Defect levels coupled with oscillations and frustrated spins by Fe^{+3} in co-precipitated Aluminum ferrites

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Short Report

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Abstract

The degradation of organic dyes determines the suitability of a photocatalyst for wastewater treatments. Metal oxides like TiO_2 , ZnO , CuO , Fe_2O_3 , Ce_2O_3 , and Al-doped Ni Ferrites can degrade dyes. However, fine-tuning of physicochemical properties of the reaction system and characteristics of the reactor plays a significant role in making photocatalytic degradation a large-scale activity. The photoactivity gets altered by altering the Fe^{+3} ion concentration. The mechanism behind such changes has been addressed here, along with a unique magnetic property of frustrated spins observed.

1. Introduction

Ferrites are insulating magnetic oxides. Their structure can be spinel, garnet, or magneto plumbite. The metal cations are at the interstitials in the oxygen lattice. The magnetism in ferrites arises from the superexchange mechanism. They have technological applications in electromagnetic devices [1]. Al-doped Ni Cu and Mn ferrites have been used for supercapacitors as electrode material [2-4]. Al^{3+} doped CuCo_2O_4 nanowire arrays also act as an enhanced positive electrode for energy storage devices [5]

They have also been reported to enhance photocatalytic behavior [6] The interconnection of cluster created macropores allow the transport of the electrolyte creating a large surface area for redox reactions [7]

For high performances, the magnetic particles should be spherical, having smooth surfaces and narrow size distribution, large surface area, and high magnetic saturation. A change in particle shape sometimes takes place due to impurity ion concentration which gets a signature in the UV absorption spectra.

The M-phase ferrites have high magnetization, high Curie temperature, high coercive force, large magnetocrystalline anisotropy, high permeability and low conduction losses, chemical resistance. The structure consists of alternate stacks of spinel $\text{Fe}_6\text{O}_8^{+2}$ and hexagonal layers $\text{MFe}_6\text{O}^{-2}_{11}$. The structure of hexaferrite consists of a hexagonal lattice containing close-packed O atoms. The intrinsic magnetic properties of the material can be improved by substituting divalent and trivalent ions in place of Fe^{+3} ions [7]. Al-based ferrites have very large coercivities [8]. The Al^{+3} is nonmagnetic and they substitute the octahedral sites at low doping levels. Replacing Fe^{+3} with Al^{+3} however by an increased level of concentration leads to the formation of secondary phases.

Nanocrystalline Al substituted $\text{SrFe}_2\text{O}_{19}$ samples have been synthesized and have however not developed any secondary phases and apart from the M-phase hexagonal structure. An increase in Al^{+3} concentrations however led to a decrease in lattice parameter. The morphology of the particles changed from disc to rod-shaped on increasing the Al^{+3} concentrations. They also changed from ferromagnetic to ferrimagnetic with an increase in Al^{+3} due to weakened exchange interaction and non-collinear spin arrangement. There is also a size and magnetocrystalline anisotropy of the particles [8].

The material Aluminum Ferrite has many industrial applications. They are used as noise suppressors in audio-video cable filters. In combination with transition metals like Co and Ni, Al ferrite shows varied magnetic properties. From a metallurgical point of view, Al addition increases the ferrite grain size leading to lower core loss. In nanomaterials, there is a difference in cation distribution. The surface ions due to incomplete coordination shells lead to ionic displacements and changes in lattice parameters.

In this research work, we have synthesized Al Ferrite by co-precipitation method with different precursor concentrations (Fe^{+3}) and tried to study its effect on the structural and optical properties.

2. Experimental Details

Aluminum Ferrite ($\text{Al}_x\text{Fe}_y\text{O}_4$) was synthesized using Aluminum Nitrite ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Ferric Nitrate with Citric Acid as fuel using the Co-precipitation method. The Ferric nitrite doping was varied from $x = 0.1$ to $x = 0.2$ as 1%, 2% and 5%. The characterizations were done using XRD (Proto A-XRD), UV-ViS spectrometer (UV 3600 Plus, Shimadzu, Japan and Photoluminescence spectrometer (Fluoromax-4, Horiba Scientific, USA).

