text{Zn}_x\text{Sb}_2$ system, where the isoelectronic substitution of Zn for Cd optimizes the electrical and thermal conductivity at $x = 0.4$.⁸ Similar

tunability is demonstrated in the $\text{Yb}_{1-x}\text{Ca}_x\text{Cd}_2\text{Sb}_2$ system, but with substitution in the cation layer.¹¹

In the case of AMg_2Pn_2 and AZn_2Pn_2 , the A-sites of these materials have been shown to exclusively contain divalent ions,³ which limits rare-earth ions to Sm, Eu, and Yb. To date no samarium containing compounds have been reported. Here we describe the synthesis and characterization of the two new phases, SmMg_2Bi_2 and SmMg_2Sb_2 . We present structural, magnetic, thermal, and electrical properties of AMg_2Bi_2 ($\text{A} = \text{Sm}, \text{Eu}, \text{Yb}$) single crystals grown from a magnesium-rich flux and compare the results with previous investigations.

Experimental

Synthesis

Single crystals of LnMg_2Bi_2 ($\text{Ln} = \text{Yb}, \text{Eu}, \text{Sm}$) were grown and isolated from a molten Mg-Bi flux. The starting materials were elemental magnesium (Alfa-Aesar, 99.98%), elemental bismuth (Gallard-Schlesinger, 6N), and elemental rare-earth (Yb, Eu, Sm) metal (Aldrich 99.9%) in the molar ratio of 25:5:1 for Mg:Bi:Ln. SmMg_2Sb_2 crystals were grown from a corresponding Mg-Sb flux with the same respective molar ratio of 25:5:1. The starting materials were loaded under ~ 1 atm Ar atmosphere into stainless steel crucibles that were subsequently welded shut and sealed in quartz ampoules under vacuum. The sealed ampoules were heated to 1000 °C in 10 hours, held for 20 hours,

and subsequently cooled to 700 °C over a period of 150 hours. At 700 °C the ampoules were removed from the furnace and centrifuged to separate the flux from the crystals.

The choice of molar ratios and heating profile is informed by the binary Mg-Bi phase diagram,¹² where the β -Mg₃Bi₂ phase (*Im3m*) region is avoided and the CaAl₂Si₂-type α -Mg₃Bi₂ phase (*P3m1*) region is targeted. Previous synthesis methods of LnMg₂Bi₂ utilized Bi-rich fluxes (Mg:Bi ratio 4:6) and cooling to 650°C,¹³ whereas the flux described in this work is magnesium rich, producing the largest crystals when cooling to 700°C. The flux is never slow-cooled into the liquid-solid two phase region, indicating that the LnMg₂Bi₂ phases must have a higher stability than the corresponding Mg(Mg₂Bi₂) phases. SmMg₂Bi₂ growth was only observed in magnesium-rich fluxes with molar ratios Mg:Bi:Sm around 25:5:1. The crystals are chemically stable, but show a decrease in metallic luster after 48 hours in ambient conditions.

Phase Identification

EDS analysis using a JEOL 5900 scanning electron microscope confirmed the stoichiometry of LnMg₂Bi₂ having a molar Ln:Mg:Bi ratio of 1:2:2 to within 5 at.% (XRF2007 Software). The crystals were structurally characterized by single crystal x-ray diffraction using an Oxford-Diffraction Xcalibur2 CCD system with graphite monochromated MoK α radiation. The as-grown crystals were transferred from the glovebox under Paratone-N oil and cleaved in the oil. Shards of appropriate size were selected, mounted in cryo-loops, and aligned in a cold nitrogen stream for data collections at 200 K. Reflections were recorded, indexed and corrected for absorption using the Oxford-Diffraction CrysAlis software making sure that reflections were observed up to $2\theta = 100^\circ$.¹⁴ Subsequent structure refinements were carried out using CRYSTALS⁵ and CIFs were deposited with ICSD (ICSD# 428792-428795).¹⁶

Magnetic, Electronic, and Physical Property Measurements

Temperature dependent magnetic susceptibility ($\chi = M/H$) measurements were carried out using a Quantum Design MPMS SQUID system in the range of 2-300 K and at a field of 0.1 to 0.5 T. The single crystals were fixed with cotton wool inside a gel capsule and attached to a brass rod using an open ended plastic straw. A Quantum Design PPMS system was used to measure the zero-field heat capacity (C_p) in a temperature range of 0.4-20 K. The crystals were embedded in Apiezon N-grease; an addendum of the N-grease was taken prior to the experiment. Electrical resistivity (ρ) was measured using Van der Pauw 4-point contact geometry in the temperature range 1.8 K to 300 K. The data agrees well with the data previously reported for thK using the same PPMS system. Gold leads were attached to single crystals using silver paste solvated in 2-butoxy-ethylacetate.

