# Effect of Sm Doping on Structural and Dielectric Properties of CoFe₂O₄ Ferrite

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Samarium doped cobalt ferrite, $CoSm_xFe_{2-x}O_4$ in which $x$ varies as 0.0, 0.1, 0.3 and 0.5 were synthesized by conventional solid state reaction method. The impact of samarium doping on structural and dielectric properties is studied. The phase formation is confirmed by using XRD technique. The reflection peak broadening increases with increase in Sm concentration. The grain size is calculated by using scanning electron microscope image. The variation in dielectric constant ($\varepsilon'$) and dielectric loss ($\tan\delta$) as a function of frequency in the range 20 Hz to 1 MHz is studied. The dielectric constant is enhanced with increase in Sm concentration and decreases with increase in frequency.

**Keywords:** Cobalt ferrite, Solid state reaction, Dielectric constant, Loss tangent.

## 1. INTRODUCTION

Since many years, the scientific community is engaged in the study of rare earth ions substituted spinel ferrites for their use in high-density magnetic recording and enhanced memory storage, magnetic fluids and catalysts [1]. Spinel ferrites with general formula $MFe_2O_4$ (M = Co, Ni, Zn or other metals) are well known as they continue to be one of the most important scientific and industrial material by virtue of their electrical and magnetic properties [2, 3]. Since many decades, these materials are in focus because of scientific interest and technological importance in electronics, optoelectronics, and microwave industry and in fabrication of sensors [4-6]. The main advantage of use of such materials is their low cost, easy manufacturing process and remarkable electric and magnetic properties [7]. In the inverse spinel structure, the tetrahedral (A) sites are occupied by the $Fe^{3+}$ ions and the octahedral sites (B) are occupied by the divalent metal ions ($M^{2+}$) and $Fe^{3+}$, in equal proportions. The angle A-O-B is closer to 180 than the angles B-O-B and A-O-A, and therefore, the AB pair (Fe-Fe) has a strong superexchange (antiferromagnetic) interaction. The synthesis of spinel ferrites by using different methods has been investigated intensively in recent years because of their remarkable electrical and magnetic properties and wide practical applications in biotechnology [5, 6].

Amongst many spinel ferrites, cobalt ferrite is a well-known inverse spinel structured hard magnetic material with high coercivity, moderate magnetization and highest magnetocrystalline anisotropy [7, 8]. The doping of rare earth (RE) in cobalt ferrite not only makes the structural distortion but also impacts largely on its properties. The substitution of RE elements in $CoFe_2O_4$ is promising to manipulate magnetic coupling as reflected in decrease of hyperfine field as well as Curie temperature to increase the sensitivity [1]. The interest in RE elements and their influence on the microstructure and magnetic properties of substituted ferrite is related to the occupancy of the $4f$ electron shell [9]. The RE elements present large ionic radii which, when substituting cations with smaller ionic radii in other types of structures, can determine a change in cell symmetry and thus generate internal stress. In this work, we aimed to study the effect of Sm doping on structural distortion and dielectric properties of cobalt ferrite.

Several methods such as sol gel, co-precipitation, combustion technique, hydrothermal, solvothermal and ceramic method are used to synthesis such materials. Among them, ceramic method has attracted much attention because of simple synthesis process, control of stoichiometry, uniform particle size distribution and less pollution. We focused on influence of samarium doping on structural and dielectric properties of cobalt ferrite.

## 2. EXPERIMENTAL

A series of Sm doped $CoSm_xFe_{2-x}O_4$ in which $x$ varies as 0.0, 0.1, 0.3 and 0.5 were synthesized by conventional solid state reaction method. The oxides such as $Co_3O_4$, $Fe_2O_3$ and $Sm_2O_3$ were used as starting materials. The oxides were mixed in required proportion and ground in agate mortar for 3 h. The powder was presintered using programmable furnace at 800 °C for 10 h in air medium. The presintered powder is again crushed for couple of hours and sintered again at 850 °C for 12 h. The phase formation is confirmed by using X-ray diffractometer (Philips, Model PW-3710) using CuKα radiation with $\lambda = 1.5406$ Å. Once the phase is confirmed, the powder is pelletized using hydraulic press with polyvinyl alcohol as a binder. The pellets were finally sintered at 850 °C for 12 h. The particle size and stoichiometry is studied by using Carl-Zeiss Scanning Electron Microscope. The frequency dependence dielectric constant and dielectric loss in the range 20 Hz to 1 MHz was studied using a precision LCR meter bridge (HP 4284 A).

