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Emerging materials with novel electronic properties for solar light harvesting and conversion IFFAT NAYYAR, TIFFANY KASPAR, MARTIN MCBRIARTY, SARA CHAMBERLIN, NIRANJAN GOVIND, SCOTT CHAMBERS, PETER SUSHKO, Pacific Northwest National Laboraotry, Richland, WA — The optical absorption and electronic transport in complex oxides can be tuned by judicious selection of the lattice structure and control of chemical composition and prevalent oxidation state of the transition metal species. Optical spectra for solid solutions of metal oxides are complex; we focus on revealing the electronic structure and orbital nature of the transitions, which is crucial for rational materials design. We applied state-of-the-art *ab initio* methods, including time-dependent DFT, to screen thermodynamically favorable configurations and determine the effects of the local environment on the transition energies and relative intensities. Here we focus on the magnetite-type $Fe_{3-x}Cr_xO_4$ mixed spinel solid-solutions, which can only be doped to $x \leq 2$, since Cr strongly prefers to occupy octahedral sites. In the interval of $0 \leq x \leq 2$, the electronic structure of $Fe_{3-x}Cr_xO_4$ undergoes transformations resulting in several qualitatively different types of optical transitions sensitive to the Cr concentration. We find the lowest band gap and high room-temperature conductivity, in agreement with experiment, for x=1 (Fe_2CrO_4), and attribute this conductivity to the thermally-driven electron hopping between the octahedral-site Fe^{2+} and tetrahedral-site Fe^{3+}. We compare $Fe_{3-x}Cr_xO_4$ with the corundum α-$(Fe_{1-x}Cr_x)_2O_3$ and α-$(Fe_{1-x}V_x)_2O_3$, where electron transfer from the Cr and V $3d$ to the unoccupied Fe $3d^*$ orbitals reduces the band gap to 1.6 and 0.6 eV (from 2.1 eV in α-Fe_2O_3).

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