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Influence of cation impurities and both cation and anion nonstoichiometry on aluminum oxide energy gap width

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At present, miniaturization of the electronic devices is achieved by increasing the dielectric constant, K, and by using low-dimentional materials [1]. In this regard, high K oxides, such as Al_2O_3 ($K = 10$) and HfO_2 ($K = 25$) are considered as promising materials for advanced electronic devices [2]. During the past decade, the optical and electronic properties of aluminum oxide with transition metal impurities have been intensively investigated [1, 3]. Almost all theoretical studies were performed within the supercell approximation with periodic repetition of atomic defects and a discrete set of impurity concentrations. The Coherent Potential Approximation (CPA) is a fundamentally different approach developed for the study of substitutional disordered alloys with a continuous interval of impurity concentrations.

In this Letter, we employed a novel CPA scheme developed in [4] using the TB-LMTO-ASA. The combination of these two approximations allows us to consider substitutional impurities, as well as vacancies in the lattice sites.

The purpose of the work was to study the effect of mono- and multi-component (Zr, Nb, Mo, Ga, Sn) doping and nonstoichiometry on the electronic spectrum of α-Al_2O_3 in the vicinity of the energy gap using the CPA approach.

When aluminum sublattice is doped with one impurity such as $Al_{1.94}Zr_{0.06}O_3$, $Al_{1.94}Nb_{0.06}O_3$, and $Al_{1.94}Mo_{0.06}O_3$, new partially occupied $4d$ paired bands (α and α', β and β', γ and γ') appear near the bottom of the conduction band (CB) of α-Al_2O_3 (Fig. 1,A), in good agreement with experimental data. The nonstoichiometry on the Al sublattice ($Al_{1.94}O_3$) does not change the electronic structure of α-Al_2O_3 in the vicinity of the energy gap because Al vacancy s-, p-states lie higher. The spectra of these compositions are found to be metallic.

We also found new insulators $Al_{1.97}Ga_{0.03}O_3$ (mono-doping), $Al_{1.96}Zr_{0.03}O_3$, $Al_{1.95}Nb_{0.03}O_3$, $Al_{1.94}Mo_{0.03}O_3$ (the latter 3 cases are multi-doping with both impurity atom and Al vacancy) with energy gap values lying in the UV range of sunlight (Fig. 1,B). Doping of the Al subblattice with isovalent Ga impurity does not form an isolated impurity band in the vicinity of α-Al_2O_3 energy gap, because the Ga s-, p-states lie higher. The electronic spectrum of $Al_{1.97}Ga_{0.03}O_3$ has a dielectric type with a large energy gap of 8.1 eV. The DOS for $Al_{1.96}Zr_{0.03}O_3$ with the energy gap of 7.2 eV is shown in Fig. 1,B. Incorporation of Nb atom and Al vacancy in the Al sublattice simultaneously allows us to suggest the $Al_{1.95}Nb_{0.03}O_3$ compound with the energy gap value equal to 5.7 eV. For $Al_{1.94}Mo_{0.03}O_3$, the calculated value of the energy gap is 4.3 eV. The $Al_{1.97}Ga_{0.03}O_3$ and $Al_{1.96}Zr_{0.03}O_3$ are potential candidates for new capacitors.

Another way to reduce the α-Al_2O_3 band gap to the values lying in the visible and IR ranges of the solar spectrum is the mono- and multi-doping of nonstoichiometric α-$Al_2O_{3-\delta}$ with d- (Zr, Nb, and Mo) and p- (Ga and Sn) impurities with the corresponding concentrations. We obtained a semiconducting state for $Al_{1.97}Ga_{0.03}O_{2.97}$ with the energy gap value of 2.1 eV. We established a semiconducting type spectrum for nonstoichiometric multi d- and p-doped compositions, $Al_{1.96}Zr_{0.03}O_{2.97}$ and $Al_{1.91}Nb_{0.03}Sn_{0.06}O_{2.97}$, with the energy gap values lying in the IR range of the sunlight, 0.4–1.6 eV. The new semiconductors can be used in photodiods.

Thus, the CPA approach allows one to predict the fundamental electronic properties of disordered nonstoichiometric multi-doped oxide compounds with arbitrary impurity concentrations and design promising materials for advanced electronic and photoelectric devices.

