Supporting Information

Alloying Induced Superionic *β*-Phase Formation in Mg_3Sb_2 based Zintl Compounds

Nagendra Singh Chauhan[1] and Takao Mori[1,2 *]

[1]International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, 305-0047, Japan.
[2]Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.

*Corresponding author: mori.takao@nims.go.jp
Tel: +81-29-860-4323; Fax: +81-29-851-6280

S1. Structural Refinement - The lattice parameters and phase identification of synthesized $Mg_3(Sb_{1-x-y}Bi_xGe_y)_2$ nanocomposites were determined using a (3+1) dimensional superspace group approach employing Le Bail analysis performed on the JANA2006 software package. The red circles correspond to the data points, the black line denotes the calculated pattern, and the difference map is shown in blue. Olive vertical ticks correspond to Bragg reflections.

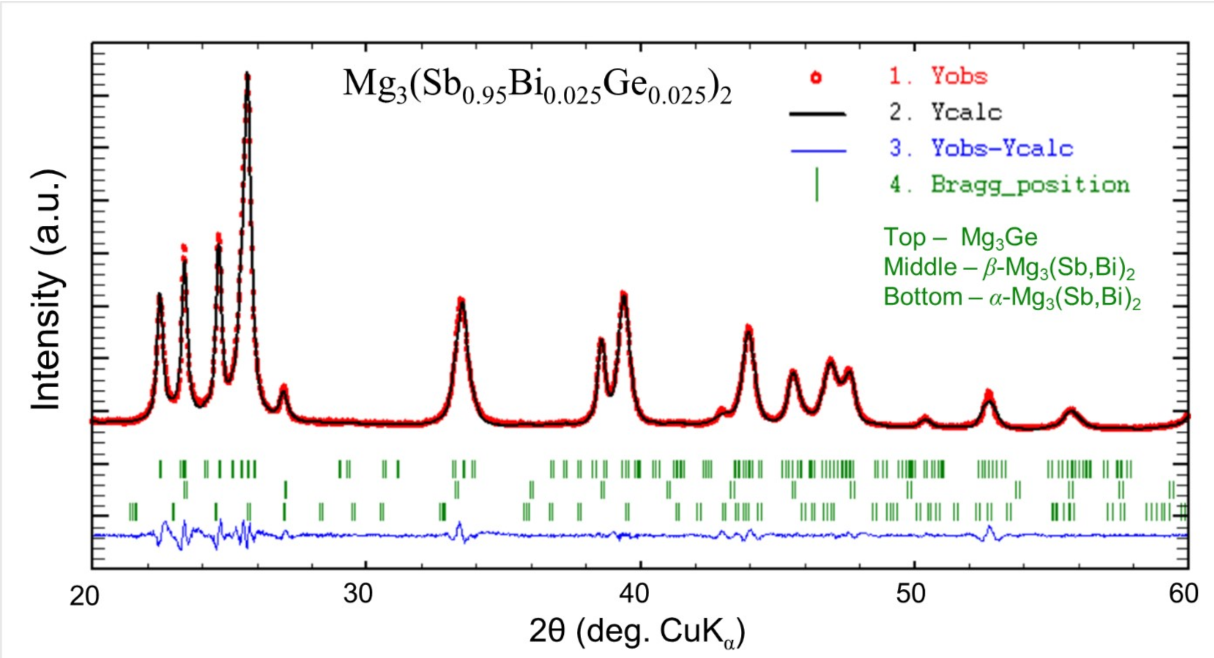

Figure S1. Le Bail analysis of XRD pattern of pulverized sintered sample with a nominal composition of $Mg_3(Sb_{0.95}Bi_{0.025}Ge_{0.025})_2$.

