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Spontaneous Non-stoichiometry and Ordering in Degenerate but Gapped Transparent Conductors

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SUMMARY

[illegible]

in Figure 1B) and then attempting heavy doping (by Sn or Al, respectively), making it concentration and optical response. Such phases (Figure 2A) could then, in principle, F r 3. S n an Va an F r a n n D n ra Ga In a ra -16.4 n-28a84 283. -5.4 6.1aa.7265n n 3Ca-3.4 a6 -1256.7265n -44.7r 5.Pr8

in $Ca_6Al_7O_{16}$, and the Ag vacancy in $Ag_3Al_{22}O_{34}$, as a function of the metal chemical potential (see Experimental Procedures). The allowed stable chemical potential regions (constructed by considering possible competing phases, see Experimental Procedures) of the respective bulk compounds are shown in Figures 3B, 3D, and 3F. We see that for the degenerate gapped compounds under cation-deficient chemical potential conditions, vacancy formation energies can be extremely low (in fact, negative). Whereas $BaNbO_3$ and $Ca_6Al_7O_{16}$ have stable chemical potential (green) zones at the respective stoichiometries indicated, $Ag_3Al_{22}O_{34}$ does not. In fact, in the latter case, the Ag vacancy formation energy (Figure 3E) is so strongly negative under all chemical potential conditions, that the CB is empty and the parent degenerate $Ag_3Al_{22}O_{34}$ phase is not stable (i.e., no green zone in Figure 3F).

D Va an Can C n n n S aB OVC F r n H a S n

The negative formation energies of dilute vacancies open the possibility of vacancy condensation and long-range ordering (Figure 2B). To examine this possibility, we have calculated the T = 0 K stable phases (“ground state diagram” or “convex hull") of such ternary structures. This entails searching for configuration versus composition that lies on the energy convex hull,[14] which defines the phases with energy lower than a linear combination of any competing phases at the corresponding compositions. We create candidate configurations by considering a base compound ($BaNbO_3$, $Ba_3Nb_5O_{15}$, $Ca_6Al_7O_{16}$, or $Ag_3Al_{22}O_{34}$), then create a replica of N such units of the base compound and add successively p metal vacancies, i.e., OVC = $N \times$ (base) + pV_m, searching via total energy minimization for stable and metastable configurations. We also include experimentally known reconstructed OVCs, the compounds that satisfy the OVC expression but do not have clearly defined vacancy sites (e.g., $Ba_3Nb_5O_{15}$, $BaNb_2O_6$, and $Ba_5Nb_4O_6$).

Available information on the experimental literature[15–30] is provided in Figure 4, and the theoretical results of this work are summarized in Figure 5. The key point to and 7B) demonstrating the phases that are stabilized as the chemical potentials of the atoms being removed are continuously changed between their allowed values. Finally, we show how a window of opportunity can be determined computationally between opposing tendencies of (1) stability (Figures 2A and 7B), (2) conductivity (Figures 6B–6D and 7C), and (3) transparency (Figure 8) to design new TCs.

Stable Phases and OVCs for the Ba-Nb-O System

Computationally, we find 25 binary and ternary ground state compounds (described in Data S1) of which $Ba_7Nb_6O_{21}$, $Ba_5Nb_4O_{15}$, $Ba_3Nb_5O_{15}$, $Ba_7Nb_8O_{24}$, $Ba_9Nb_{10}O_{30}$, $Ba_{26}Nb_{27}O_{81}$, and $BaNb_2O_6$ are OVCs (Figure 5). Here, 7:8:24, 9:10:30, and 26:27:82 phases have clearly defined vacancy sites, and 1:2:6, 3:5:15, and 5:4:15 OVCs are excluded."[18] Indeed, several potential experimental compositions (i.e., $Ba_{0.95}NbO_3$ and $Ba_{0.97}NbO_3$) nearly match predicted phases ($Ba_{26}Nb_{27}O_{81}$ Ba unstable with respect to competing phases. Our experimental attempts to reduce synthesized $Ag_3Al_{22}O_{34.5}$ to $Ag_3Al_{22}O_{34}$

complexity of material synthesis. In our own work on 3:5:15 OVC, we see the preferential formation of the secondary reconstructed 1:2:6 and 5:4:15 OVCs over the targeted compound (Note S2). This reflects the narrow stability region of the 3:5:15 phase versus the reconstructed OVCs. Hence

frequency but also changes the interband transition, which is illustrated in the absorption spectra of 6:7:16 and its OVCs (see Figure 8 acceptor states. As a result, the negative electron-hole recombination energy offsets the positive energy associated with vacancy bond breaking. Our results thus explain

$40 \times 40 \times 40$, $20 \times 20 \times 20$, $20 \times 20 \times 20$, $8 \times 24 \times 8$, $16 \times 12 \times 8$, $20 \times 20 \times 20$, $8 \times 8 \times 8$, and $8 \times 8 \times 8$ Γ-centered k-point grids were used for $BaNbO_3$, $Ba_7Nb_8O_{24}$, $Ba_7Nb_6O_{21}$, $Ba_3Nb_5O_{15}$, $BaNb_2O_6$, $Ca_6Al_7O_{16}$, $Ca_{23}Al_{28}O_{64}$, and $Ca_{11}Al_{14}O_{32}$, respectively. The Drude contribution to optical properties was included by utilizing kram code[48] with plasma frequencies calculated from first-principles calculations and the damping coefficient of 0.2 eV, which is analogous to traditional TCs.[49]

Defect Calculation

Supercells with 116, 135, and 236 atoms were used to calculate defect energetics in $Ca_6Al_7O_{16}$, $BaNbO_3$, and $Ag_3Al_{22}O_{34}$ systems, respectively. The defect formation energies (Figures 3A, 3C, and 3E) and finite size corrections were computed within the framework described by Lany and Zunger[50,51] and implemented in the pylada-defects code.[52] For the defect calculations, the ranges of chemical potentials were determined using only experimentally known stoichiometric crystal structures as described above. It should be noted that unlike conventional insulators where the Fermi energy can span the full range of the gap (Figure 1B), thus controlling the balance between different charges, if the Fermi energy resides inside a continuum band, as is the case in Figure 1A, it represents the energy to add or remove an electron from the host system, not from point defects in the gap. Thus, the conventional calculation of charged defects versus E_F is not meaningful in degenerate gapped materials.

DATA AND SOFTWARE AVAILABILITY

All data needed to evaluate the conclusions in the paper are present in the paper and the Supplemental Information. Additional data related to this paper may be requested from the authors.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.matt.2019.05.014.

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AUTHOR CONTRIBUTIONS

O.I.M. carried out the theoretical calculations. M.T.Y. fabricated the samples and carried out structure analysis by X-ray powder diffraction. A.Z. directed the design of the research, analysis of the results, and writing of the paper. O.I.M. contributed most to writing of the paper, with contributions from all co-authors. K.R.P. supervised the experimental work. C.P. and A.Z. supervised all theoretical studies.

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