Qualitative Seebeck measurements were carried out using a nano-voltmeter and heat source; the same type of gold leads and paste used in the resistivity experiments were used here.

Results and Discussions

Figure 1. (a) Crystal structure with unit cell outlined of LnMg₂Bi₂ compounds. (b) Image of as grown SmMg₂Bi₂ crystal placed on a millimeter grid, the flat face is the (001) plane.

Structural Properties

The single crystals are metallic in appearance with a silver luster and plate-like morphology (Figure 1b). The large flat face is determined to be the (ab)-plane. The phases LnMg₂Bi₂ crystallize in the CaAl₂Si₂ structure type (trigonal, No. 164, *P3m1*); results of the structure refinements are given in Table 1, atomic and thermal parameters in Table 2, and selected bond angles and distances in Table 3. The unit cell parameters of SmMg₂Bi₂ ($a = 4.7745(1)\text{\AA}$, $c = 7.8490(2)\text{\AA}$) and EuMg₂Bi₂ ($a = 4.7702(1)\text{\AA}$, $c = 7.8457(2)\text{\AA}$) are similar, with SmMg₂Bi₂ having slightly larger unit cell parameters in all directions, as expected from ionic radii considerations (Sm²⁺ 1.36 $\text{\AA}$ compared to Eu²⁺ 1.31 $\text{\AA}$). For comparison, the ionic radius of Yb²⁺ is 1.16 $\text{\AA}$ ¹⁷ resulting in smaller unit cell parameters for YbMg₂Bi₂ ($a = 4.7317(2)\text{\AA}$, $c = 7.6524(3)\text{\AA}$). The similarity in ionic radii of Eu²⁺ and Sm²⁺ provides these analogs with very similar structural properties and potentially, mixed phases should be possible.¹³ Our structural data agrees well with the data previously reported for the LnMg₂Bi₂ and LnMg₂Sb₂ compounds.^{13,30}

Table 1: Single crystal diffraction data and collection parameters for LnMg₂Bi₂, and SmMg₂Sb₂ (T = 200K)

Space group: $P\bar{6}m1$ (#164) $Z = 1$		Parent Structure: CaAl ₂ Si ₂		
Formula	SmMg ₂ Sb ₂	SmMg ₂ Bi ₂	EuMg ₂ Bi ₂	YbMg ₂ Bi ₂
ICSD#	428793	428792	428795	428794
a (Å)	4.6861 (1)	4.7745 (1)	4.7702 (1)	4.7317 (2)
c (Å)	7.7192 (2)	7.8490 (2)	7.8457 (2)	7.6524 (3)
vol (Å ³)	146.800 (6)	154.954 (7)	154.611 (6)	148.375 (10)
calc. density (g/cm ³)	5.005	6.611	6.643	7.158
Data collection range	5.02 < θ < 54.04	4.93 < θ < 53.92	4.94 < θ < 66.46	4.97 < θ < 54.01
Reflections	4660	4899	7102	4652
Independent refl.	742	769	1104	745
Parameters refined	10	9	9	10
R _w , wR ₂ (all data)	0.0362, 0.0409	0.0447, 0.0529	0.0597, 0.0641	0.0381, 0.0447
Goodness-of-fit	0.9782	1.0651	1.0914	1.0890

Table 2: Refined structural parameters

	atom	atomic coordinates			U ₁₁ = U ₂₂	U ₃₃	U _{eq}
		x	y	z	Å ²	Å ²	Å ²
SmMg ₂ Sb ₂	Sm	0	0	0	0.00889(8)	0.00829(10)	0.0087
	Mg	1/3	2/3	0.6304(2)	0.0105(4)	0.0098(6)	0.0103
	Sb	1/3	2/3	0.25380(3)	0.00748(7)	0.00765(9)	0.0075
SmMg ₂ Bi ₂	Sm	0	0	0	0.01208(11)	0.01183(16)	0.0120
	Mg	1/3	2/3	0.6279(4)	0.0142(7)	0.0129(10)	0.0138
	Bi	1/3	2/3	0.25032(3)	0.01033(8)	0.01103(10)	0.0106
EuMg ₂ Bi ₂	Eu	0	0	0	0.01391(10)	0.01517(13)	0.0143
	Mg	1/3	2/3	0.6283(5)	0.0159(6)	0.0174(9)	0.0164
	Bi	1/3	2/3	0.25009(3)	0.01216(7)	0.01434(8)	0.0129
YbMg ₂ Bi ₂	Yb	0	0	0	0.01846(13)	0.01643(17)	0.0092
	Mg	1/3	2/3	0.6313(5)	0.0174(8)	0.0164(11)	0.0087
	Bi	1/3	2/3	0.24123(4)	0.01466(8)	0.01446(11)	0.0073