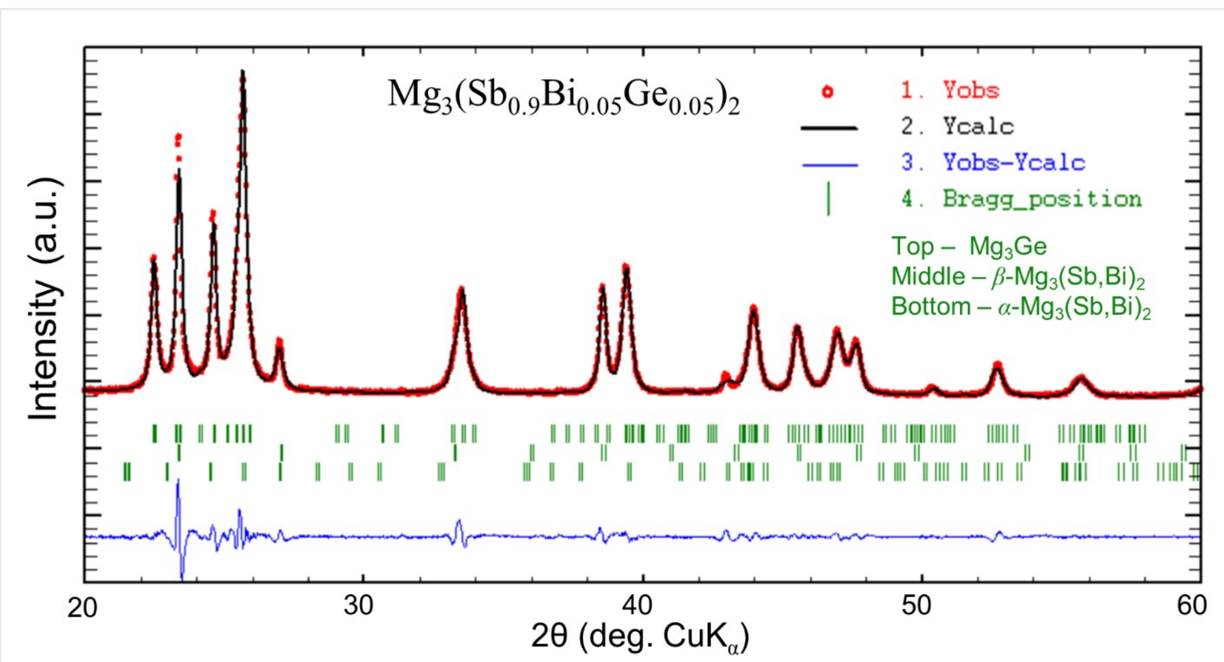

Figure S2. Le Bail analysis of XRD pattern of pulverized sintered sample with a nominal composition of $Mg_3(Sb_{0.8}Bi_{0.05}Ge_{0.05})_2$.