For Al Ni Zn Ferrite synthesis, Zinc nitrate 7.57 g was dissolved in 20 ml distilled water making a 0.5 M solution. A similar solution Nickel nitrate (7.30 g) was also prepared with the same molarity. A 1.5 M solution of Aluminum nitrate (8.5 g), Ferric nitrate (7.25 g) was also prepared. A 3M solution of Citric acid (11.52 g) in 20 ml is taken, which acts as a fuel. The nitrates were mixed and the citric acid solution was added dropwise during stirring for 30 min. Ammonia was also added dropwise to make the pH neutral ($\text{pH} = 7$). The total solution was heated at 300°C , till the formation of gel which was left open to absorb water to make a hard mass. The mixture was then ground with mortar pestle and calcined in the furnace at 600°C for 5 hrs. The powder was obtained as a further ground to make fine particles.

3. Results

The XRD plots of synthesized Al Ferrite powders with different doping are shown in Fig. 1. The plots showed no major peaks but a hump around 30° indicating amorphous nature (Fig. 2).

The M-H plot of Al Ferrite is shown in Fig. 2 which resembles that of a spin glass. Spin glass is a disordered magnet with a magnetic spin component not aligned in a regular pattern. The individual atomic bonds in a spin glass are a mixture of roughly equal numbers of Ferromagnetic bonds and Antiferromagnetic bonds. These patterns create *frustrating interactions* and result in distortion of atomic bond geometry. By frustration, it is meant that the atoms stick to a non-trivial position on a regular lattice. Magnetic Spin glass is very good conductor. Spin glass characteristics have been observed in CuMn and AuFe systems. We are first time reporting this property in Al-Fe systems.

The total magnetic moment is due to uncompensated upward spin. Al^{+3} replaces Fe^{+3} from sites having upward spin directions causing a reduction in saturation magnetization. Surface defects are also

responsible for lowering of exchange interaction. The hysteresis loop is a mixture of ferromagnetic and paramagnetic samples. The critical size of a single domain particle is given by

$$D_m = \frac{9\sigma_m}{2\pi M_s^2}$$

where $\sigma_m = \sqrt{\frac{2K_B T_c |K_1|}{a}}$ is the wall density energy, K_1 is the magnetocrystalline anisotropy constant, T_c is the Curie temperature, M_s the saturation magnetization, K_B Boltzmann constant, and a is the lattice parameter. For $D > D_m$, the particles have multi-domain and an increase in D_m takes place due to an increase in Al concentration.

For small concentrations of nonmagnetic ions like Al^{+3} , the saturation magnetization is $M_s = M_B - |M_A|$ where M_B and M_A denote the magnetization of A and B site ions in Spinel Ferrite (AB_2O_4). Due to polarization effects, the nonmagnetic ions prefer octahedral and tetrahedral sites causing an enhancement in M_s values. The preferential attainment of the octahedral and tetrahedral sites by the non-magnetic ions also causes Fe^{+3} ions to migrate to the B sites giving rise to an anti-parallel spin coupling which causes weakening of A-B exchange interactions and increases the M_s . The magnetic moment per formula unit $\eta_B = M_A(x) - M_B(x)$ [9].

In spinel structure, A^{+2} ions occupy tetrahedral sites and B^{+3} ions occupy the octahedral sites. $FeAl_2O_4$ has a spinel structure. The inverse spinel is written as $B(AB)O_4$ or $(A^{+2})(B^{+3})_2O_4$. In this half of the B^{3+} ions occupy tetrahedral sites and the other half, as well as A^{2+} ions, occupy the octahedral sites.

In inverse spinel structures, the Fe^{+3} ions are equally shared by tetrahedral and octahedral sites whereas the divalent metal ion (Fe^{+2} in case of Fe_3O_4) is at the tetrahedral site giving ferri-magnetic properties. In the compound $MgAl_2O_4$ from where the term spinel is taken, the Al^{+3} is at the octahedral sites.

