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Enduring effect of rare earth (Nd^{3+}) doping and γ- radiation on electrical properties of nanoparticle manganese zinc ferrite

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ABSTRACT

Rare earth (Nd^{3+}) doped Manganese-Zinc Ferrite nanoparticles with composition $Mn_{0.65}Zn_{0.35}Fe_{2-x}Nd_xO_4$ (x = 0.04, 0.05 and 0.06) were prepared using combustion method of materials preparation. Formation of pure spinel phase was confirmed using X-ray diffraction (XRD) and Fourier transforms infra red spectroscopy (FTIR). The samples were exposed to various doses of γ-radiation (500Gy, 750Gy and 1000Gy) after recording the data on structural and electrical transport properties of as prepared samples, in order to study the effect of γ-radiation on these properties of the nanoparticles. Lattice constant '*a*' that showed a moderate increment with Nd^{3+} doping was found to show a further increase after γ-radiation exposure with nearly a 30%–40% reduction in crystallite size. Transmission electron micrographs showed a decreasing trend of particle size that was nearly proportional to increasing dose of γ-radiation. The samples which showed enhancement in resistivity profile with increasing Nd^{3+} concentration showed a reverse trend of decrease in the resistivity values with increasing γ radiation dose thus contributing to the conduction process. The dielectric constant of Nd^{3+} doped samples showed a multifold increase in the dielectric constant with a further increase in its values for radiated samples, when referred to the values reported for undoped Mn-Zn nanoparticle ferrite materials.

1. Introduction

Magnetic nanoparticles of Manganese- Zinc ferrite have attracted tremendous interest in recent years due to their highly unique physical, electrical and magnetic properties, which remarkably vary from the bulk properties of the respective materials [1–3]. These materials play a very important role in numerous applications such as medical technologies, catalysis, absorbent, magnetic recording media, radiofrequency circuits, wave guides etc [4–7]. Ferrites also known for their usefulness in miniature electro-optic modulators piezoelectric sensors, high quality filters etc as a result of their unique magnetic and electrical properties. These properties are dependent on several factors such as method of preparation, doping material, raw materials used as well as external property altering factors like electromagnetic radiation etc [8,9]. The high electrical resistivity at room temperature, incomparably low eddy currents and dielectric losses, high permeability and saturation magnetization along with adjustable Curie temperature, immense chemical stability are some of the very important properties of these ferrite materials that are responsible for emerging technological applications of ferrite nanoparticles [10–13]. Mn-Zn ferrite has a spinel structure which is highly stable and exhibits variation in lattice constant on changing the concentration of the constituents. The unit cell comprises of eight formula units generally referred *Fd*3*m* space group. Cations occupy special positions 8a and 16d. The geometry of a unit cell is monitored by the tetrahedral (A-O) and the octahedral (B-O) bond lengths [14–16]. Most of the properties of these materials are normally governed by the cation distribution over the tetrahedral site (A-site) and the octahedral site (B-Site) inside the unit cell. Appropriate additives or appropriate alternate methods can be used to bring about effective and irreversible changes in cation distribution [17] which can effectively enhance several useful properties of these materials.

Numerous methods of material preparation are being employed by researchers for preparing materials some of which include solvo-thermal method [18,19], co-precipitation method [20,21], the hydrothermal precipitation processing [22], the sol–gel synthesis [23], the micro-emulsion approach [24,25] combustion synthesis [26–28], and spray pyrolysis [29]. It is found that the properties of the ferrite nanoparticles largely depend on preparative method as

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the conditions under which the raw materials are subjected to, in obtaining the final product differ in every method which can be linked to cation distribution in the final product [30,31].

According to the reports one can alter these properties in several ways. Rare earth doping is one of the very sensitive and effective methods where in the smallest level of rare earth inculcation replacing Fe ion at the octahedral site can alter the structural, magnetic and electrical properties to a great extent [32]. Rare earths have unpaired 4f electrons shielded by $5s^2$ and $5p^6$ electrons. When rare earth ions are introduced in spinel ferrite a coupling between 4f electrons of rare earth ions and 3d electrons of transition element occurs which plays a decisive role in setting the magnetic and electrical properties on the ferrite material. However the inculcation of rare earths in the structure is not an easy task as the solubility of rare earth in the host material is poor. However low amounts of rare earth material could be included in the host matrix by employing conventional simple methods of material preparation [33].

Earlier investigations on interaction of high energy radiations with nanoparticle material has shown that significant amount of variation in the cation distribution can be achieved leading to sizeable variations in various properties of the material [17,34]. Gamma (γ) rays and heavy ion beam are some of the radiations that can be employed to bring about such changes in the materials. These high energy radiations can bring about several changes like creation of defects in the structure, excitations and ionizations in atoms which can help to alter the material properties [35,36]. The present treatise comprises of interesting findings on investigations carried out on Nd^{3+} doped Mn0.65Zn0.35Fe2-xNdxO4 (x = 0.04, 0.05 and 0.06) and gamma radiated nanoparticle samples prepared using combustion route which is an effective method for synthesizing magnetic nanoparticles with a uniform particle size distribution at low cost The compositional values of Mn, Zn, Fe and Nd have been selected in light of available reports showing optimum values of magnetic and electrical properties for Mn-Zn ferrites [17,26,27,33]. The investigations show that inclusion of Nd^{3+} in Mn-Zn ferrite nanoparticles significantly increases its resistivity with increasing ‘x’ thereby lowering the dielectric constant. On the other hand γ radiation is seen to induce a reverse effect. However Nd^{3+} doping and exposure to γ radiation show an increase in lattice constant of the materials under investigation. The investigation thus demonstrates that one could choose the right method to optimize the required properties on the basis of suitability.