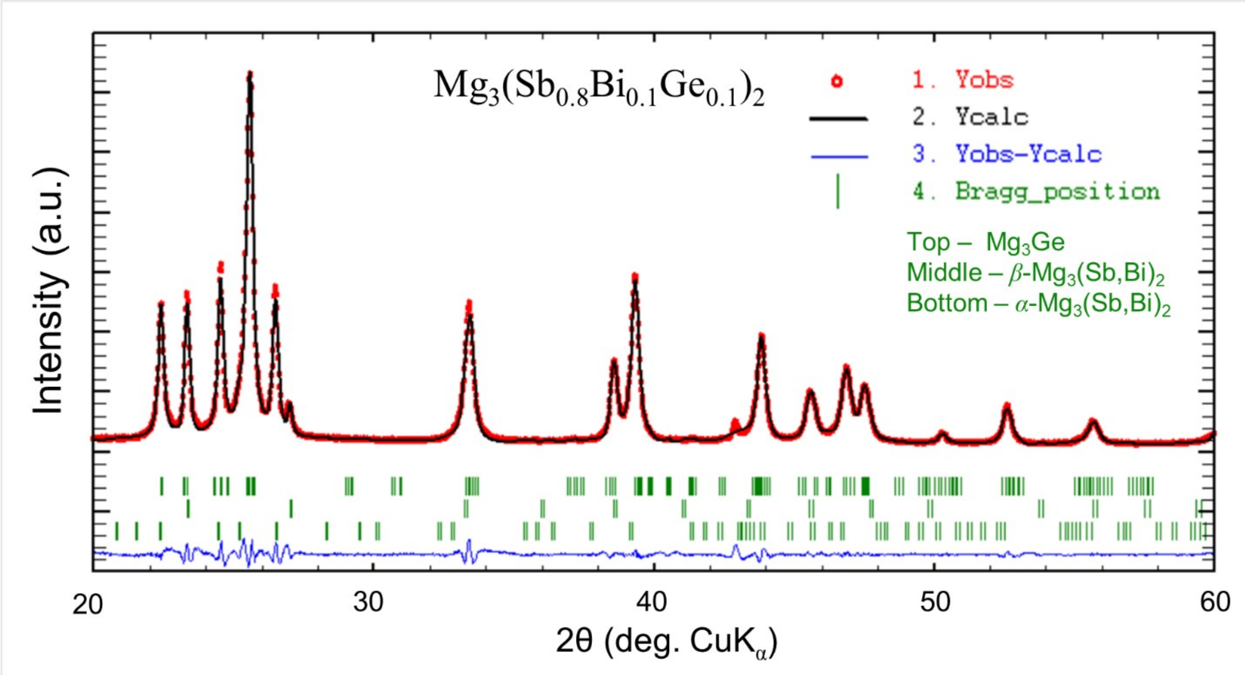

Figure S3. Le Bail analysis of XRD pattern of pulverized sintered sample with a nominal composition of $Mg_3(Sb_{0.8}Bi_{0.1}Ge_{0.1})_2$.

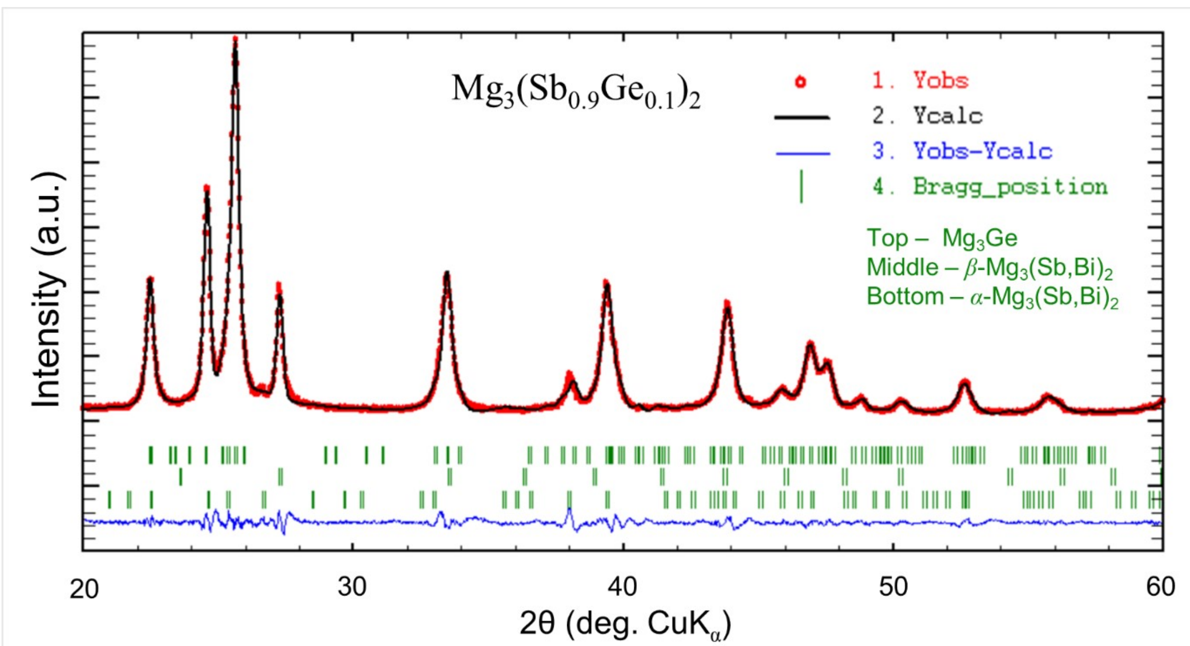

Figure S4. Le Bail analysis of XRD pattern of pulverized sintered sample with a nominal composition of $Mg_3(Sb_{0.9}Ge_{0.1})_2$.

