A comparison between Curie temperature of nano and bulk Al doped nickel ferrite (NiAlFeO₄)

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Abstract: Nanocrystalline Al-doped nickel ferrite NiAlFeO₄ has been synthesized by sol-gel method. The X-ray diffraction (XRD) revealed that the powder obtained is single phase with spinel structure. Average crystallize size has been calculated by Scherrer's formula. The morphology of the sample was investigated by TEM and the mean particle size of the sample was obtained, which was 65 nm. Magnetic hysteresis loop was measured at room temperature with a maximum applied field of 3000 Oe. The Curie temperature (Tc) obtained by Faraday balance. The results show that magnetization decreases whit decreasing of particle size and Curie temperature increases. The magnetization of the sample is lower than the bulk one. The reduction of magnetization compared to bulk one is a consequence of surface spin disorder. The Curie temperature of the powder was determined using a Faraday balance and the result shows that the Curie temperature of the sample is higher than the bulk counterpart.

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1. Introduction

There are many methods for preparation of fineparticle ferrites [1]. The preparation technique plays an important role in surface properties and the Curie temperature (Tc) can also be varied by substitution of non-magnetic cations[2]. In the present investigation, we have employed sol-gel method to synthesize Aldoped nickel ferrite nanoparticles. This method offers a significant saving in time and energy consumption over the traditional methods, and requires less sintering temperature. This method is employed to obtain improved powder characteristics, more homogeneity and narrow particle size distribution, thereby influencing structural, electrical and magnetic properties of spinel ferrites. Ni ferrite and substituted ones are technologically important materials, which have been studied in many experimental and theoretical works. NiFe₂O₄ spinel ferrite combines a wide range of useful magnetic properties with relatively low electrical conductivity. Thus, unlike the metallic magnetic materials, they display low eddy current loss in alternating current applications and they are particularly useful in the radio frequency range. Therefore, this ferrite has numerous applications in recording heads, core materials for various transformers, inductors and TV deflection units.

In this work, NiAlFeO₄ fine powder was prepared by sol-gel method. It has been shown that single-phase Ni-Al ferrite fine particles can be prepared by this method, at a temperature much lower than is associated with the conventional ceramic method. In the inverse spinel

Structure of NiFe₂O₄ the tetrahedral sites are occupied by ferric ions and octahedral, by ferric and nickel ions. Substitution of Al ions in above structure is for Fe ions.

2. Experimental procedure

Nanocrystalline powder of NiAlFeO₄ was prepared by sol-gel method. The citric acid (C₆H₈O₇.H₂O), nickel (Ni (NO₃)₂.6H₂O), ferric nitrate (Fe nitrate $(NO_3)_3.9H_2O$, and aluminum chloride $(AlCl_3.6H_2O)$ were used as starting materials. The metal nitrates were dissolved together in a minimum amount of de-ionized water to get a clear solution. A clear solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7. The mixed solution was heated on a hot plate with continuous stirring at 90-100°C. During heating the solution became viscous and finally formed a very viscous green gel and began to bubble, after 1h a hard black mass was remained. The as-prepared powder was heat treated at 1100°C for 2h to get the final product. The structural characterization of the as prepared ferrite powder was carried out, using Bruker D8 XRD system with CuK α radiation (wavelength, λ =1.5406Å). The average particle size D was calculated using XRD data, employing the Scherrer's formula:

D=0.9λ/βCosθ

Where β is the angular line width at half maximum intensity and θ is the Bragg angle of the peaks.

Magnetic measurements were performed using the AGFM. Magnetic hysteresis loop was measured at room temperature with maximal applied magnetic fields up to 3000 Oe.

The Curie temperature of the sample was measured by Faraday balance.

The morphology of the nanopowders was studied by a transmission electron microscope; Philips CM-12.

