

Fe Doping Effects on the Optical and Magnetic Properties of Indium Oxide

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Powders of $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ ($x=0, 0.02$ and 0.15) synthesized from mixtures of aqueous solutions of InCl_3 and FeCl_3 exhibited the x-ray diffraction pattern of In_2O_3 and the $\text{Fe } 2p_{3/2}$ electron spectrum due to the Fe^{3+} state. The optical absorption peak energies of the samples with $x=0, 0.02$ and 0.15 were 3.44, 3.54 and 3.17 eV, respectively. For the samples with $x=0.02$ and 0.15 , additional absorption structure at around 2.3 eV was observed below the optical gap of the $x=0$ sample. Model cluster calculations by discrete variational- $X\alpha$ method for the Fe^{3+} ions at $8b$ and $24d$ sites of the In_2O_3 crystal lattice showed asymmetric spin density of states in the vicinity of the valence band maximum. The $x=0.15$ sample showed a divergence between the zero-field-cooled magnetization and the field-cooled magnetization at 250K. A sharp peak at ≈ 30 K was observed in the history dependent magnetization.

Key words: Fe, In_2O_3 , light absorption and reflection, glassy magnetism, DV- $X\alpha$ computation

1. Introduction

It is of great interest to integrate the asymmetric electron spin density of states (DOS) of $3d$ transition metal ions with the wide band gap (E_g) of In_2O_3 for leading to developments of a high-performance monolithic flat-panel display. The asymmetric electron spin DOS in the vicinity of the valence band maximum (VBM) should enable a low field extraction of spin-polarized electrons with uniform energy distribution. Therefore, it is important to study the electronic structure of $\text{In}_{2-x}\text{M}_x\text{O}_3$ (M: trivalent $3d$ transition metal ions) to characterize the optical and magnetic properties of multifunctioned In_2O_3 .

In_2O_3 crystallizes to form the C -type rare-earth structure with the cubic cell lattice constant (a) of 1.0117 nm. The space group symmetry of the unit cell is $Ia\bar{3}$, and it contains sixteen In_2O_3 formula units with fluorite-type unit cells accompanying systematic O vacancies: In atoms occupy Wyckoff positions $8b$ and $24d$, and O atoms occupy Wyckoff positions $48e$. There have been many studies on substitution effects for trivalent In ions of In_2O_3 by di- or tetra-valent foreign ions¹⁻³ to obtain a high electrical conductivity with high transmissivity in the visible region.⁴⁻⁷

In this paper, we report how the Fe doping effects on the optical and magnetic properties of In_2O_3 . A high spin state Fe^{3+} ion has the magnetic moment of $S=5/2$, and its ionic radius (0.079 nm) is smaller than that of In^{3+} (0.094 nm). So, it is expected that the $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ with smaller a value shows the larger optical and magnetic effects due

to introduction of the d^5 electrons into the octahedral coordination field of the transparent and diamagnetic In_2O_3 .

2. Experiment

Powder samples of $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ ($x=0, 0.02$ and 0.15) were synthesized from mixtures of aqueous solutions of InCl_3 and FeCl_3 .⁸ The mixtures were stirred at room temperature, dehydrated thermally for 48 h, and then calcinated at 900 °C for 1 h in flowing O_2 gas. X-ray diffraction patterns measured with a Rigaku CN2013 diffractometer using $\text{Cu } K\alpha$ radiation were similar to each other, and we could not find any other peaks from the In_2O_3 crystal lattice. Peaks shift toward the higher angles with increase of x , which implies to a reduction of the lattice constant due to the Fe^{3+} ion substitution for In^{3+} ion of the In_2O_3 lattice. The a value of the samples with $x=0, 0.02$ and 0.15 were 1.0117, 1.0100 and 1.0088 nm, respectively. The powders can be expressed as $\text{In}^{3+}_{2-x}\text{Fe}^{3+}_x\text{O}_3$.

The chemical state of doped Fe was examined by X-ray photoelectron spectroscopy (XPS). We used a Surface Science Laboratories SSX-100 spectrometer with monochromatized Al $K\alpha$ source at room temperature. The spectrometer was calibrated utilizing the Au $4f_{7/2}$ electrons (83.79 eV) and the full width at half-maximum (FWHM) of the Au $4f_{7/2}$ peak was 1.03 eV. The experimental uncertainty is estimated to be $\pm 0.1_5$ eV in this experiment. The $\text{Fe } 2p_{3/2}$ peak was observed at 711.1 eV, which can be assigned to

the Fe^{3+} ion state.⁹ The $\text{Fe } 2p_{1/2}$ peak was masked by an intense background of the $\text{In } 3p_{1/2}$ peak (703.8 eV).^{10,11} It is obvious that doped Fe^{3+} ions substituted for In^{3+} ions in In_2O_3 lattice and the $\text{Fe } 3d$ orbitals hybridized strongly with the $\text{O } 2p$ orbitals in the octahedral coordination field. Thus, the Fe^{3+} (d^5) ions incorporated in the In_2O_3 lattice should add some optical and magnetic effects to transparent and diamagnetic In_2O_3 . Therefore, the electronic structure of the $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ powders has to be examined theoretically in order to analyze their optical and magnetic properties.

