Supporting Informations:

Phase purity and the typical solid solution behaviors of $Mg_3Sb_{2-x}Bi_x$ ($0 < x < 0.4$) was verified by XRD (Figure 1 in the main text) and obeying Vegard's law generated from XRD data. The Vegard's plot was observed to be well satisfied by all solid solutions $Mg_3Sb_{2-x}Bi_x$ ($0 < x < 0.4$) as shown in Figure S1

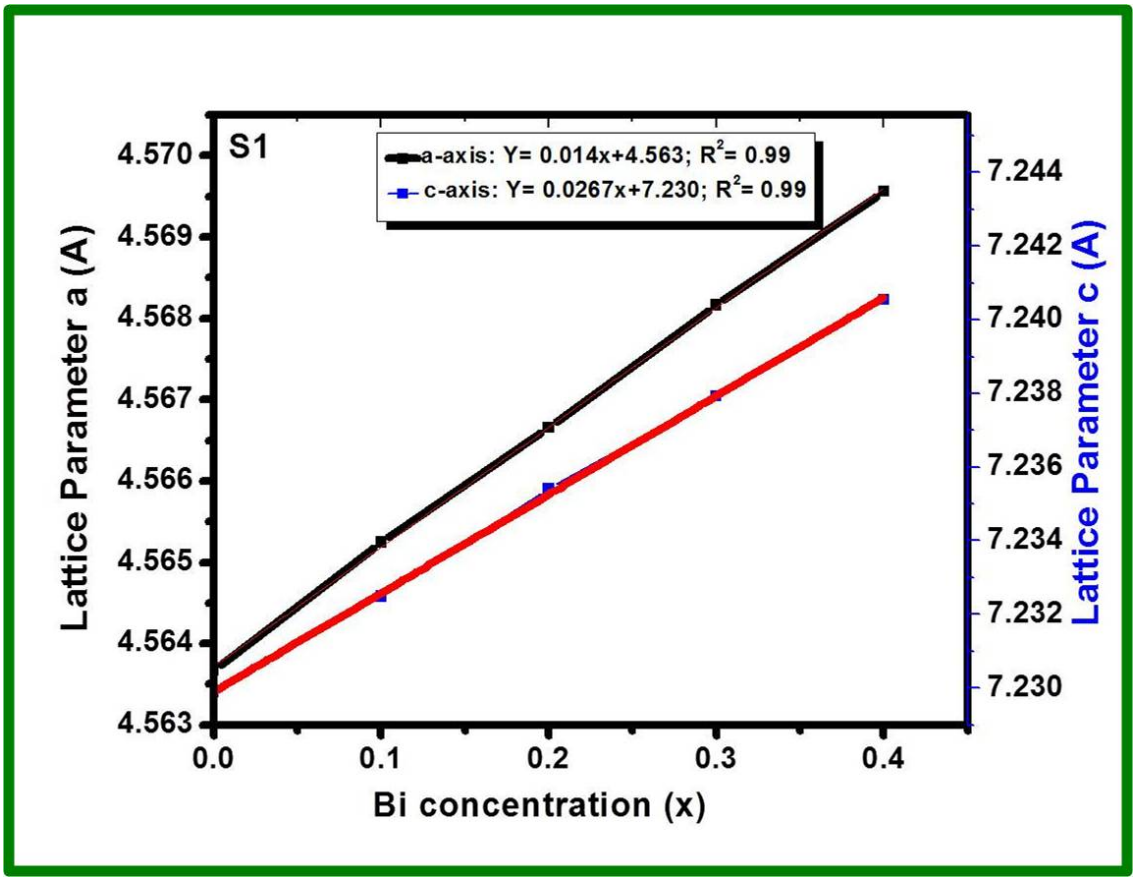
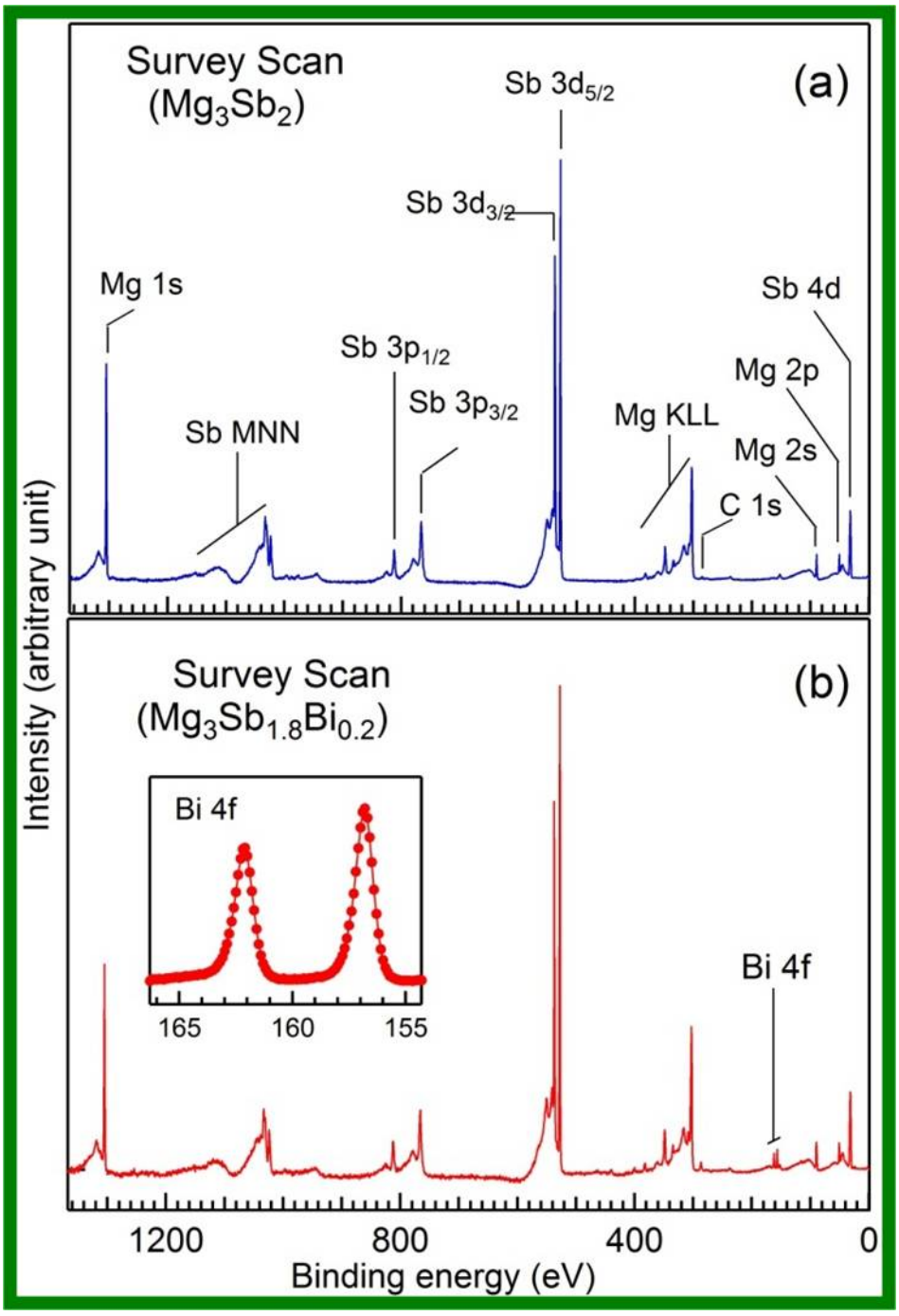