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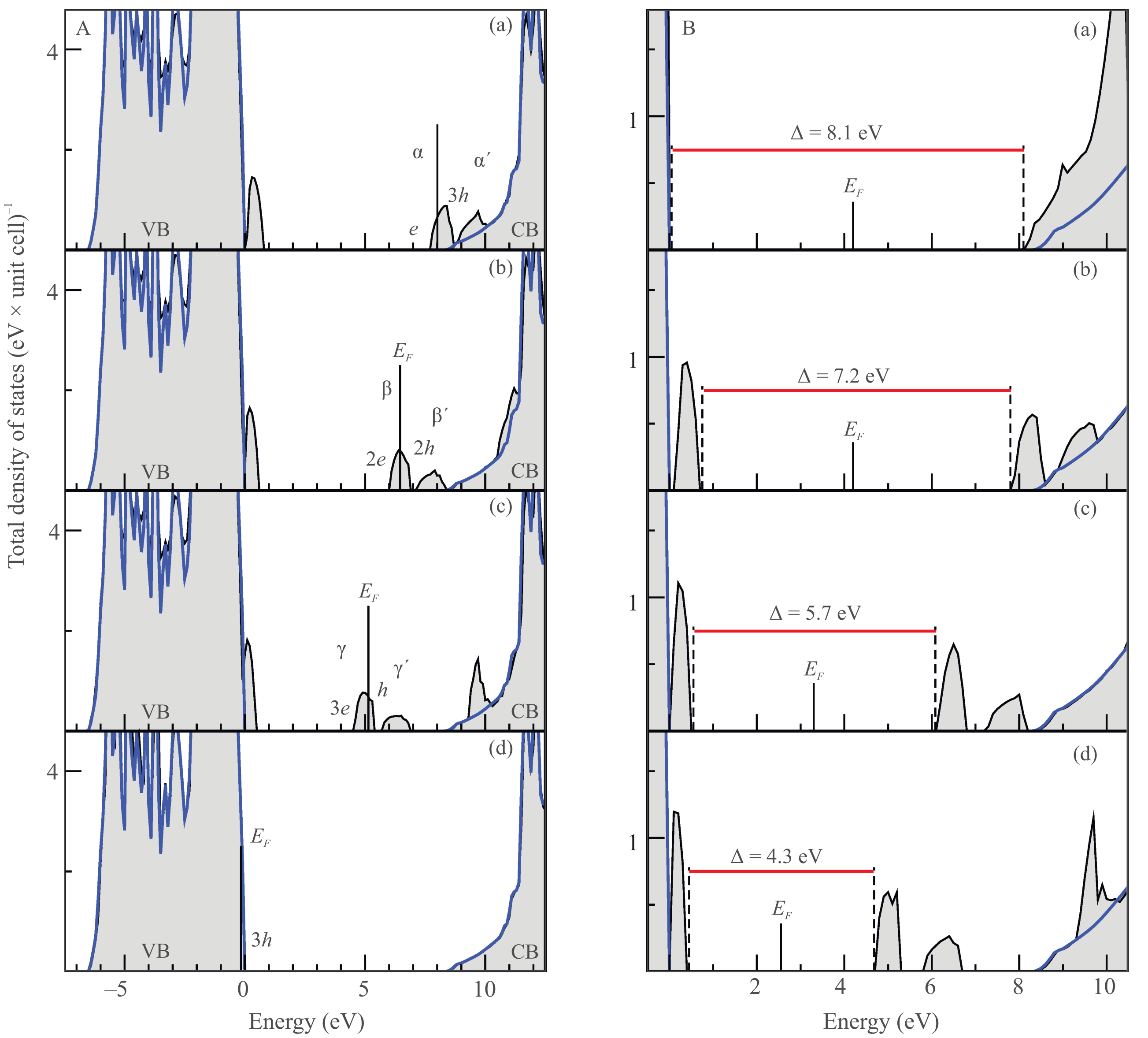

Fig. 1. (Color online) A – Calculated total (grey area) densities of states (DOS) for $Al_{1.94}Zr_{0.06}O_3$ (a), $Al_{1.94}Nb_{0.06}O_3$ (b), $Al_{1.94}Mo_{0.06}O_3$ (c), and $Al_{1.94}O_3$ (d). (B) – Total DOS (grey area) for $Al_{1.97}Ga_{0.03}O_3$ (a), $Al_{1.96}Zr_{0.03}O_3$ (b), $Al_{1.95}Nb_{0.03}O_3$ (c), and $Al_{1.94}Mo_{0.03}O_3$ (d) in the vicinity of the energy gap of α-Al_2O_3. The red horizontal segment shows the energy gap interval. The value of the energy gap Δ is given in red. The Fermi level is denoted by a vertical solid line and E_F mark. The energy interval from 0.0 to 8.3 eV corresponds to the interval of α-Al_2O_3 energy gap. Blue color shows the DOS for α-Al_2O_3

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