The non-magnetic Al^{+3} ions introduced to ferrites, if replace the octahedral Fe^{+3} ions, the effective magnetic moment will decrease. However, Al^{+3} replacing the tetrahedral site ions has also been reported which will eventually cause an increase in the total magnetic moment of the sample. The most probable possibility seems to be an intermediate structure $(Fe_x^{3+} Al_{1-x}^{3+} [Fe_{2-x}^{3+} Al_x^{3+}] O_4)$ where the Al^{+3} atoms are shared between the A (tetrahedral) and B (Octahedral) sites. Al^{+3} replacing Fe^{+3} has been reported to a reduction in M_s , M_r and superexchange interaction $(Fe^{+3}_A)^{tet} - O - (Fe^{+3}_B)^{oct}$ which causes noncollinear spin alignment.

The reflectance spectra of all the samples are given in Fig. 3. It can be observed that in the wavelength range 380 – 640 nm, the Al Ferrite showed an increase in reflectance with an increase in Ferrite concentration from 1–2% followed by a decrease of 5%. After 640 nm, the reflectance value in the case of

5% Ferrite showed an increase. The band edge showed an increase in wavelength (redshift) for an increase in Ferrite concentration. The change in slopes around 450 nm was observed for 2% and 5% Ferric Nitrate concentrations due to the formation of defects. The bandgap energy can be calculated by Kubelka–Munk equation:

$$\alpha = F(R) = \frac{(1-R)^2}{(2R)} \quad (1)$$

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where, α is the absorption coefficient, R is reflectance, $h\nu$ is the incident photon energy; A is a constant, and n depends on the type of transition: $n = 1/2$ and 2 for direct and indirect transition, respectively.

The bandgap increased from 1.9 eV to 2.2 eV for an increase in Fe^{+3} concentration from 1–2%. Due to the formation of defects, a bandgap at 2.5 eV is also obtained. The bandgap showed a decrease to 2.1 eV for 5% doping also there were no prominent other band gaps which indicates decreased energy difference between the defect levels and the conduction band (Fig. 4).

Increasing the Fe^{+3} concentrations may create positive ion vacancy due to the higher positive charge of Fe^{+3} compared to Al^{+3} . The positive ion vacancy again is an effective negative ion which causes the nearby positive ions to move inward and negative ions to move outwards creating polarization. The dipole moment due to this polarization again interacts with the electric field of the incoming light wave. The higher is the interaction of the electric field of the incident light with the dipole moment, the higher will be the rate of optical transition. Each particle is assumed as a dipole oscillator of the displaced electron cloud and positively charged matrix region. The oscillations are due to perturbation by light. When two particles come together, coupled oscillations of lower frequency (higher wavelength) take place due to increased effective length (Fig. 5). So an increase in Fe^{+3} to 5% seems to bring the crystallites together to form a larger crystallite and lower the bandgap.

4. Conclusions

The synthesized Al Ferrite showed amorphous nature. The shift in absorption edge and corresponding changes in bandgap with increased Ferrite concentrations were attributed to changes in particle shape and formation of excitons. Aluminum Ferrite was synthesized by the Co-precipitation method with different Ferric Nitrite concentrations. XRD studies showed amorphous nature. Magnetic studies showed spin-glass properties of Al Ferrite. Higher Fe^{+3} concentrations caused increased dispersion of the excited energy states and the bandgap showed variation due to defect levels formed and coupled oscillations of lower frequency which may lead to increased photocatalytic activity. These observations open the doors for further research in Al ferrites as a smart multi-functional material.

Declarations

CONSENT FOR PUBLICATION

Not Applicable

FUNDING

Not Applicable

CONFLICT OF INTEREST

Nil

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Figures

Figure 1

XRD of synthesized Al ferrite

Figure 2

M-H plot of Aluminum Ferrite

Figure 3

Reflectance spectra of Aluminum Ferrite

Figure 4

Band gap determination using Kubelka–Munk equation

Figure 5

Coupled oscillations of atomic dipoles