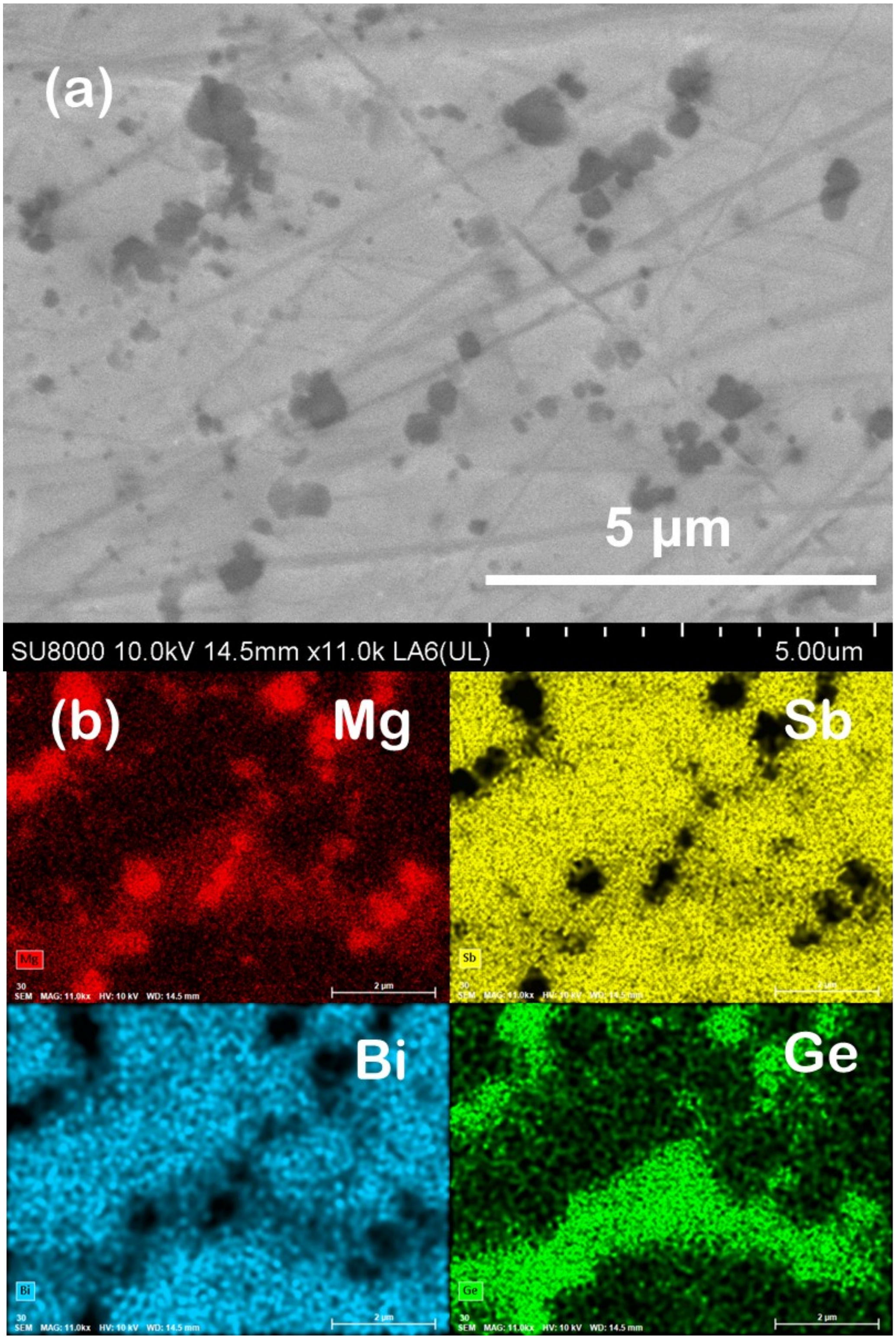

Figure S5. (a). BSE-SEM micrographs displaying the polished surface of the sintered bulk of representative $Mg_3(Sb_{1.9}Bi_{0.05}Ge_{0.05})_2$ constituting nanoprecipitates corresponding to Mg_3Ge phase. (b) The elemental mapping indicating Mg and Ge rich domains within the microstructure.