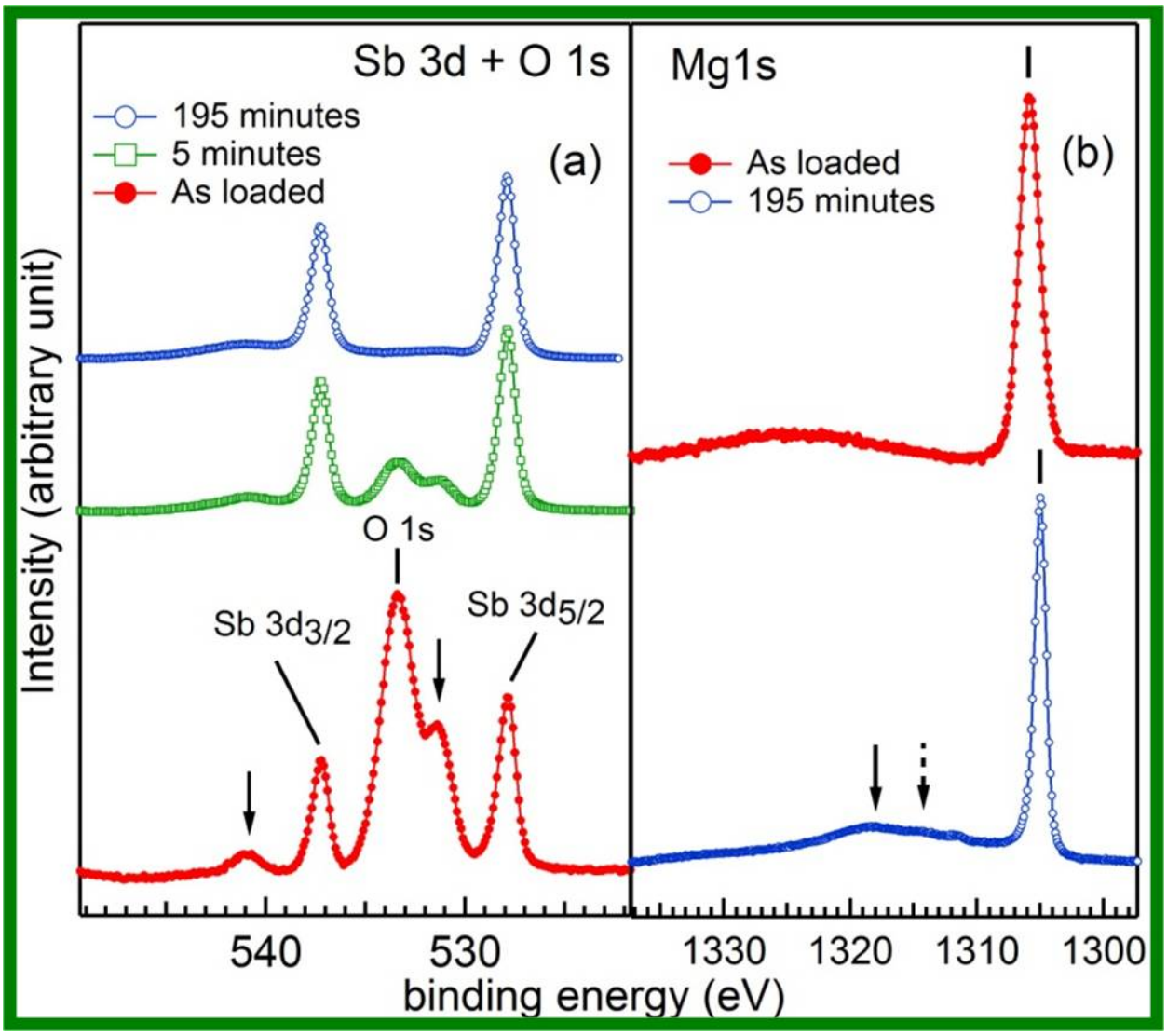
Figure S1: Plot for Vegard's law following linear trend of cell parameters with increasing Bi concentration showing complete solid solution phase formation of $Mg_3Sb_{2-x}Bi_x$ alloys.

