Origin of n-type conductivity of polycation compound Mg_2SnN_2 and polyanion compound Zn_2NBr in wurtzite phase

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The wurtzite structure is a typical crystal structure of traditional semiconductors, such as GaN and ZnO. Polycation compounds Zn-IV-N_2 (IV = Si, Ge, Sn) and II-Sn-N_2 (II = Mg, Ca) are obtained on the basis of GaN via cation mutation [1]. Similarly, polyanion compounds Zn_2NX (X = Cl, Br, I) are derived from ZnO by anion mutation [2]. Zn-IV-N_2 (IV = Si, Ge, Sn) thin film have been synthesised, and proposed as photovoltaic absorbers [3]. However, among them, $ZnSnN_2$ suffers from high carrier concentration which can change the onset of the light absorption spectrum due to the Burstein-Moss effect and exceed the optimal range of carrier concentrations for photovoltaic applications (10^{16}–10^{18} cm^{-3}) [3-4]. In contrast to the intense research on Zn-IV-N_2 (IV = Si, Ge, Sn), investigation on II-Sn-N_2 (II = Mg, Ca) and Zn_2NX (X = Cl, Br, I) has only been started recently. Their properties, especially their potential as photovoltaic absorbers deserve further exploration due to their earth abundant composition. Here, we study the phase stability and defect properties of two representative compounds: the polycation $MgSnN_2$ and polyanion Zn_2NBr in the wurtzite structure via first-principles calculations. We find that both $MgSnN_2$ and Zn_2NBr show n-type conductivity but with different origins. The low-energy donor-type antisite defect, Sn_{Mg}, is the primary source of the high electron carrier concentration (10^{16} cm^{-3} – 10^{18} cm^{-3}), which leads to self-doped *n*-type conductivity in $MgSnN_2$. On the contrary, the compensation between the donor-type defect V_{Br} and acceptor-type N_{Br} pins the Fermi level close to the conduction band for the whole chemical potential range, resulting in intrinsic *n*-type conductivity in Zn_2NBr with a carrier density level around 10^{15} cm^{-3}. Our results would be useful for future study of adjusting electrical conductivity for poly-element wurtzite compounds.

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