Structure and Properties of Single Crystalline $CaMg_2Bi_2$, $EuMg_2Bi_2$, and $YbMg_2Bi_2$

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Supplemental Information

Synthesis

Single crystals were obtained via the metal-flux method using nominal melt compositions of AMg_4Bi_6, where A = Ca, Yb, or Eu. The growth occurred in either 2 or 5 mL Al_2O_3 crucibles, using one additional crucible filled with quartz wool to catch the molten metal expelled during centrifugation. High-purity elements were loaded into the crucibles inside a He glove box, which were then placed inside a quartz ampoule and quickly transferred to a vacuum line for sealing after purging with argon. The sealed ampoules were heated to 900°C in 8 h, then cooled to 850°C in 1 h, then to 750°C in 10 h, and finally to 650°C in 24 h. The sealed ampoules were removed from the furnace at 650°C and quickly transferred to a centrifuge to remove the excess molten metal. Signs of reaction between the magnesium vapor and silica ampoules were evident, though fast cooling

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to 750°C appeared to reduce this process and only a slight brown coating was generally present on the silica. No crystals were obtained when the melt was centrifuged at 750°C, suggesting the complete solubility of the crystals at this temperature. The effect of cooling rate between 750°C and 650°C was briefly investigated, with faster and slower rates considered but neither providing noteworthy changes in crystal growth (as observed by the naked eye). It is believed that the fairly fast growth is beneficial as it limits the vapor phase loss of Mg. We note the effect of cooling rate on the transport properties has not been investigated. Elemental Yb and Eu were obtained from the Ames Research Laboratory, dendritic Ca from Alfa Aesar, and magnesium slugs and Bi shot were employed.

Powder diffraction refinement results

Figure 1 contains representative powder diffraction data for hand-ground crystals of AMg$_2$Bi$_2$ grown from the Mg-Bi flux, with a nominal composition AMg$_4$Bi$_6$. The Rietveld refinements results are presented in Table 1; these refinements included data up to 135°2Θ. A Bi impurity peak is detected near 27.2°2Θ, this is most likely due to excess flux on the crystal surfaces. The region between 26 and 29°2Θ has not been included in the fit, and is thus shown in grey. Powder x-ray diffraction data were collected at ambient conditions on a PANalytical X'Pert Pro MPD using an incident beam Cu K$_{\alpha,1}$ monochromator, and were refined using the program FullProf.[1]

Table 1: Selected parameters from refinements of powder x-ray diffraction data for CaMg$_2$Bi$_2$, YbMg$_2$Bi$_2$, and EuMg$_2$Bi$_2$ collected at room temperature.

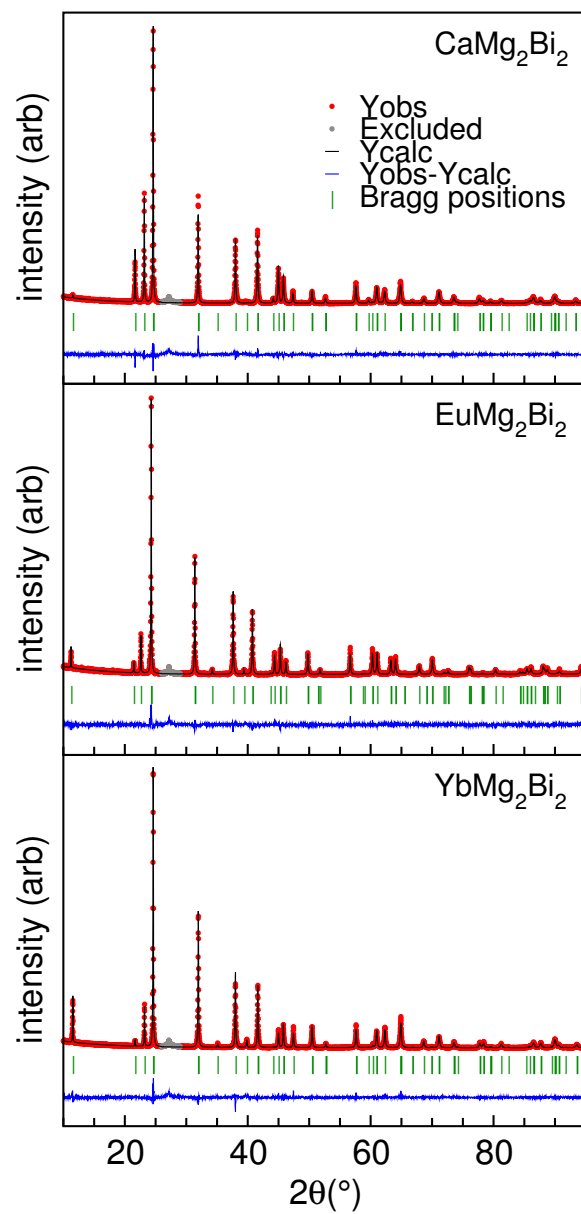| empirical formula	CaMg$_2$Bi$_2$	EuMg$_2$Bi$_2$	YbMg$_2$Bi$_2$
a (Å)	4.7308(1)	4.7771(1)	4.7321(1)
c (Å)	7.6720(2)	7.8524(1)	7.6606(1)
vol (Å^3)	148.704(5)	155.189(5)	148.560(4)
Bi position z	0.2408(2)	0.2503(3)	0.2415(2)
Mg position z	0.6288(9)	0.625(1)	0.6310(9)
B$_{ov}$	0.78(2)	0.32(3)	0.39(2)
χ^2	2.46	1.70	2.27
R_p / R_{wp}	10.1 / 13.6	7.74 / 9.93	9.90 / 13.2
Bragg R-factor	5.11	6.45	4.77

Figure 1: Powder x-ray diffraction data and Rietveld refinements for the title compounds. Data were collected on hand-ground crystals at room temperatures.

Electronic structure calculations

The present calculations were performed relativistically with the all-electron general potential linearized augmented planewave (LAPW) method,[2] using the WIEN2k code[3] and include spin-orbit coupling for all elements. Dense samplings of the Brillouin zone and well converged LAPW basis sets were used with local orbitals to relax linearization errors and include semicore states.[4] The zone samplings were done with uniform 32x32x16 grids, while the cut-offs for the basis set K_{max} were obtained with the criterion $RK_{max}=9$, where R is the smallest LAPW sphere radius. The LAPW sphere radii were 2.5 bohr for Ca and Mg, and 2.8 bohr for Bi.

The approach is the same as we used in our prior study of halide scintillators with the TB-mBJ functional.[5] Specifically, a standard generalized gradient approximation (GGA) functional is used to relax the internal coordinates in the unit cell by total energy minimization. This was done using the experimental lattice parameters of Reference 6 and the GGA of Perdew and co-workers (PBE).[7] The relaxed coordinates were within 1% of those in Table 1. We then used the resulting structural parameters to calculate the electronic structure and optical absorption (optical package of the WIEN2k code) using the recently developed modified Becke Johnson functional of Tran and Blaha, denoted TB-mBJ here.[8] Unlike standard GGA functionals, which are designed to reproduce total energies and structures but underestimate the band gaps of semiconductors,[9] the TB-mBJ functional cannot be used for total energy calculations, but does yield very much improved band gaps in a wide variety of materials.[8,10]

References

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