1. Introduction

A_2BX_4[1] spinels (X = O, S, Se, Te)[2,3] comprise a broad group of chalcogenides containing two metal atoms (A and B), being either III-valent and II-valent cations (giving the III_2-II-VI_4 spinel group,e.g., Al_2MgO_4) or II-valent and IV-valent cations (giving the II_2-IV-VI_4 spinel group,e.g., Cd_2SnO4. There are about 1000 known spinels including ~130 oxides, some of them explored previously for ferroelectricity,[4] ferromagnetism,[5] superconductivity,[6] thermoelectricity,[7–10] and catalytic properties.[11,12] Only recently this large group of materials has been tapped for its potential in electronic and optoelectronic applications.[13–16] Such applications would require first and foremost that these materials can be doped n-type and/or p-type, even though the perfectly stoichiometric III_2-II-VI_4 or II2-IV-VI_4 systems generally form a closed-shell octet, and hence tend to be insulators.

It is important to realize that doping in spinels can follow different rules from doping in traditional electronic materials, such as Si or GaAs. The main rea-

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exploitation as electronic materials. Attempts have been previously made[13–15] to distill some phenomenological expectations from the few known examples, establishing what makes a spinel n- or p- type. It was thought that (i) oxygen vacancy V(O) is the cause of n-type conductivity,[14,15,37] as supported by the fact that oxygen deficiency is correlated with electron conductivity, and that (ii) cation vacancy V(A) or V(B) is the cause of p-type conductivity, as supported by the general knowledge that cation vacancies are usually acceptors. Concomitantly, it was thought that (iii) excess of the high-valent cation (e.g., III in III_2-II-VI_4) will enhance n-typeness and defeat p-typeness[28,39] of a spinel because III-on-II substitution is expected to be an electron-producing (hole-killing) donor. iii) Interstitial defects in the closed pack spinel structure are tought to be unlikely and hence do not affect its electrical properties.[40,41] Extra cation in an interstitial position lead to metal–metal bonding or metal–oxygen underbonding,[42] hence energetically they are difficult to form. These phenomenological principles have been guiding the search and optimization of doped spinels, but with little success. Previous first-principle calculations[22,28] were limited to a few specific compounds, and no attempts have been made so far to extract general understanding and general rules of doping in this family of oxides.

a high concentration of V(O), comparable to the concentration of anti-site donors are Ga_2ZnO_4 and Cr_2MnO_4 but the corresponding donor levels are energetically deep so oxygen vacancy is not the leading cause of n-type conductivity, even in these two spinel oxides (for example, the V(O) is double donor (0/2+) meaning the energy where V(O) changes from having charge . = 0 to . = +2 in Ga_2ZnO_4 and it occurs at E_c – 2.4 eV, whereas in Cr_2MnO_4 its a single donor (0/1+) meaning the energy where V(O) changes from having charge . = 0 to . = +1 and it occurs at E_c – 2.8 eV, with E_c being the short-hand notation for conduction band minimum). Similar to the oxygen vacancy, cation vacancies are not the leading source of p-type behavior, as can be seen from the survey of V(A) and V(B) vacancy concentrations in Figure 1. In a few spinels, such as Fe_2FeO_4, it has been shown experimentally that oxygen vacancies are not the main defects.[44,45] Since oxygen, cation vacancies, and interstitial defects are not the