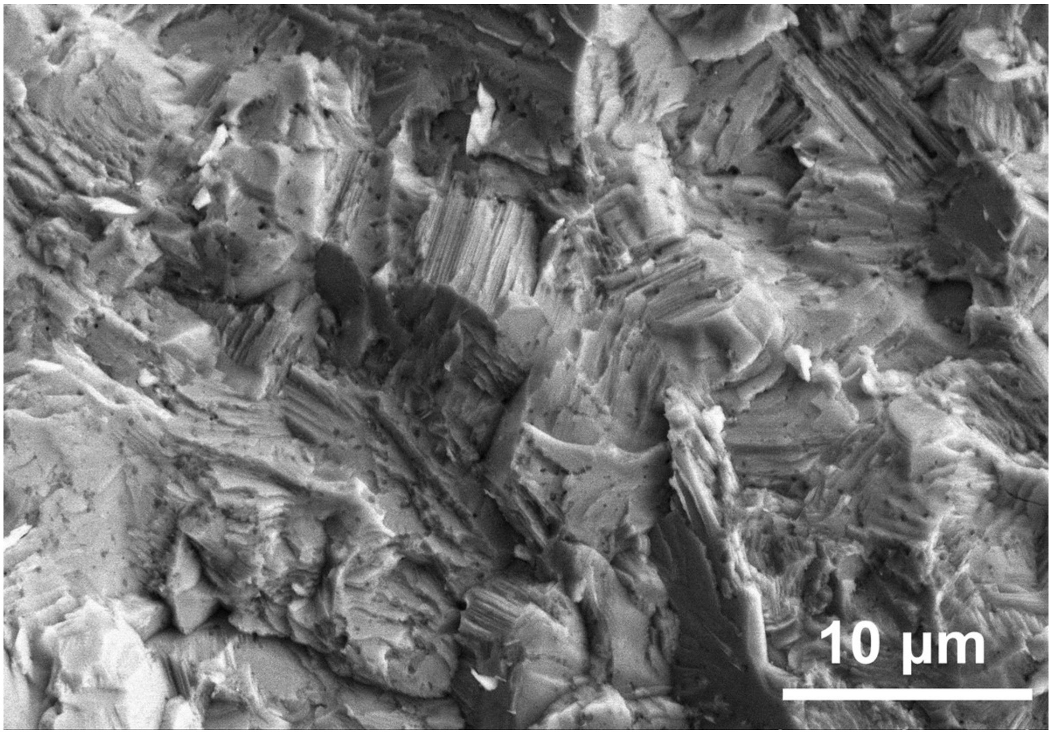

Figure S6. BSE-SEM micrographs showing the fractured surface of representative $Mg_3(Sb_{1.9}Bi_{0.05}Ge_{0.05})_2$ indicating embedded nanoprecipitates corresponding to Mg_3Ge phase within the layered α-$Mg_3(Sb, Bi)_2$.

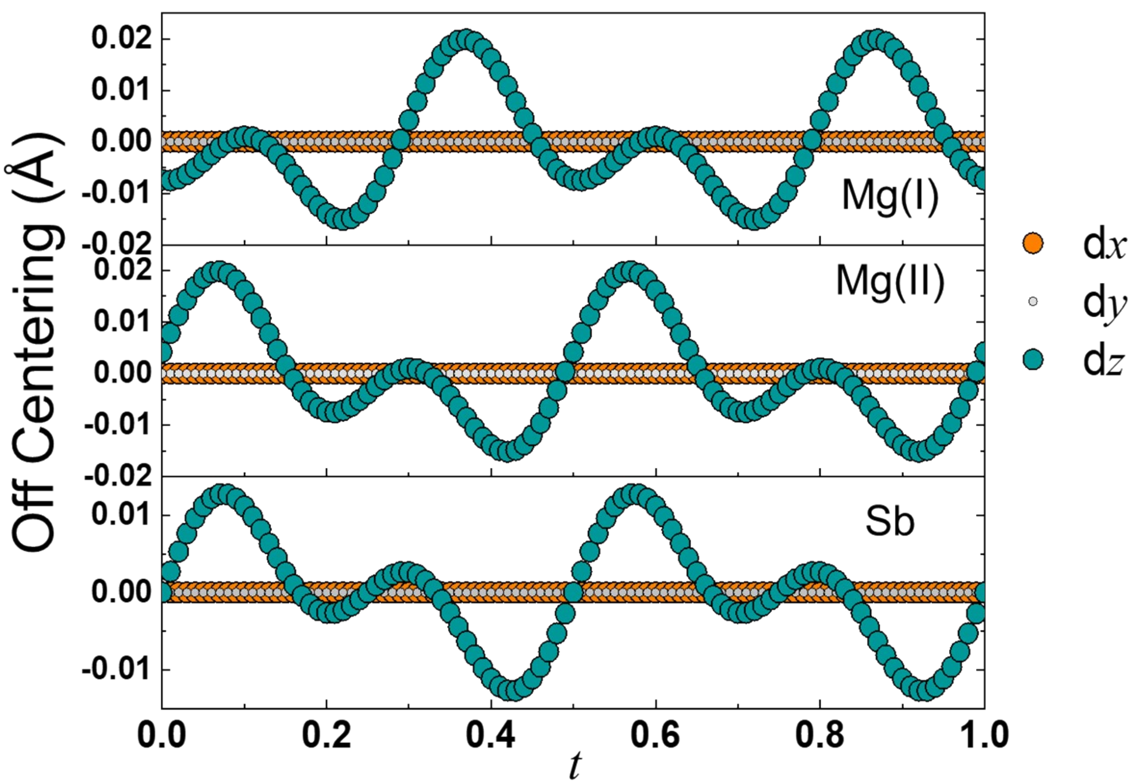

Figure S7. Evaluated off-centering for Mg(I), Mg(II) and Sb atoms along *x*, *y,* and *z* directions for the synthesized $Mg_3(Sb_{0.95}Bi_{0.025}Ge_{0.025})_2$.