Table 3: Bond distances and angles for LnMg₂Bi₂ and SmMg₂Sb₂

	bond distances (Å)		bond angles (deg)	
SmMg ₂ Sb ₂	Sm – Sb (1)	3.3404(2)	Sb – Sm – Sb (β)	89.080(5)
	Mg – Sb (2)	2.8494(6)	Sb – Mg – Sb (α)	110.583(3)
	Sm – Sm (3)	4.6861 (1)		
SmMg ₂ Bi ₂	Sm – Bi (1)	3.3851(1)	Bi – Sm – Bi (β)	89.699(5)
	Mg – Bi (2)	2.918(1)	Bi – Mg – Bi (α)	109.807(6)
	Sm – Sm (3)	4.7745 (1)		
EuMg ₂ Bi ₂	Eu – Bi (1)	3.382(1)	Bi – Eu – Bi (β)	89.714(4)
	Mg – Bi (2)	2.915(1)	Bi – Mg – Bi (α)	109.825(7)
	Eu – Eu (3)	4.7702 (1)		
YbMg ₂ Bi ₂	Yb – Bi (1)	3.2966(2)	Bi – Yb – Bi (β)	91.709(7)
	Mg – Bi (2)	2.899(2)	Bi – Mg – Bi (α)	109.285(8)
	Yb – Yb (3)	4.7317 (2)		

Physical properties

SmMg₂Sb₂:

Single crystals of SmMg₂Sb₂ were sufficiently large for x-ray diffraction studies; however the electronic property studies of this material were hampered by the size limitations.

SmMg₂Bi₂, EuMg₂Bi₂, YbMg₂Bi₂:

Magnetism

The magnetic susceptibility data $\chi = M/H$ ($H = 0.5T$) versus temperature for single crystal SmMg₂Bi₂ is shown in Fig. 2. Van Vleck paramagnetic behavior is observed with a susceptibility plateau between 10K and 100K and a Curie tail developing below 10K. The plateau region is typical of ions with electron configuration 4f⁶ and is seen in compounds containing Eu³⁺ ions,¹⁸ but is also notable in Sm²⁺ systems such as the samarium monochalcogenides¹⁹ or SmB₆.²⁰ The Curie tail is likely attributed to magnetic impurities within the sample such as Sm³⁺ cations or contamination from the stainless steel crucibles.

The magnetic susceptibility temperature dependence was modeled for SmMg₂Bi₂ using a Russel-Saunders coupling scheme for the spin-orbit interaction, where $\lambda L \cdot S$ represents the separation in ⁷F_J multiplets in divalent Sm²⁺. The following Van Vleck model is used to fit the data:

$$\chi_m = \frac{N_A \mu_B^2}{k_B} \left(\frac{1}{2J+1} \sum_{J=0}^6 \frac{J(J+1)}{J(J+1) - \lambda^2} + \frac{1}{2J+1} \sum_{J=0}^6 \frac{J(J+1)}{J(J+1) - \lambda^2} \right) \quad (1)$$

The expression is summed over the various multiplet states ($J = 0$ to 6) with $J(J+1) = J(J+1) - 1$.¹⁸ The coupling constant λ is the energy difference between the ground state and first excited state, and J is the total angular momentum for Sm²⁺. The χ_m term is a second order Zeeman term which represents the mixing of multiplet states for J and $J \pm 1$.²¹ This is defined as:

with

A modified Curie law is added to model the susceptibility due to impurities. Assuming the presence of Sm³⁺, the following simple expression can be applied:

$$\chi_m = \chi_{\text{Curie}} + \chi_{\text{Van Vleck}} \quad (2)$$

Here, χ_0 is attributed to coupling between the $J=5/2$ ground state and the $J=7/2$ state allowed due to the small energy difference between the multiplets.²¹⁻²³ The total magnetic susceptibility is therefore:

$$\chi_m = \chi_{\text{Curie}} + \chi_{\text{Van Vleck}} \quad (3)$$

The susceptibility data is shown in figure 2 with orientation $H \perp c$ and $H \parallel c$ under a field of 0.5T.

