

論文の内容の要旨

論文題目: First-principles calculations of the electronic structures and optical absorption spectra of functional metal oxides

(機能性金属酸化物の第一原理電子状態計算及び吸光スペクトル)

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Introduction

Our laboratory has reported functional metal oxides, e.g., epsilon iron oxide ($\epsilon\text{-Fe}_2\text{O}_3$) exhibiting a large coercive field over 25 kOe and millimeter wave absorption property, and lambda titanium oxide ($\lambda\text{-Ti}_3\text{O}_5$) exhibiting external-stimuli-induced phase transitions at room temperature. In this work, to investigate the electronic structures and optical properties of functional metal oxides, first-principles calculations and optical measurements were conducted. The calculated electronic structure and the measured optical absorption spectrum of $\epsilon\text{-Fe}_2\text{O}_3$ showed that $\epsilon\text{-Fe}_2\text{O}_3$ has a wide band gap and exhibit light color. Furthermore, first-principles calculations and optical measurement of Al- and Ga-substituted epsilon iron oxide, $\epsilon\text{-Al}_{0.5}\text{Fe}_{1.5}\text{O}_3$ and $\epsilon\text{-Ga}_{0.5}\text{Fe}_{1.5}\text{O}_3$, were carried out. The obtained results showed that Al- and Ga-substitution enlarge the band gap and lighten the color of $\epsilon\text{-Fe}_2\text{O}_3$.

Experimental

Figure 1 shows the crystal structure of $\epsilon\text{-Fe}_2\text{O}_3$, Al- or Ga-substituted epsilon iron oxide used in the periodic structure calculations. These crystal structures are orthorhombic in the $Pna2_1$ space group and have four cation sites (A–D site). A–C sites are octahedral sites, and D site is a tetrahedral site. In $\epsilon\text{-Fe}_2\text{O}_3$, Fe^{3+} ions occupy A–D sites. For the calculations of $\epsilon\text{-Al}_{0.5}\text{Fe}_{1.5}\text{O}_3$ and $\epsilon\text{-Ga}_{0.5}\text{Fe}_{1.5}\text{O}_3$, the crystal structure with D site substituted by Al^{3+} or Ga^{3+} ions were used. First-principles calculations were conducted using Vienna *Ab initio* Simulation

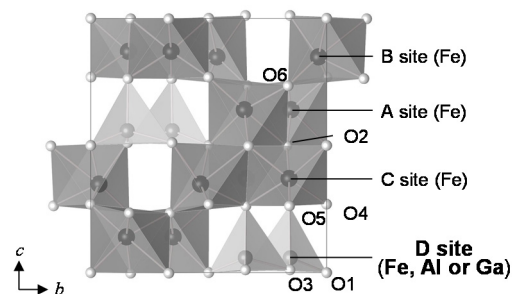


Figure 1. Crystal structure of $\epsilon\text{-Fe}_2\text{O}_3$, $\epsilon\text{-Al}_{0.5}\text{Fe}_{1.5}\text{O}_3$ or $\epsilon\text{-Ga}_{0.5}\text{Fe}_{1.5}\text{O}_3$.

Package. The exchange-correlation functional was approximated with the generalized gradient approximation. The Hubbard U was taken into account in order to describe the Coulomb repulsion of Fe 3d orbitals. U - J value of 5 eV was selected. The basis set was regulated by a cutoff energy of 520 eV, and the k -mesh was set to $7 \times 5 \times 5$.

Crystal structures were obtained by X-ray diffraction (XRD) and Rietveld analyses. The magnetic properties were measured by superconducting quantum interference device magnetometer (SQUID). Optical spectra were measured by UV-vis spectrometer using highly dispersed polymer solutions of epsilon iron oxide, which were prepared by mixing the powder sample and an organic solvent containing urethane resin, polyvinyl chloride, toluene and methylethelketone.