Ultraviolet-visible (UV-vis) diffuse reflectance spectra of the samples were measured with a resolution of 0.002 eV using a JASCO V-550 spectrometer. Magnetic measurements were carried out using a Quantum Design MPMS 5S superconducting quantum interference device (SQUID) magnetometer. In order to demonstrate the doping effect, we have measured the dc magnetization below 300 K in $H=100$ G.

3. The optical and magnetic properties

The diffuse reflectance spectra of the samples are shown in Fig. 1. The absorption peak energy of the $x=0.02$ sample was 3.54 eV which is larger by 0.1 eV than that of the $x=0$ sample, though the absorption peak energy decreased to 3.17 eV as the x increased to 0.15. New structure at around 2.3 eV grew with increasing x below the absorption edge of the $x=0$ sample. Variation of the absorption peak energy and appearance of the new structure should correspond to changes in the energy splitting between the valence band (VB) and the conduction band (CB) and to formation of the localized electronic states of Fe^{3+} (d^5) incorporated with the In_2O_3 crystal, respectively. Theoretical computations of the electronic structure by tight-binding method,¹² by first-principles,¹³ and by discrete variational (DV)- $X\alpha$ model clusters¹⁴ have been reported. Though, the electronic structure of In_2O_3 has not been analyzed in detail since the unit cell includes 80 atoms and the crystal structure is so complicated.¹⁵

In order to simulate substitution effects on the

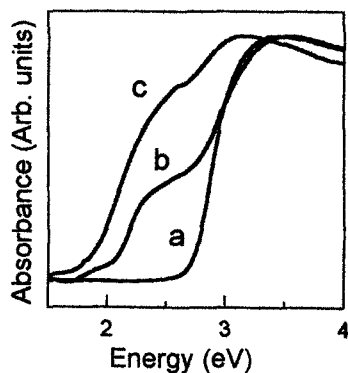


Fig.1 UV-vis diffuse reflectance spectra of the $\text{In}_{2-x}\text{Fe}_x\text{O}_3$ powders with $x=0$ (a), 0.02 (b) and 0.15 (c).

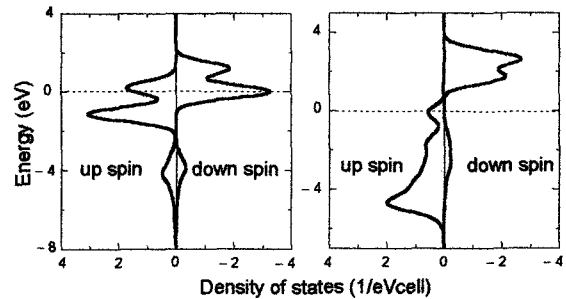


Fig.2 Calculated spin DOS for the Fe^{3+} (d^5) ion at $8b$ site (a) and $24d$ site (b).

optical and magnetic properties of the $\text{In}_{2-x}\text{Fe}_x\text{O}_3$, we have performed the DV- $X\alpha$ computation¹⁶ for the $(\text{FeIn}_{12}\text{O}_{42})^{45-}$ clusters with Fe^{3+} ions centered at $8b$ and $24d$ sites. The number of the sampling points was 500 per atom. Used minimal basis sets were $1s-2p$ for O, $1s-5p$ for In, and $1s-4p$ for Fe. The DOS were made by broadening the discrete energy eigenvalues by Gaussian functions with the full width at half-maximum of 0.3 eV. Computation for the $(\text{In}_{13}\text{O}_{42})^{45-}$ cluster yielded the DOS of a non-doped reference. The VB and CB of the non-doped In_2O_3 are predominantly consisted of the filled $\text{O } 2p$ and unoccupied $\text{In } 5s$ states, respectively. The optical transition (E_g) of non-doped In_2O_3 corresponds to the electron transition energy from the $\text{O } 2p$ to $\text{In } 5s$ states. We observed half-filled DOS of the $\text{Fe } 3d$ states with octahedral coordination at around the center of the optical E_g of non-doped In_2O_3 . It is obvious that Fe^{3+} ions positioned at $8b$ and $24d$ sites generate new DOS due to the $\text{Fe } 3d$ localized states in E_g . According to DV- $X\alpha$ computation, the peak at around 2.3 eV in absorption spectrum can be predicted by the formation of Fe^{3+} ion localized states at around the center of E_g .

