STRUCTURAL AND THERMOELECTRIC POWER STUDIES OF Sm^{3+}-SUBSTITUTED Li-Ni-SPINEL FERRITE

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Nanocrystalline spinel ferrite with chemical composition $Li_{0.15}Ni_{0.5}Sm_{0.1}Fe_{2.15}O_4$ was prepared using co-precipitation method and investigated under different annealing temperatures from 800°C to 1200°C for 6 hours. Structural analysis was done by employing the following techniques: X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM). The XRD patterns and IR spectra confirmed biphase except at 1100°C. The average crystallite size calculated using the Scherer formula was in the range of 21.3–55.2 nm. An increase in the crystallite size was observed with increase of annealing temperature. The images of scanning electron microscope revealed the grain size which was in consistent with the X-ray diffraction results. Differential method was used to investigate the thermoelectric power studies of synthesized ferrites at room temperature. The seebeck coefficient (**α**) was found 4.2×10^{-6} V/K which indicated its p-type semiconductor behavior.

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1. Introduction

Nanomaterials got great attention in the recent years due to their tremendous properties and versatile applications in the fields of microwave absorption, microwave devices, designing of radio frequency coils, and devices for telecommunication [1]. Nanoferrites also have applications in the field of thermoelectric power generation and their properties can be altered by method of preparation and annealing temperature [2]. Rare earth cation substitution also emerged as a great source of tuning the electrical and thermoelectric properties of ferrites. The rare earth doped Li-Ni-ferrites have extensively been studied due to their high frequency applications. Many studies report tuning of structural properties of ferrites by substituting trivalent ions such as Sm^{3+} on octahedral sites in the crystal structure [3,4]. Spinel ferrite nano particles are being synthesized via various methods such as co-precipitation, hydrothermal method, sol gel method and micro emulsion method [5-8]. Among these, co-precipitation method has been used widely during the last few years. This process has many advantages over other methods such as low temperature digestion process and better control over the size and structure of synthesized nano particles. The

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objective of this work is to study effect of annealing temperature on the structural and thermoelectric properties of $Li_{0.15}Ni_{0.5}Sm_{0.1}Fe_{2.15}O_4$ ferrite prepared via co-precipitation method.

2. Experimental procedure

The starting materials used for synthesizing nano ferrite are $LiNO_3$, Ni $(NO_3)_2.6H_2O$, Sm $(NO_3)_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$. First of all stoichiometric calculations were made. The prepared aqueous solution was stirred at hot plate. The pH 11 was maintained by adding NaOH drop wise. After getting precipitates the beaker was put in preheated water bath for digestion and then filtered with deionized water 3 to 4 times. The obtained precipitates were dried in electric oven at 95 ^oC for overnight. The dried powder was grind with pestle and mortar for 30 minutes. For structural analysis, the prepared samples were sintered at different temperature 800-1200 ^oC for 6 hours. The X-ray diffraction (XRD) patterns were recorded at room temperature using Xpert Pro PANalytical diffractometer with Cu-Kα radiation (λ=1.54056 Å) at 40 kV and 30 mA. Step counting method was used to collect the intensity data with a scanning speed 0.05°/s in the 2θ range from 20^o-75^o. The Fourier transform infrared spectra (FTIR) were obtained using Jasco-310 spectrometer over the range 400 - 4000 cm^{-1}. The SEM images were obtained to study the surface morphology and microstructure of the grown nano particles using JSM-6490 JEOL scanning electron microscope (SEM). To investigate the thermoelectric properties of Li-Ni ferrites, Seebeck's coefficient was determined using a homemade setup. A gradient of 20 $^{\circ}C$ was maintained across the disk shape pellets and induced electromotive force (emf) was recorded in the temperature range of 375 - 675 K. A digital voltmeter (HC-9020) having accuracy ± 0.05% V was used to measure the induced emf.