First-principles calculations and optical measurement of ϵ -Fe₂O₃

Density of states of ϵ -Fe₂O₃ showed that O2p band is located below the Fermi energy (E_F) in valence band, and Fe3d occupied band is located below the O2p band. Fe3d unoccupied band is located above the E_F . Figure 2a shows the band structure of ϵ -Fe₂O₃. The band structure of ϵ -Fe₂O₃ suggested that ϵ -Fe₂O₃ has a band gap of 2.0 eV for down-spin transition and 2.4 eV for up-spin transition. By calculation of transition moments, this down-spin transition was assigned to the transitions from the 4 top energy states in the valence band to 6 bottom energy states in the conduction band. FeD site and neighboring O sites mainly contributed to 4 top energy states in valence band, and FeC site mainly contributed to 6 bottom energy states in conduction band. Figures 2b,c show the calculated and observed optical spectra of ϵ -Fe₂O₃. The calculated results well reproduced the observed spectrum. The observed optical spectrum showed that ϵ -Fe₂O₃ has a weak transition with a gap of 2.4 eV and a strong transition with a gap of 2.9 eV. These results indicated that ϵ -Fe₂O₃ exhibits a light color with a large band gap.

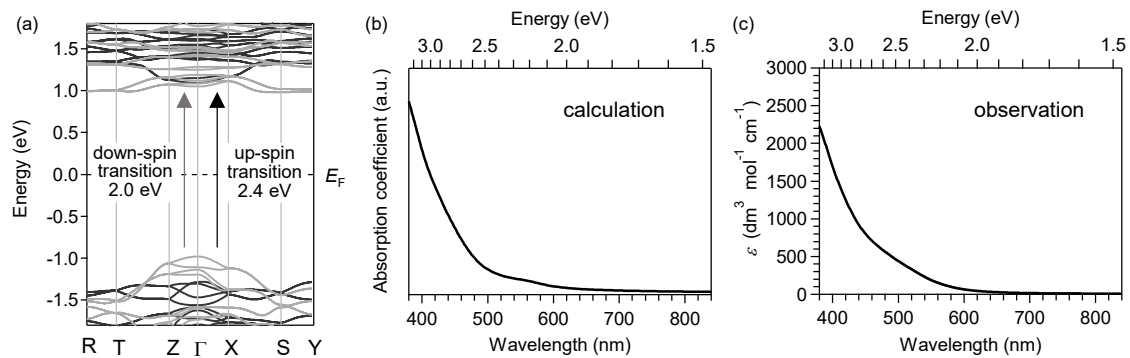


Figure 2. (a) Band structure of ϵ -Fe₂O₃. Black and gray lines denote the up-spin and down-spin states, respectively. Calculated (b) and observed (c) optical spectra of ϵ -Fe₂O₃.

Al- and Ga-substitution effect on epsilon iron oxide for optical absorption

Fe³⁺ ions of ϵ -Fe₂O₃ can be substituted by Al³⁺ ions, which selectively occupy the tetrahedral D sites. First-principles calculations and optical measurement of Al-substituted epsilon iron oxide were conducted.

Density of states of ϵ -Al_{0.5}Fe_{1.5}O₃ showed that O2p band is located below the E_F in the valence band, and Fe3d occupied band is located below the O2p band. Fe3d unoccupied band is located above the E_F . Al2p band and Al3d band are located below and above these bands, respectively. Figure 3 shows the band structure of ϵ -Al_{0.5}Fe_{1.5}O₃. The band structure indicated that this material has a band gap of 2.5 eV for down-spin transition and 2.6 eV for up-spin transition. The band gaps were enlarged from ϵ -Fe₂O₃ by Al-substitution. This enlargement can be explained as follows. Comparing the band structures of ϵ -Fe₂O₃ and ϵ -Al_{0.5}Fe_{1.5}O₃, 4 down-spin states of the valence band and 4 up-spin states of the conduction band near the E_F disappeared by Al-substitution of D site. This disappearance enlarged the band gap. In

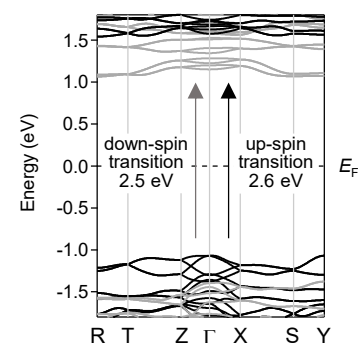


Figure 3. Band structure of ϵ -Al_{0.5}Fe_{1.5}O₃. Black and gray lines denote up-spin and down-spin states, respectively.

comparing the band structures of ϵ -Fe₂O₃ and ϵ -Al_{0.5}Fe_{1.5}O₃, 4 down-spin states of the valence band and 4 up-spin states of the conduction band near the E_F disappeared by Al-substitution of D site. This disappearance enlarged the band gap. In

ϵ -Fe₂O₃, the charge density maps showed that the down-spin state of valence band top and the up-spin state of conduction band bottom are mainly contributed by D site. Figure 4a shows the calculated optical spectrum of ϵ -Al_{0.5}Fe_{1.5}O₃. Compared with the calculation result of ϵ -Fe₂O₃, the absorption peak of ϵ -Al_{0.5}Fe_{1.5}O₃ shifts to a higher energy by 0.1 eV, and the absorption is inhibited by half above 500 nm, which indicate that the present material has a higher transparency than ϵ -Fe₂O₃.