Magnetic anisotropy is seen, with a slightly larger susceptibility resulting from H applied $\parallel c$. The results of the fit (eq. 3) are presented in table 4. The coupling constants λ for $H \parallel c$ and $H \perp c$ are 409K and 450K respectively, which are in agreement with Van Vleck's theoretical work of 418K for free ions with the configuration [Xe]4f⁶.²¹ In figure 2 the solid lines are the susceptibility fits (eq. 3), the Sm²⁺ contribution (eq. 1) is plotted as a dashed line, and the impurity susceptibility (eq. 2) is plotted as the dotted line below the break. Sm²⁺ ions dominate the behavior of the magnetic susceptibility providing more than 95% of the overall moment. The most notable contribution from the impurities appear below 10K. Using the effective moment for Sm³⁺ ($\mu_{\text{eff}} = 0.85\mu_B$)²¹ with the obtained Curie constant C , the amount of Sm³⁺ impurities is found to be of the order of 0.7%. If the experimental moment for Sm³⁺ free ions ($\mu_{\text{eff}} = 1.54\mu_B$)²¹ is used, a lower concentration of the order of 0.2% is found.

Figure 2: χ vs T for SmMg₂Bi₂ single crystal at a field of 0.5T. The solid curves are the total fits using equation (3), the Curie fit equation (2) is represented by the dotted line, and the Van Vleck fit equation (1) is represented by the dashed line. The parameters resulting from the fit are given in table 4.

Table 4: Fit parameters for SmMg₂Bi₂ magnetic susceptibility

	$H \perp c$	$H \parallel c$
λ (K)	450	409
C (cm ³ /mol·K)	7.32×10^{-4}	5.57×10^{-4}
χ_0 (cm ³ /mol)	1.21×10^{-4}	3.65×10^{-4}
Sm ³⁺ ($\mu_{\text{eff}} = 0.85\mu_B$)	0.81%	0.62%
Sm ³⁺ ($\mu_{\text{eff}} = 1.54\mu_B$)	0.25%	0.18%

Single crystals of EuMg₂Bi₂ show Curie-Weiss behavior followed by antiferromagnetic ordering with $T_N \approx 7K$ (Fig. 3). The larger susceptibility of the samples with c -

axis orientation $\perp$ to the field indicates the magnetic moments are aligned along the c-axis. A Curie-Weiss fit to the paramagnetic region yields an effective moment of $7.98 \mu_B$ per Eu atom, in agreement with Hund's rules. The Weiss temperature of $-3.6K$ is consistent with the ordering temperature, and previously reported values.¹³

Figure 3: χ_m vs T for EuMg_2Bi_2 single crystal at a field of 0.1 T. An antiferromagnetic transition is observed at 7 K. The inset is a plot of χ_m^{-1} vs T with a linear fit yielding $\mu_{\text{eff}} = 7.98 \mu_B$ and a Weiss temperature of $-3.6 K$

Heat capacity

Results from heat capacity for LnMg_2Bi_2 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) are shown in Figure 4. The results for the non-magnetic compounds (Sm, Yb) are typical for semi-metal compounds. The inset in figure 4 illustrates the temperature dependence of the specific heat plotted as C_p/T vs T^2 . This data is fitted to the relation

$$\frac{C_p}{T} = \gamma + \beta T^2$$

where γ denotes the Sommerfeld coefficient of the electronic contribution and β denotes the coefficient of the lattice contribution. The fit yields the values $\gamma \approx -0.0016(20) \text{ J/mol}\cdot\text{K}^2$ and $\beta \approx 0.0020(20) \text{ J/mol}\cdot\text{K}^4$ for SmMg_2Bi_2 with $\gamma \approx -0.0013(20) \text{ J/mol}\cdot\text{K}^2$ and $\beta \approx 0.0024(20) \text{ J/mol}\cdot\text{K}^4$ for YbMg_2Bi_2 . The essentially zero gamma term indicates an electron poor system with little electronic contribution to the heat capacity. A Debye integral fit of the nonmagnetic data provides Debye temperatures of $\Theta_D = 138 K$ and $130 K$ for SmMg_2Bi_2 and YbMg_2Bi_2 , respectively. This result suggests that the lattice is quite soft, by comparison to typical ternary rare-earth intermetallics such as TbCu_2Si_2 which provides a $\Theta_D = 201 K$ ²⁴.