## 3. RESULTS AND DISCUSSION

The XRD patterns of the undoped and Sm doped $CoFe_2O_4$ is shown in Fig. 1. All samples revels the cubic structure with (311) as dominant intense peak. As expected, the intensity of diffraction peaks decreases with

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the increase in Sm concentration, which indicates lattice distortion in the sample. When Sm ions are replaces the Fe ions, a strain is induced in the system, resulting in the alteration of the lattice periodicity and decrease in crystal symmetry. For higher percentage of Sm doping, few $Sm_2O_3$ peaks appear in the pattern which reflects the forbidden of high doping, not to complete the solid state reaction. The lattice parameter is found to be decreasing with increase in Sm concentration. It is known that ionic radii of $Sm^{3+}$ (0.96 Å) is larger than ionic radii of $Fe^{3+}$ (0.67 Å). Therefore, the doping of Sm can leads to the Fe vacancies and distort the tetrahedral and octahedral symmetry and affects the lattice parameter and bond length [10-14].

Another possibility is that $Sm^{3+}$ ions may reside at grain boundaries, which hinders the grain growth and exerts a pressure on grain, causing to decrease the lattice parameter. The broadening in the diffraction peaks is also observed as the Sm doping increases.
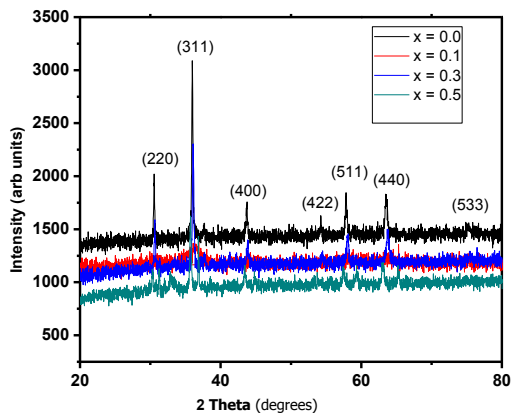


**Fig. 1** – XRD patterns of $CoSm_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.3 and 0.5)

Fig. 2 shows the surface morphology of the samples. The average size of particles varies from 0.22 to 0.74 μm. The Sm doped samples are distinguished by heterogeneous morphology composed of particles of a micrometer size. The particle size is found to be decreasing with increase in Sm concentration. The decrease in particle size is also reflected in XRD analysis as the peak broadening increases with increase in Sm concentration.
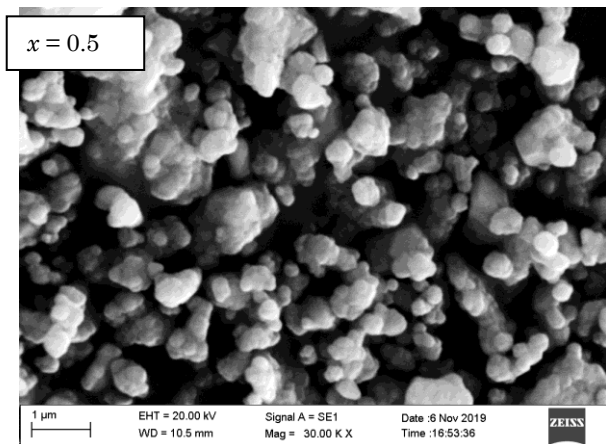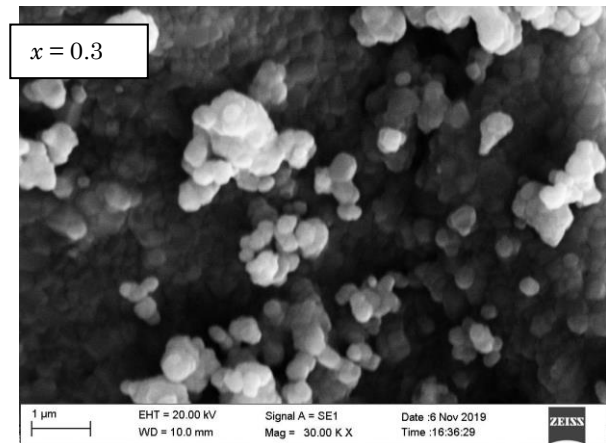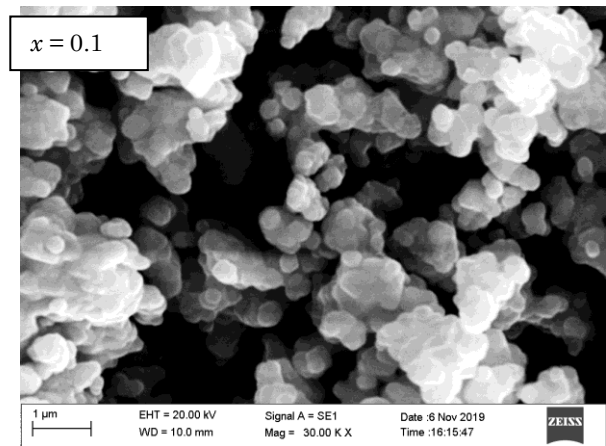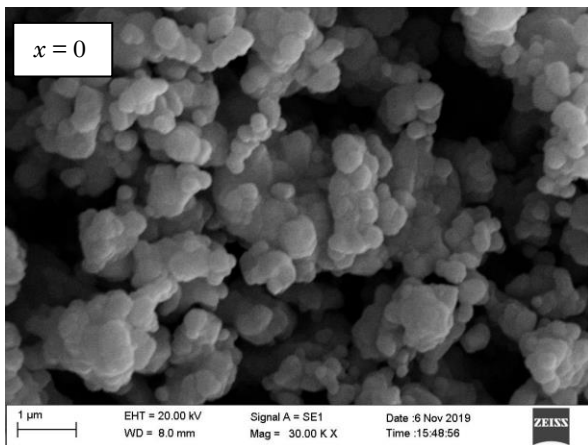