3. Results and discussions

Fig. 1 shows XRD pattern of NiAlFeO₄ sample. The XRD pattern clearly indicates that the prepared sample contains cubic spinel structure only. Average crystallite size has been calculated by Scherrer's formula. The results are as showed in table 1.

superexchange interactions, which tends to align the neighboring dipoles antiparallelly. This substitution decreases the magnetization of the sample, compared to $NiFe_2O_4$ as was reported in other works [4].

In the inverse spinel structure of NiFe₂O₄, the tetrahedral sites are occupied by ferric ions with a magnetic moment of 5 μ_B and octahedral sites are occupied by both ferric and nickel ions together with a magnetic moment of $7\mu_B$ in opposite direction to that of tetrahedral sites.

This leads to a net magnetic moment of $2\mu_B$. The substitution of diamagnetic Al^{3+} , which has strong preference for occupying the octahedral sites for Fe⁺³, decreases the magnetic moment of octahedral site. This leads to a decrease in the net magnetization of the sample.



Fig1. X-ray diffraction pattern of NiAlFeO4 nanoparticles .

Table 1: Structural and Magnetic properties of NiAlFeO4 nanoparticles .

NiAlFeO ₄			
D(nm)	a(Å)	M(3000 Oe)(emu/gr)	Tc(∘c)
21.42	8.23	0.7	670

TEM image of the sample is illustrated in Figs. 2, indicating the nanoscale nature of ferrite particles. The image also shows that mean particle sizes of the powders are about 65 nm.

 Al^{3+} ion has strong preference to occupy octahedral sites [3]. The removal of magnetic Fe^{3+} ion from magnetic sublattice in NiFe₂O₄ and substitution of the nonmagnetic Al^{3+} ion in its place weakens the



Fig. 2. TEM photograph of the NiAlFeO₄ nanopowders.

Magnetic hysteresis loop of Al-doped nickel ferrite NiAlFeO₄ nanoparticles measured at room temperature using AGFM are shown in Fig. 3. At maximal applied field of 3000 Oe, the saturation was not achieved.

The value of magnetization at applied magnetic field of 3000 Oe for NiAlFeO₄ nanoparticles was measured to be 0.7 emu/gr. This is approximately lower than the value of the bulk sample at room temperature[5].



H(Oe)

Fig.3. Magnetic hysteresis loop of NiAlFeO₄ sample.



Fig.4. M-T curve of NiAlFeO₄ nanopowders.

This is due to particle size reduction of this sample in which the surface to volume ratio has been increased. In this case surface spin disorder will be increased as particle size are reduced and leads to a decrease in magnetization [6-7]. Beside the canting of the surface spin caused by broken exchange bonds, the core spins could also have canted spin structure due to the large magnetocrystalline anisotropy resulting from the occupation of the tetrahedral sites by Ni²⁺ ions [8].

Fig. 4 shows the result of measuring Curie temperature by Faraday balance.

Perhaps most noteworthy of our results is that the Curie temperature measured for NiAlFeO₄ nanoparticles, approximately 670° C, is higher than the measured bulk value of 510° C [9].

This result can be very valuable for industry purposes. The finite size scaling [10] can be used to explain the behavior of Tc. In order to explain the increase of Tc transition temperature of the bulk, it should depend on the dimension of the system in the following manner: $[T_C(D)-T_C(\infty)]T_C^{-1}(\infty) = \pm (D/D_0)^{-\lambda}$ where the exponent is predicted to be related to the correlation length exponent by $\lambda=1/\nu$, the system dependent sign may be either positive or negative, and D_0 should be of the order of the characteristic microscopic dimension of the system [10].

4. Conclusion

In this work we have prepared single phase Ni–Al ferrite nanopowders by the sol-gel method. Measured magnetic parameters of the sample show that

magnetization of Al substituted Ni ferrite nanopowders are lower than those related to bulk ones. This is because of the surface spin disorder an increase in surface to volume ratio in nanoparticles. The Curie temperature of the sample is higher than the one related to bulk counterpart, which is a result of a reduction in superexchange interaction.

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