In order to confirm the calculation results, optical measurement of Al-substituted epsilon iron oxide (ϵ -Al_{0.66}Fe_{1.34}O₃) was conducted. XRD pattern and Rietveld analysis showed that this material has an orthorhombic structure with space group of *Pna*2₁, and the lattice constants are $a = 5.0385(5)$ Å, $b = 8.6648(9)$ Å, $c = 9.3457(9)$ Å, and $V = 408.01(7)$ Å³. Al³⁺ ions mainly occupied D site with Al : Fe = 84.0(12)% : 16.0(12)%. The occupancies of the other sites are 16(3)% : 84(3)% at A site, 9.9(17)% : 90.1(17)% at B site, and 22.1(17)% : 77.9(17)% at C site. The magnetic measurement of ϵ -Al_{0.66}Fe_{1.34}O₃ powder showed a magnetic hysteresis loop at 300 K with a saturation magnetization (M_s) value of 16.5 emu g⁻¹ and a coercive field (H_c) value of 7.4 kOe. At 10 K, the magnetic hysteresis loop increases with an H_c value of 17.5 kOe and an M_s value of 29.7 emu g⁻¹.

Figure 4b shows the UV-vis spectrum of ϵ -Al_{0.66}Fe_{1.34}O₃. An absorption coefficient (ϵ) around 3.1 eV is $\epsilon = 870$ dm³ mol⁻¹ cm⁻¹ and that of a weak optical absorption centered at 2.6 eV is $\epsilon = 300$ dm³ mol⁻¹ cm⁻¹. These absorption coefficients are half the values of ϵ -Fe₂O₃. The observed spectra agree well with calculation results. Therefore, Al-substitution lightens the color of the ϵ -Fe₂O₃ based magnet.

In addition, Ga-substitution also lightens the color of the ϵ -Fe₂O₃ based magnet with the same mechanism as Al-substitution.

Conclusion

In this work, optical absorption of ϵ -Fe₂O₃ was investigated. ϵ -Fe₂O₃ has a wide band gap of 2.0 eV for down-spin transition and 2.4 eV for up-spin transition. Therefore, this ferrite magnet exhibits high transparency. In addition, first-principles calculations of ϵ -Al_{0.5}Fe_{1.5}O₃ and ϵ -Ga_{0.5}Fe_{1.5}O₃ were carried out. The electronic structure was calculated by substituting Fe³⁺ ions of the tetrahedral D sites with Al³⁺ ions or Ga³⁺ ions. The calculated results show that the band gaps are larger than ϵ -Fe₂O₃. This expansion of the band gap can be understood by the disappearance of the energy states in the conduction band and the valence band, which are originated from the tetrahedral D site.

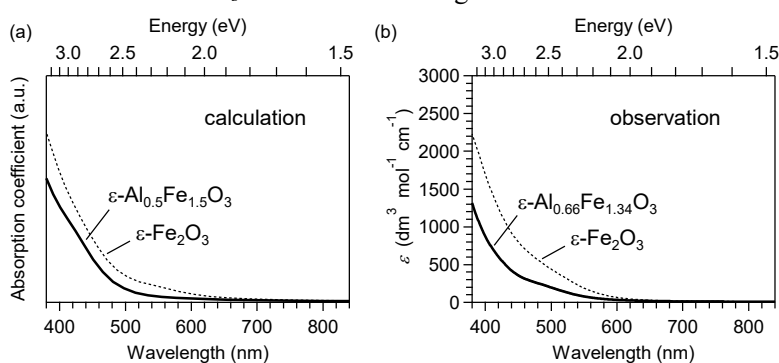


Figure 4. (a) Calculated optical spectra of ϵ -Al_{0.5}Fe_{1.5}O₃ and ϵ -Fe₂O₃, and (b) observed optical spectra of ϵ -Al_{0.66}Fe_{1.34}O₃ and ϵ -Fe₂O₃.