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is further subdivided into four doping types, depending on the positions of the defect energy levels with respect to band edges (Figure 3). Compensated defects occur in materials where cross-substitution causes the donor level to be above the acceptor level (Figure 2a), and uncompensated defects occur when the acceptor level is above the donor level (Figure 2b). In the former case of donor-above-acceptor (Figure 2a), the Fermi energy can be pinned into a narrow range because of a negative feedback mechanism that counteracts intentional doping. We call materials with pinned Fermi level doping-type 1 (DT-1) materials. As shown in Figure 2a, right panel, in DT-1 materials, intentional n-type doping will initially shift the Fermi level [illegible] in the gap, causing an easier formation of native hole-producing acceptors such as B^{2+}-on-O_h due to lowering of their formation energy (and a less-easy formation of A^{3+}-on-T_d donors), thus shifting the Fermi energy [illegible] in the band gap. Conversely, intentional attempts of p-type doping of such a material would initially shift E_F [illegible] the gap, but this will cause the easier fromation of native electron-producing donors such as A^{3+}-on-T_d due to lowering of their formation energy (and a less-easy formation of B^{2+}-on-O_h acceptors), thus shifting the Fermi level [illegible] in the gap. External dopants will also behave similar as the intrinsic dopants. For example, adding external n-type dopants to the T_d site will shift E_F towards the CBM and thus cause formation of additional B^{2+}-on-O_h anti-site defects, but there is no requirement that an equal amount of A^{3+}-on-T_d would form. In fact, the Fermi level change in response to external n-type doping would even raise the formation energy of A^{3+}-on-T_d, thereby reducing their numbers. The shaded green region in Figure 2a, right panel illustrate the narrow range over which such pinning can occur in a material with comparable formation energy and transition levels of both donors and acceptors. Asymmetry in the energetic properties of defects may cause this narrow region to move closer to one of the band edges or even inside of the band, as will be discussed below in more details. In the case of acceptor-above-donor (Figure 2b, right panel), the Fermi level

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base in a normal spinel) remains low-valent when it is moved from a T_d to an O_h site, then such a substitution to B^{2+}-on-O_h could lead to an acceptor level, capable of releasing holes.

iv) Finally, if B raises its valence when it is moved from a T_d to an O_h site, then such substitution to B^{3+}-on-O_h will be electrically neutral.

In the remaining part of this paper we will use DFT calculations of the donor and acceptor levels

free carriers. The balance of carriers, whether n-type prevails over p-type or vice versa, depends critically on the relative concentration of the two anti-sites and on the position of their energy levels with respect to the band edges. We distinguish the following generic behaviors:

i) If the number of the A^{3+}-on-T_d donors and B^{2+}-on-O_h acceptors are comparable than: a) one expects net n-type behavior as exemplified by materials like In_2CdO_4 and Ga_2ZnO_4 (Figure 4) if the donor level lies closer to the CBM than the acceptor level is to the VBM. These are n-type compensated spinels. b) If the acceptor level lies closer to VBM than the donor level is to the CBM, signaling that the energy to ionize the acceptor is smaller than that needed to ionize the donor, (a case we call DT-1(p)), and exemplified by Co_2FeO_4, a net p-type behavior might be expected. We call these materials p-type compensated spinels. c) Finally, if the donor level position of the CBM is approximately equal to the acceptor level position of the VBM and if they lie either around the band edges, as exemplified by Al_2MgO_4 and Sc_2CdO_4, or at the mid gap, exemplified by Fe_2CoO_4, we have an electrically inactive intrinsic compensated spinel.

ii) However, if the number donor defects far exceeds the number of acceptors: a) net n-type behavior is expected when the donor is shallow, as exemplified by Fe_2ZnO_4, Fe_2MgO_4 and In_2MnO_4, or even if it is relatively deep compared to the acceptor; b) net insulating behavior is expected when donor is really deep; and similarly, if the number of acceptors far exceeds the number of donors, then: c) net p-type behavior is expected when the acceptor is shallow, as exemplified by In_2FeO_4 and Ga_2FeO_4, or if it is relatively deep compared to the donor, as exemplified by Ga_2FeO_4; and d) insulating behavior is expected when acceptor is really deep as exemplified by Ga_2MnO_4 and Sc_2MnO_4.

n-Typeness in this family of compounds can be enhanced by growing the compounds in an A-rich environment, as it promotes A substituting B in T_d sites, creating electrons. Similary p-typeness can be enhanced by growing the compounds in a B-rich environment, as it promotes B substituting A in O_h sites, creating holes. Furthermore, extrinsic doping in these spinels is unlikely to be effective:

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