The XPS survey spectra of Mg_3Sb_2 and $Mg_3Sb_{1.8}Bi_{0.2}$ over large binding energy (BE) range are shown in supplementary Fig. S2 (a) and S2 (b) respectively. For Mg_3Sb_2, we observe that all the features in the spectrum belong to either Mg or Sb only. Repeated in-situ mechanical scrapping of the sample also resulted in contamination free surface as can be seen from negligible signal of O 1s (will be shown in more detail in Fig. S3) and C 1s in the spectrum. It reflects the absence of impurities in the sample. Additional Bi 4f peaks have been observed in the Bi doped sample as shown in the inset of Fig. S2(b). Figure S3(a), (b) are showing the changes in the Sb 3d, O1s and

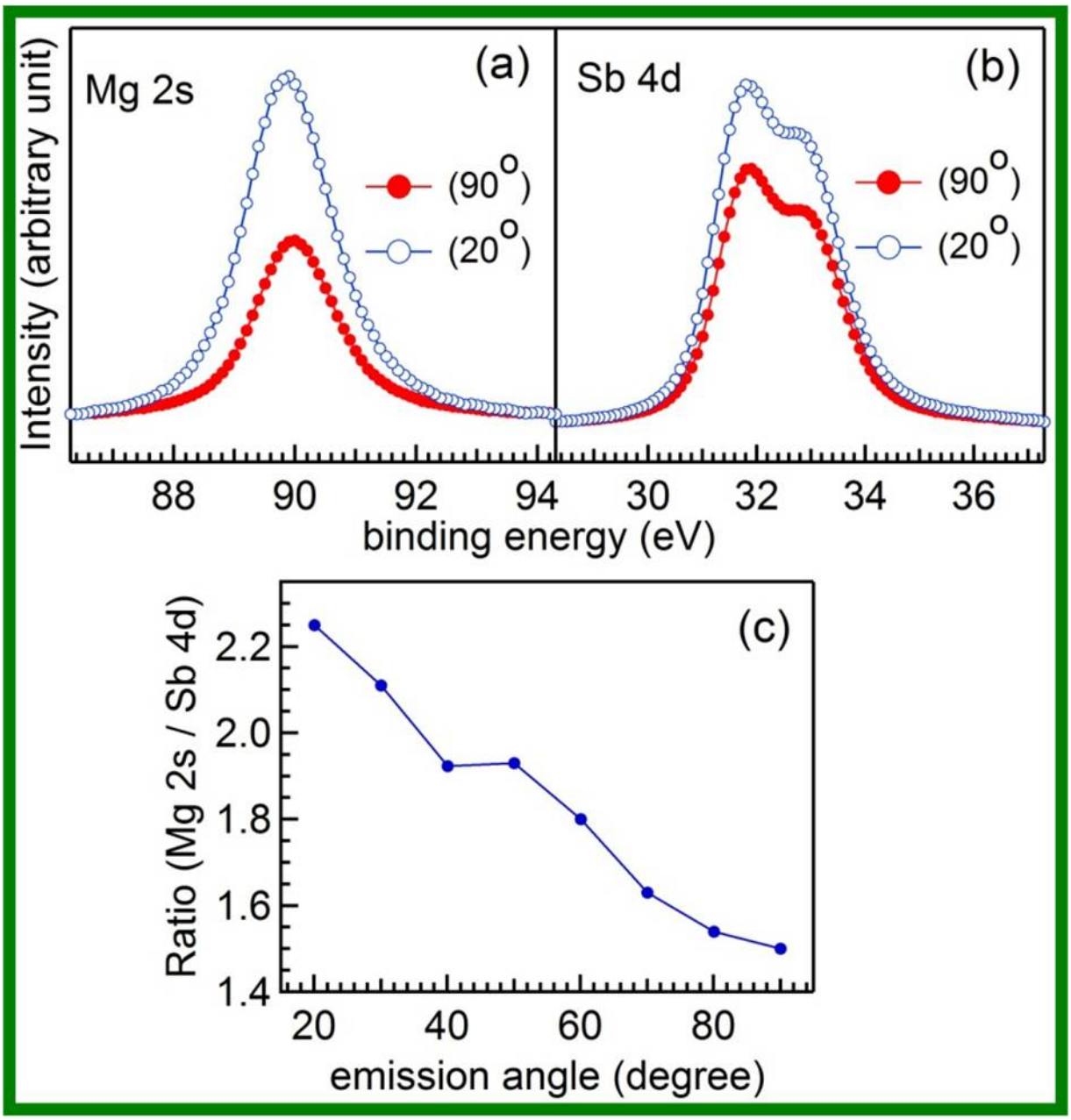
Mg 1s core level of Mg_3Sb_2 with progressive mechanical scrapping of sample. For the convenience of comparison, all the spectra in S3 (a) are normalized to have the same Sb 3d5/2 peak height and spectra shown in Fig. S3 (b) have been normalized to have same Mg 1s peak height. For as loaded sample, Sb 3d5/2 and 3d3/2 have been found at 527.9 and 537.3 eV BE with 9.4 eV spin orbit splitting. Sb oxide peaks corresponding to 3d5/2 and 3d3/2 have been observed at 531.3 and 540.7 eV BE respectively. Energy position of oxide peak indicates that it has contribution from Sb_2O_3, Sb_2O_4 and Sb_2O_5.[1] Intense O 1s peak overlapped with Sb oxide (3d5/2) peak is also marked by a tick in Fig. S4 (a). Energy position of O 1s peak also indicates that it has contributions from Mg-O and Mg-OH bonding.[2] Presence of intense O 1s and Sb oxide peaks verify that as loaded sample was highly oxidized. 5 minutes of in-situ mechanical scrapping resulted in dramatic decrease in the O 1s and Sb oxide peaks. However, it took many more repeated scrapings to obtain the surface free of oxygen as indicated in the top spectra of Fig. S3 (a). Mg 1s core level of pure Mg metal is usually accompanied by multitude of plasmon (quanta of conduction electron gas) loss features (as shown in the Figure 8(a) of main text) excited during the propagation of photoelectron in the solid.