Metal to Semi-metal Transition in CaMgSi Crystals Grown from Mg-Al Flux

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Introduction
Magnesium alloys and intermetallics are being widely investigated as potential aerospace and hydrogen storage materials because of their low expense and mass. This has led to growing interest in the properties of compounds in the ternary Mg-Ca-Si system; these ternaries often occur as adventitious byproducts in Mg-based composites. CaMgSi is commonly observed as a precipitate in Mg alloys which increases tensile strength. However, synthesis of single phase samples (particularly formation of single crystals) is problematic. In this work large single crystals of CaMgSi were reproducibly synthesized in a molten Mg/Al mixture flux. A variety of other synthetic techniques and fluxes were explored, but these produced multi-phase products of polycrystalline CaMgSi, Mg_2Si, Ca_2Si and CaMg_{2-x}Si_x. In addition to its mechanical properties, the electronic behavior of CaMgSi is of particular interest. From its stoichiometry, this compound would appear to be related to the Zintl phases Mg_2Si and Ca_2Si; it is in fact a substitutional variant of Ca_2Si. CaMgSi is therefore expected to be a Zintl phase. However, our findings indicate that this phase spans the boundary between charge balanced semiconducting Zintl phases and fully delocalized intermetalics.

Experimental
Single crystals of CaMgSi were produced using the metal flux synthesis method in a Mg/Al (1:1) flux mixture. The elements Mg/Al/Ca/Si were weighed out in a 15/15/3/3 mmol ratio and placed into a niobium crucible which was welded shut under argon and sealed in a silica tube. After quickly heating to 950 ºC, the ampoule was cooled to 750 ºC in 60 hours and then removed from the furnace and centrifuged to separate the crystals from the molten flux. Elemental analysis by SEM-EDS and single crystal XRD studies were carried out to confirm the identity of the products. Si MAS-NMR spectra were collected and density of states calculations carried out. Variable temperature powder XRD data were collected using the low temperature diffractometer in the Wiebe lab (NHMFL). Transport and heat capacity measurements were carried out using the PPMS system in the Tozer research lab in NHMFL. Magnetic susceptibility data were collected on a SQUID; variable temperature EPR spectra were obtained with assistance from the Hill group (NHMFL).

Results and Discussion
CaMgSi grows from Mg/Al flux as large rod-shaped crystals up to 7 mm in length. This phase crystallizes with the orthorhombic TiNiSi structure type (space group Pnma; a = 7.4752(2) Å, b = 4.42720(10) Å, c = 8.3149(2) Å; R_1 = 0.021). Despite its relationship to semiconducting Zintl phases Mg_2Si and Ca_2Si, CaMgSi is metallic at room temperature; this produces a positive (~150 ppm) Si MAS NMR chemical shift and is supported by DOS calculations. An electronic transition at around 50 K is evident in the resistivity, magnetic susceptibility and electron paramagnetic resonance measurements. Low temperature powder X-ray diffraction data indicates a structural distortion accompanies this transition. The electronic heat capacity coefficient (0.4695 mJ/molK^2) determined from low temperature heat capacity data supports the designation of CaMgSi as a semi-metal at low temperature. The transition at 50 K therefore appears to be a metal-to-semimetal transition accompanied by a very subtle structural distortion. The hydrogen storage capacity of the crystals is negligible (≤0.5 wt.% hydrogen), although exposure to hydrogen does destabilize the structure, inducing decomposition at 500 ºC.

Acknowledgements
This research was supported by the National Science Foundation (grant award number DMR-05-47791). C.R.W. acknowledges support from the NSF (DMR-0084173). Use of the Tozer group Open Door Laboratory facilities at NHMFL is made possible by support from DOE/NNSA (grant number DE-FG52-06NA26193, NSF and the State of Florida).

References