2.1. Calculation

The recorded XRD patterns were used to calculate the lattice constant "a", unit cell volume "V_{cell}" X-ray density "D_x" and the crystallite size "D". The mathematical relations used to caluculate the above mentioned parameters are given below:

$$a = \frac{\lambda}{2Sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{1}$$

$$V_{cell} = a^3 \tag{2}$$

$$Dx = \frac{ZM}{N_A\, a^3} \tag{3}$$

$$D = \frac{k\lambda}{\beta_{hkl}\, Cos\theta} \tag{4}$$

where h, k, and l are the Miller indices, Z is representing of molecules per unit cell and its value for spinel structure is 8, N_A is the Avogadro's number and M is the molecular weight of the nano-ferrite, where k is the shape factor, λ is the X-ray wavelength; θ is the Bragg's diffraction angle and β_{hkl} represent full width half maxima. To measure the Seebeck's coefficient, the powered nano ferrites were pressed to form pellets using hydraulic press. Silver paste was used on either side of the pellet to ensure the good electric contact. The pellets were placed between two electrodes of the sample holder. A temperature difference of 20 ^oC was maintained between two ends of the pellets to develop a thermo electromotive force (emf) across the sample. The following relation was used to calculate the thermoelectric power or Seebeck coefficient (α) [9]

$$\alpha = \Delta E / \Delta\, T \tag{5}$$

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of $Li_{0.15}Ni_{0.5}Sm_{0.1}Fe_{2.15}O_4$ ferrite which was synthesized via co-precipitation route and sintered at different temperatures. The biphase structure was observed. The observed patterns have prominent diffraction peaks with reflection planes of (220), (311), (400), (422) and (511) which were indexed by computer software Jade 5 [10]. The lattice constant "a" was calculated using the Eq.1 and the obtained values were listed in Table 1. The calculated values of lattice constant were found in the range 8.4146 - 8.4501Å. It is observed that the lattice constant "a" increases with the increase in annealing temperature and resulted in an expansion of the unit cell. It is also observed that the average crystallite size on the annealing temperature and was found to be in the range of 21.2–55.1 nm. Also it can be seen from table 1 that the maximum value of crystallite size is observed at 1200 °C because it is an established fact that heat treatment of spinel ferrites at higher temperatures promotes the grain growth. In this research paper, the fine nanoparticles having average crystallite size under 50 nm are successfully prepared that are suitable to use as high density recording media to achieve high signal-to noise ratio. [11]. The Fig. 2 also depicts that the crystallite size increases with the raising of annealing temperature. The similar trend of the growth of nano particles with increasing annealing temperature had been reported previously by different researchers for the multiphase spinel ferrites prepared via different methods [12, 13].

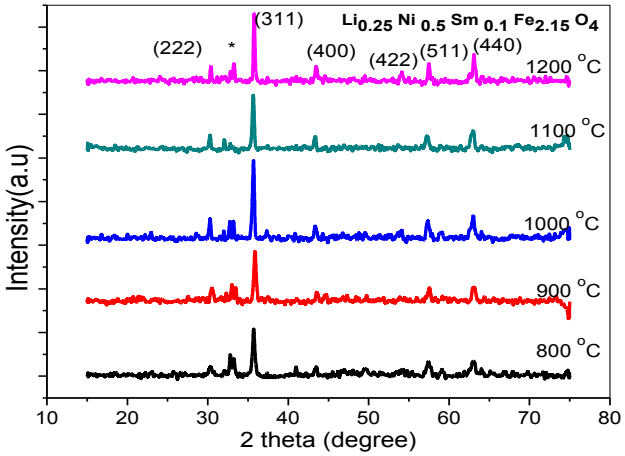


Fig. 1. XRD Patterns of $Li_{0.15}Ni_{0.5}Sm_{0.1}Fe_{2.15}O_4$ ferrite at different temperatures 800 - 1200 °C

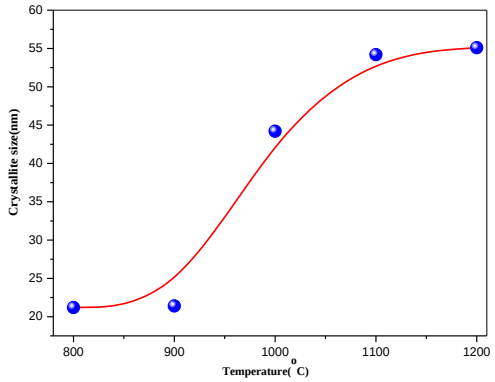


Fig. 2. Crystallite size (nm) vs annealing temperature

Table 1. Lattice constant (a), crystallite size, unit cell volume and X-ray density of Sm^{3+} doped Li-Ni ferrite sintered at different temperatures