The antiferromagnetic ordering of EuMg_2Bi_2 at 7 K is clearly observed in the heat capacity measurements. The entropy change ($\Delta S = R \ln(2J+1)$ and $J = 7/2$) for the magnetic transition is predicted to be $17.3 \text{ J/mol}\cdot\text{K}$ for Eu^{2+} .²⁵ Since the phonon contributions to heat capacity for both EuMg_2Bi_2 and SmMg_2Bi_2 are similar due to similar structure parameters, SmMg_2Bi_2 is used as a nonmagnetic reference to find the entropy change of the antiferromagnetic phase transition, resulting in $\Delta S =$

$16.7 \text{ J/mol}\cdot\text{K}$. However, it can be observed from figure 4 that some residual entropy remains below 7 K, possibly due to some remaining spin degrees of freedom. Similar antiferromagnetic behavior has been observed in other rare-earth containing compounds of various crystal structures.²⁶⁻²⁸

Figure 4: C_p/T versus T^2 for the measured compounds from 0.4 – 20 K. The inset provides low temperature data for the non-magnetic compounds.

Electronic Transport

All phases measured behaved similarly showing semi-metallic behavior with a positive coefficient of temperature. These materials are expected to be semiconductors as determined by electronic structure calculations.¹³ Previous Hall probe transport measurements identified the carriers to be p-type.^{5,13} In SmMg_2Bi_2 the qualitative Seebeck measurement also showed p-type behavior.²⁹

In EuMg_2Bi_2 the antiferromagnetic transition can be seen as a gradual increase in resistivity as the temperature decreases towards 7 K, with an abrupt decrease in resistivity below 7 K as expected from the magnetic ordering of the sample removing magnetic scattering of the carriers. Both SmMg_2Bi_2 and YbMg_2Bi_2 show similar behavior in resistivity, with Yb having a slightly higher resistivity. RRR values were determined by taking $\rho(300 K)/\rho(10 K)$; giving 2.04, 2.40, and 1.57 for SmMg_2Bi_2 , YbMg_2Bi_2 , and EuMg_2Bi_2 respectively. The RRR values for these samples are larger than those previously obtained¹³ indicating higher purity. The increased resistivity of these samples compared to the previous samples follows the assertion that the conductivity arises from impurities. The presence of Ln^{3+} could account for the p-type conductivity seen in these materials^{6,13}.

Figure 5: Resistivity of all Bi-containing compounds between 1.8K and 300K exhibiting semi-metallic behavior.

Conclusion

Two new compounds SmMg_2Bi_2 and SmMg_2Sb_2 along with the previously discovered YbMg_2Bi_2 and EuMg_2Bi_2 analogs were synthesized as single crystals using Mg-rich Mg-Bi/Sb fluxes. Divalent samarium is stabilized in SmMg_2Sb_2 and SmMg_2Bi_2 crystals grown from magnesium-rich fluxes.

The magnetic behavior of SmMg_2Bi_2 was modeled using Van Vleck theory for ions in a $[\text{Xe}]4f^6$ electronic state, proving the presence of Sm^{2+} . The magnetism data was further used to estimate the existence of 0.2% to 0.7% Sm^{3+} ions in the system. Electronic transport studies show that the materials behave as poor metals with p-type conductivity, suggesting conduction arises from sample impurities such as Ln^{3+} . The similarity between the structures for SmMg_2Bi_2 and EuMg_2Bi_2 allowed accurate determination of the entropy of the antiferromagnetic transition of EuMg_2Bi_2 . The electronic properties of the Sb analogs are expected to be similar to the Bi analogs. In addition SmMg_2As_2 and SmMg_2P_2 may also exist.³⁰

Furthermore the highly reducing nature of the magnesium-rich flux is shown to produce the single crystals of LnMg_2Bi_2 from lanthanide starting materials in the form of Ln_2O_3 . The reaction ratios of 25:5:1; Mg:Bi: Ln_2O_3 produced the single crystals, albeit at lower yields with significant amounts of MgO from the reduction of Ln_2O_3 to Ln.

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Table of Contents Caption: Magnetic susceptibility data for SmMg_2Bi_2 , modeled using Van Vleck Theory for temperature independent magnetism. The model proves the electron configuration for the samarium ions to be $[\text{Xe}]4f^6$ and therefore Sm^{2+} . The model is modified to include impurities which can be used to estimate an impurity concentration of 0.2% Sm^{3+} ions.