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approximation (GGA) are treated in rotationally invariant GGA+U formalism,<sup>13,14</sup> with the onsite Coulomb interaction ( $U$ ) determined in such a way that it correctly reproduces relative stability of competing binaries.<sup>15</sup> In a supercell approach defect calculation is performed using a 56-atom cubic cell with  $2 \times 2 \times 2$  Monkhorst-Pack<sup>16</sup>  $k$  points with kinetic energy cutoff of 300 eV and oxygen soft pseudopotentials.

The chemical potential involved is determined using the thermodynamic consideration that a compound exists and all other possible binaries and elemental phases do not exist under a given growth condition. Energy of formations are calculated assuming thermodynamic equilibrium.

The calculated enthalpy of formation includes the corrections<sup>17</sup> due to the image charges, potential alignment, and band filling effects. The dielectric constants necessary in the image charge correction are calculated using the density functional perturbation approach.<sup>18</sup> The number of defects are calculated by minimizing the Gibbs free energy with respect to the number of defects assuming formation enthalpy is independent of the number of defects. The number of defects depends upon the Fermi energy, whereas the Fermi energy itself depends upon the number of carriers, part of which are coming from the ionized defects, so we determine self-consistently the defect density, Fermi energy, and carrier density requiring overall charge neutrality.

## B. Experimental details

Thin-film composition gradient samples (libraries) of Co-Zn-Ni-O were grown on 2 in.  $\times$  2 in. fused silica glass substrates by sputtering from separate targets of CoO, ZnO, and NiO.<sup>19</sup> The sputter sources were inclined at 30° to the substrate normal to achieve a two-dimensional (2D) composition gradient. The chamber base pressure was  $10^{-7}$ – $10^{-6}$  Torr prior to deposition. Films were deposited in a 50/50 O<sub>2</sub>/Ar gas mix at a total pressure of 20 mTorr. To cover the full Co<sub>3</sub>O<sub>4</sub>-Co<sub>2</sub>ZnO<sub>4</sub>-Co<sub>2</sub>NiO<sub>4</sub> ternary composition spread, the relative power on the CoO, ZnO, and NiO sources is varied with a constant total power of 150 W. For each library, the 240-min deposition is preceded by a 30-min burn-in. Additional, single-composition Co<sub>2</sub>ZnO<sub>4</sub> and Co<sub>2</sub>NiO<sub>4</sub> samples were grown by pulsed laser deposition (PLD) on 100-oriented SrTiO<sub>3</sub> substrates heated to 350 °C placed 7 cm from the targets in a chamber with  $10^{-10}$  atm base pressure. lled with  $2.6 \times 10^{-6}$  atm of oxygen without addition of argon. Co<sub>2</sub>ZnO<sub>4</sub> and Co<sub>2</sub>NiO<sub>4</sub> targets with Ni/(Ni + Co) = 0.33, 0.38, 0.43 were ablated using a 248-nm excimer laser beam with 2.5 J/cm<sup>2</sup> energy density and 10 Hz repetition rate.

Materials analysis focused on measuring a grid set of 44 locations on each substrate in a 4 row  $\times$  11 column format. The electrical, optical, and structural analysis all focused on the same 44 points on each library, allowing for combinatorial analysis of the results. The rows were located 12.5 mm apart and the columns were 4 mm apart. X-ray fluorescence mapping was utilized to measure the relative Co:Ni:Zn atomic ratio and thickness. Sheet resistance values were characterized with automated four-point probe mapping. Crystallographic and phase composition were measured by x-ray diffraction (XRD) in a mapping fashion using a large Bruker diffractometer equipped with a 2D area detector.<sup>20</sup>

Bulk and powder samples of Zn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> and Mg- and Ni-substituted Zn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> were fabricated using an aqueous route, in order to make syntheses at an atomic level more rapid than can be achieved by conventional solid state processing at low temperatures. For the Zn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> samples, stoichiometric amounts of Co nitrate hexahydrate, 99.999%, and Zn nitrate hexahydrate, 99.998% (both Alfa Aesar, Ward Hill, MA) were

The Seebeck coefficient of PLD-grown  $\text{Co}_2\text{ZnO}_4$  and  $\text{Co}_2\text{NiO}_4$  films was measured at room temperature as detailed in Ref. 24. The Hall effect was measured at room temperature using a Van der Pauw method<sup>25</sup> and a variable magnetic field up to 15 T with a 1.7-Hz alternating current source using lock-in techniques, and averaging four up-and-down magnetic field sweeps of both polarities. The data between 0 and 1 T have been removed as they represent pure instrumental noise.

### III. DESIGN AND REALIZATION OF *p*-TYPE TRANSPARENT CONDUCTING OXIDE: THE THREE STEPS

We have applied the three-step inverse design approach to the challenging problem of increasing the hole concentration in *p*-type transparent conductors. In particular, first is the formulation and application of general design principles to select a promising class of materials. Second, high-throughput calculations are used to select the best candidate materials. Then third, further calculations and corresponding experiments are used to verify and optimize the chosen best of class materials. Each of these steps is described in more detail below.

#### A. Step 1: Formulation of design principles for *p*-type transparent conductors

The following four design principles must be achieved in order to create *p*-type transparent conductors.

(1) *Minimize hole killers.* For oxide base materials this generally requires a low concentration (i.e., high formation energy) of oxygen vacancies which are normally donors (hole killers), as well as a low concentration of antisite defects of the high-valent metal on the low-valent site. If the concentration of potential hole killers is not low, it is then necessary to design such donor transition levels to be resonant inside the valence band, in which case they are electrically inactive and so cause no harm to holes even if they are abundant. This latter special case has been recently termed doping type II.<sup>26</sup>

(2) *Maximize hole producers.* This can imply maximizing the number (i.e., minimizing the formation energy) of cation



in an octahedral environment. In octahedral symmetry the  $t_2$  orbitals are nonbonding with lobes pointing in between the oxygen ligands, and are thus expected to yield rather narrow sub-bands with heavy mass. In contrast, the  $e$  orbitals are bonding and thus expected to lead to broader bands with lighter mass. In  $\text{Co}_2\text{ZnO}_4$ , Co is a  $\text{Co}^{3+}$   $d^6$  ion having full occupied spin-up as well as spin-down  $t_2$  orbitals. Thus, unfortunately, the highest occupied state is the nonbonding  $t_2$ .

These considerations are borne out by calculations of the density of states at the valence band maximum, showing high effective masses (the calculated effective density of states  $N_v = 2 \times 10^{21}/\text{cm}^3$



Figure 5 shows the predicted hole concentration  $n_h$  (solid line) as a function of Mg content at  $T =$

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<sup>1</sup>N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990).

<sup>2</sup>J. G. Bednorz and K. A. Müller, *Z. Physik B: Condens. Matter*