Annealing Temperature (^oC)	Crystallite Size (nm)	Lattice Constant (Å)	Volume (Å)^3	Density g/cm^3
800	21.2	8.4146	595.79	5.13
900	21.4	8.4285	598.76	5.10
1000	44.2	8.4390	601.00	5.09
1100	54.2	8.4478	602.88	5.07
1200	55.1	8.4501	603.37	5.06

3.2. Morphological analysis

Fig. 3 (a-d) shows the morphology of the material which reveals the homogeneous grain size distribution. It is pertinent to mention here that the SEM images were recorded without gold coating. SEM images shown confirm the growth of shape and size that lies in the micron range.

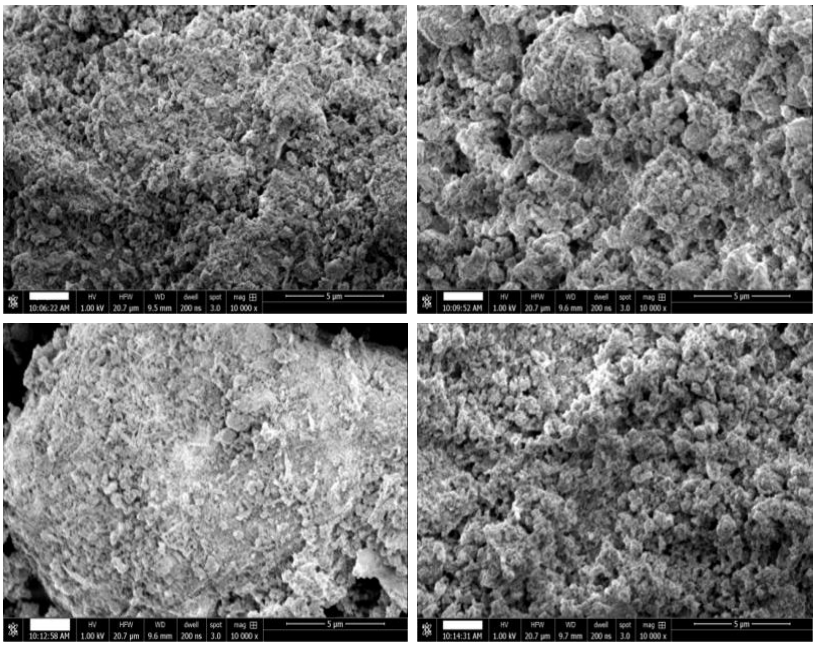


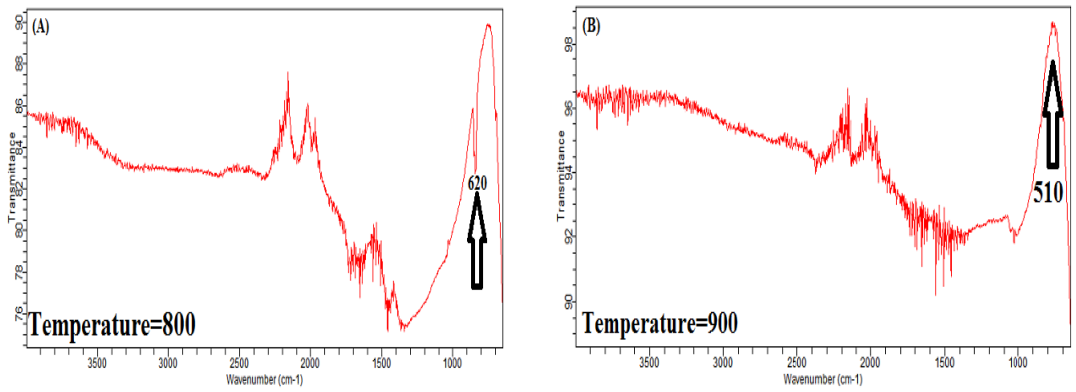
Fig. 3. SEM images of Sm^{3+} doped Li-Ni ferrite at different temperature (a) 800°C, (b) 1000°C (c) 1100°C and (d) 1200°C.