[2-3] However, we could observe only one bulk plasmon and corresponding weak surface plasmon for Mg 1s core level of clean surface of Mg_3Sb_2 as indicated by solid and dashed arrows respectively in Fig. S3 (b). Suppression of plasmons could be related to the suppression of conduction electron gas in the semiconducting Mg3Sb2. Comparison of Mg 1s core level (Fig. S3 (b)) of as loaded (oxidized) and clean surface of Mg3Sb2 shows three clear differences: for oxidized sample, core level is shifted by 0.9 eV towards higher BE, more broadened and a broad hump is observed between 10 to 25 eV BE. It has been reported that oxidation of Mg results in 1 – 2 eV shift towards higher BE side, broadening of the core level and plasmon loss features of MgO were observed between 10 to 28 eV higher BE side of main peak (Mg 1s).[2-5] Therefore, all the differences between Mg 1s core level of as loaded sample and clean sample can be attributed to the highly oxidized surface of as loaded sample. Supplementary figures S4 (a) (b) are showing Mg 2s and Sb 4d core-levels of Mg_3Sb_2 collected at 90^0 and 20^0 photoemission angle with same acquisition settings. It is evident that relative intensity of core levels is changing with photoemission angle. Figure S4 (c) is showing the variation in Mg 2s/Sb 4d ratio with photoemission angle which indicates slight enrichment of Mg at surface compared to bulk.



S2: X-ray photoemission spectra (XPS) over a wide binding energy range for (a) Mg_3Sb_2 and (b) $Mg_3Sb_{1.8}Bi_{0.2}$. All the features are identified and indexed. Bi 4f energy region is shown in the inset of (b).



S3: Evolution of core levels for Mg_3Sb_2 as a function of mechanical scrapping time. (a) Sb 3d+O1s, ticks are showing the energy positions of Sb 3d and O 1s peaks and Sb oxide peaks are marked by solid arrows. (b) Mg 1s core level, solid and dashed arrows indicate the energy positions of bulk and surface plasmons respectively. Spectra have been vertically staggered for clarity of presentation.



S4: (a) Mg 2s and (b) Sb 4d core levels of Mg_3Sb_2 recorded at 90^0 (filled circle) and 20^0 (open circle) photoemission angle with respect to surface parallel and (c) ratio of integrated intensity of Mg 2s and Sb 4d of Mg_3Sb_2 as a function of photoemission angle.

References:

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