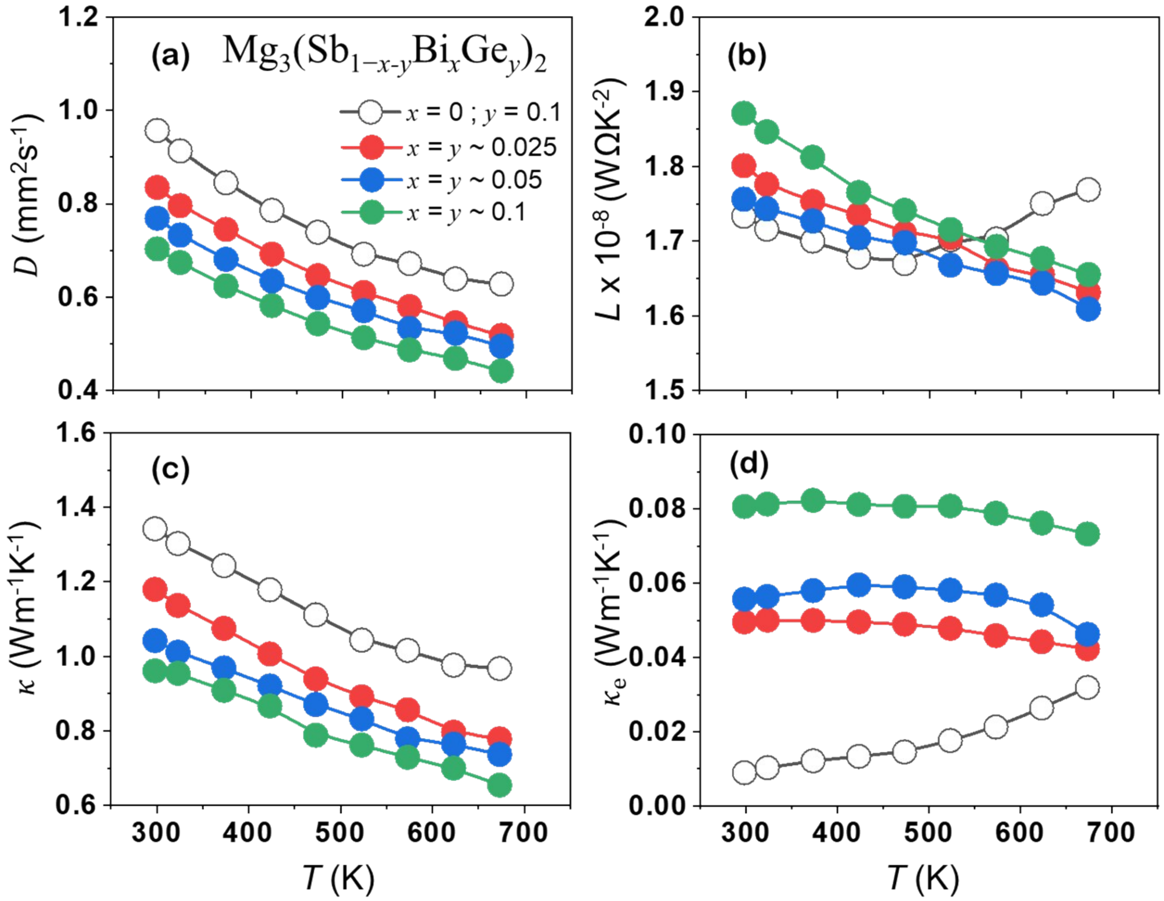

Figure S8. Temperature dependence of **(a).** Thermal Diffusivity, **(b).** Lorenz Number, **(c).** Total Thermal Conductivity, and **(d).** Electronic thermal conductivity of nominal $Mg_3(Sb_{1-x-y}Bi_xGe_y)_2$ polycrystals.