2. Experimental

2.1. Sample preparation

Ferrite powders with composition Mn0.65Zn0.35Fe2-xNdxO4 (x = 0.04, 0.05 and 0.06) were prepared using combustion route [37,38]. The metal salts in the form of acetates and nitrates were taken as raw materials in stoichiometric proportion along with Nitrilotriacetic acid (NTA) as complexing agent and Glycine as fuel. The reactants were dissolved in distilled water at an elevated temperature of 80 °C. The clear solution thus obtained was subjected to volume reduction through conventional heating until a dry mass is obtained and fuel ignition temperature is reached. The residual product obtained after combustion of dry mass was crushed into fine powder and used for characterization and study of various investigations. The powdered samples were pressed into pallets of diameter 10 mm and 2.5 mm thickness. Three sets of pallets were irradiated with γ radiation for doses 500Gy, 750Gy and 1000Gy respectively obtained from ^{60}Co source. These pallets were then crushed into fine powder and used for characterization and various other investigations.

2.2. Characterization, γ-irradiation and electrical property investigation

The X-ray diffraction patterns for rare earth (Nd^{3+}) doped Manganese Zinc ferrite powders with composition $Mn_{0.65}Zn_{0.35}Fe_{2-x}Nd_xO_4$ (x = 0.04, 0.05 and 0.06) were obtained on Rigaku X-Ray diffractometer (Cu Kα, λ = 1.5418 Å) and the formation of monophasic cubic spinel was confirmed using Rietveld refinement. Fourier transforms infra red spectra for as prepared nanocrystalline samples were taken on Simadzu FTIR 8900 setup.

Further these ferrite samples were exposed to three different doses of γ radiation obtained from ^{60}Co source. The γ radiations of wavelengths λ = 0.0106 Å with energy E_1 = 1.17 MeV and wavelength λ = 0.009 Å with energy E_2 = 1.33 MeV obtained from ^{60}Co source were used to irradiate these samples for different time durations in order to obtain the radiation dose of 500Gy, 750Gy and 1000Gy. Gamma irradiated samples were again characterized using X-ray diffraction (XRD) for investigating structural alterations if any.

Transmission electron micrographs were obtained on Hitachi transmission electron microscope to investigate the variation in the particle size before and after γ-irradiation. The variation of dielectric constant ‘ε’ of as prepared and γ-irradiated samples as a function of temperature and frequency was determined using Wayne Kerr precision component analyzer 6440B. DC resistivity ‘ρ’ variation of the as prepared and γ irradiated samples was measured using a two probe setup.

3. Results and discussion

3.1. X-ray diffraction

X-Ray diffraction patterns for as prepared and γ irradiated were recorded over the 2θ range of 20° to 80° and found to exhibit pure cubic spinel phase without any structural distortion before and after γ radiation exposure.

Fig. 1a shows XRD patterns obtained for $Mn_{0.65}Zn_{0.35}Fe_{2-x}Nd_xO_4$ before γ irradiation. It may be seen that the intensity of the 311 peak increases with increase in Nd^{3+} doping with a minor shrinkage in its width and a small shift in the peak positions towards the lower angle. The positional shifts essentially indicate variation in the lattice parameter and shrinkage in the peaks is a result of reduction in the crystallite sizes. These variations should

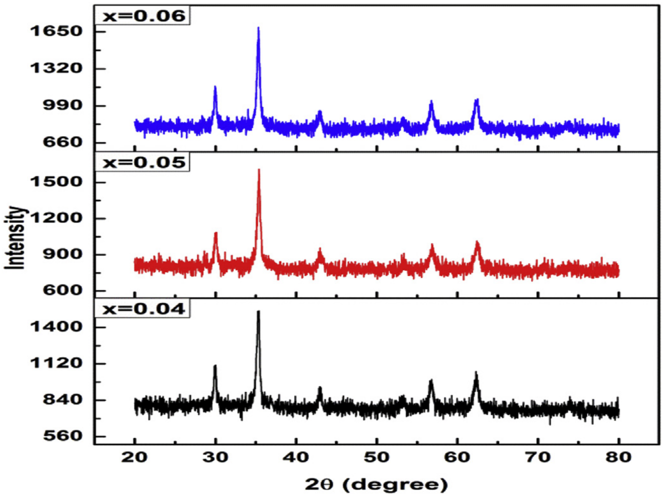

Fig. 1. X-ray diffraction pattern for as prepared $Mn_{0.65}Zn_{0.35}Fe_{2-x}Nd_xO_4$.