Some voids can also be seen in the SEM micrographs which may be the result of different annealing temperatures. Moreover, it is observed that the grain size increases with the increase of temperature in samarium doped lithium nickel ferrite.

3.3. FTIR spectra

FTIR spectra are considered finger prints of the materials. The rising of annealing temperature greatly shows influence on the hydroxyl group, carboxyl group and metal oxide group. Fig. 4 shows the FTIR spectra of Li-Ni nano ferrites annealed at different temperatures recorded in the frequency range of 600 - 4000 cm^{-1}. The absence of any band in the range 2500 - 4000 cm^{-1} confirms that no hydroxyl group is present and synthesized material is fully dried. The spectra of the samples show bands below 1000 cm^{-1} which is the common characteristic of spinel ferrites and are related to M-O vibration mode [14]. It is observed that the high frequency bands

vary from 527 – 550 cm^{-1} and low frequency bands vary from 405 – 457 cm^{-1}. This variation may be attributed to different annealing temperatures. A small peak corresponding to asymmetric carboxyl group at 1744 cm^{-1} is also observed. The peaks observed around 1359 cm^{-1} are corresponding to υ_{as} (COOH) and symmetric stretching for the respective carboxyl groups [15]. Ashiq et al. [16] also reported the similar results showing the effect of annealing temperature on vibration modes in the FTIR spectra of spinel ferrites.



a) *b)*

Fig. 4. FTIR spectrum of Sm^{3+} doped Li-Ni ferrite at (a) 800 °C and (b) 900 °C.

3.4 Thermoelectric studies

Fig. 5 shows the representative measurement of Seebeck coefficient of the sample annealed at 1000 ^{o}C in the range 375 - 675 K by employing differential method. The Seebeck coefficient was measured by plotting the induced thermo (e.m.f) of the samples versus temperature gradient across the samples. The values of emf and temperature were recorded during cooling cycle, due to better thermal stability as compared to heating cycle. The value of the Seebeck coefficient for the representative sample was observed α = 4.2 μV/K.

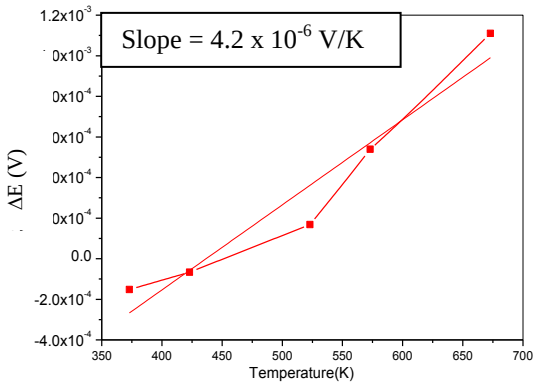


Fig. 5. Induced emf (ΔE) versus temperature for the sample annealed at 1000 ^{o}C

It has been observed that the samples show positive Seebeck coefficient that indicates the p-type nature of the samples. However, with increasing temperature, the n-type conduction mechanism dominates in spinel ferrites. The transfer of p-type conductivity to n-type conductivity can be attributed to the hopping of electrons between Fe^{+2} and Fe^{+3}. It was observed that with increasing temperature, the Seebeck coefficient of samples increases. It indicates the potential of spinel ferrites to use as efficient thermoelectric materials at high temperatures. As the heating and

cooling direction can be controlled by the polarity of applied voltage, so these devices can be used as temperature controllers.

4. Conclusions

The effect of increasing annealing temperature on the structure of synthesized samples was observed. The x-ray diffraction analysis confirms the cubic spinel formation and broadening of (311) reflection indicates the formation of growth of appropriate material. These reflections at low temperature indicate the formation of smaller nano particles. It was also observed that the crystallite size increases with increasing annealing temperature.

The M-O bond confirmation was studied by using FTIR spectroscopy and it revealed the formation of spinel ferrites. Scanning electron microscope analysis showed the formation of agglomerated particles at higher temperatures. At low temperature, the results of Seebeck coefficient indicate the p-type semiconducting behavior while at higher temperature the sample acts like an n-type semiconductor.

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