**Fig. 2** – SEM images of $CoSm_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.3 and 0.5)

Energy dispersive X-ray analysis is carried out in order to confirm the elemental composition and to test the presence of impurities. The stoichiometry is well maintained in all samples.

The dielectric properties depend on different factors such as synthesis, grain size and chemical composition. The frequency dependence of real part of dielectric constant is shown in Fig. 3. From Fig. 3 it is seen that the dielectric constant decreases with increasing frequency. The decrease is rapid at lower frequencies showing dispersion in the lower frequency region. The dielectric dispersion observed at lower frequencies is attributed to the interfacial polarization due to the two mediums that have different permittivities and conductivities [15].
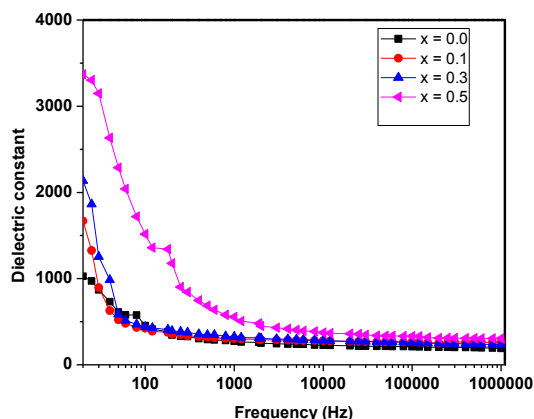
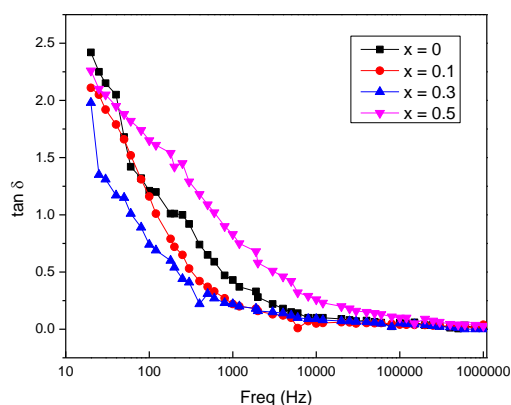**Fig. 3** – Variation of dielectric constant with frequency



**Fig. 4** – Variation of dielectric loss with frequency at room temperature

Since permittivity and resistivity are electrical properties of ferrites and depends upon the conduction phenomenon, hopping of electron between $Fe^{2+}$ and $Fe^{3+}$ is main cause for this conduction. This hopping is responsible for polarization at grain boundaries due to local charge displacement. Such kind of dielectric dispersion in ferrites can be explained by Maxwell-Wagner model [17] and Koops theory [18], which suggests that ferrite system consist of a combination of highly conducting grains separated by poorly conducting grain boundaries. Electrons by hopping pile up at grain boundaries due to high resistance and polarization takes place there. At high frequencies this hopping frequency does not follow up the field variation thereby making the relative permittivity a constant [16].

The loss tangent of the samples is shown in Fig. 4. From Fig. 4 it is clearly seen that dielectric loss tangent has the same trend as permittivity losses. It decreases with increasing frequency and becomes constant up to 1 MHz due to decreased polarization at high AC fields [16].

## 4. CONCLUSIONS

Sm doped $CoSm_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.3 and 0.5) were synthesized successfully by solid state reaction method. The peak width becomes broadening with increase in Sm concentration, which indicates the decrease in particle size. The homogeneity is distorts with increase in Sm doping concentration. The dielectric constant is also found to be decreasing with increasing frequency.

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