We have calculated the electron spin DOS for Fe^{3+} ions at $8b$ and $24d$ sites in the vicinity of VBM. Figures 2(a) and (b) demonstrate the calculated d^5 spin DOS for the Fe^{3+} ions at the $8b$ and $24d$ sites, respectively. The both spin DOS are apparently asymmetric. Exchange interaction between the spins of $\text{Fe } 3d$ (t_{2g}) nonbonding orbitals in the octahedral coordination field results in parallel spin ordering both between the $24d$ sites with the distance of ≈ 3.4 Å and between the $8b$ and $24d$ sites with the distance of ≈ 3.3 Å. Though, superexchange interaction between the spins of $\text{Fe } 3d$ (e_g) antibonding orbitals via the filled $\text{O } 2p$ states in the octahedral coordination field results in antiparallel spin ordering between the $8b$ and $24d$ sites with the distance of ≈ 4.3 Å.^{17,18} Therefore, the direct t_{2g} interactions between Fe^{3+} ions occupied $24d$ sites are ferromagnetic. The t_{2g} interactions between Fe^{3+} ions in the $24d$ and $8b$ sites also becomes ferromagnetic, although the Fe^{3+} ($24d$) - O^{2-} ($48e$) - Fe^{3+} ($8b$) zigzag chains force the indirect e_g interactions of Fe^{3+} ions between the $24d$ and $8b$ sites to be

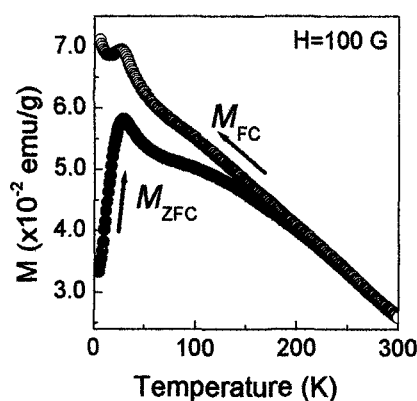


Fig.3 Temperature dependent the M_{FC} (○) and the M_{ZFC} (●) of the $In_{2-x}Fe_xO_3$ ($x=0.15$) powders.

antiferromagnetic. Thus, Fe^{3+} ion substitution at both $8b$ and $24d$ sites should result in a frustration in the spin ordering. Random substitution of Fe^{3+} ions at the $8b$ and $24d$ sites may introduce a randomness in the spin ordering. The frustration and randomness in the spin ordering introduced by the Fe^{3+} ion substituted for In^{3+} ion should result in a spin glass or cluster glass-like behavior.¹⁹⁻²¹

The temperature dependent magnetization of the samples with $x=0$ and $x=0.02$ showed a diamagnetism and a paramagnetism, respectively. The temperature dependent magnetization in $H=100$ G of the $x=0.15$ sample is shown in Fig.3. The zero-field-cooled magnetization (M_{ZFC}) is smaller than the field-cooled magnetization (M_{FC}) below 250 K. Both M_{ZFC} and M_{FC} exhibited a sharp peak at ≈ 30 K. The broad divergence of the history dependent magnetization below the bifurcate temperature suggests that there was ferromagnetic ordering of Fe^{3+} spins. The sharp peak at ≈ 30 K looks like antiferromagnetic ordering of the spins. This cluster glass or spin glass-like behavior due to the Fe^{3+} ions substituted for In^{3+} ions of In_2O_3 should correlate with a disordering of Fe^{3+} ions. A larger glassy behavior is expected for the sample with larger x value. Further magnetization measurements including frequency dependence of the linear susceptibility and the third order non-linear susceptibility (χ_3) with the more detailed crystal structure analysis are necessary to elucidate clearly the magnetization of the $In_{2-x}Fe_xO_3$.

4. Summary

The optical and magnetic properties of the $In_{2-x}Fe_xO_3$ were supported well by the DV- $\chi\alpha$ computation for the $(FeIn_{12}O_{42})^{45-}$ clusters with Fe^{3+} ions centered at $8b$ and $24d$ sites. A new structure at around the center of E_g was due to the Fe^{3+} (d^5) states in the octahedral coordination field. The observed glassy behavior in magnetism is a result of frustrated interaction between randomly introduced Fe^{3+} spins in the In_2O_3 lattice.

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