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Nd:YAG laser irradiation effects on electrical properties of polycrystalline $Li_{0.5}Fe_{2.5}O_4$

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ABSTRACT

The polycrystalline spinel structured $Li_{0.5}Fe_{2.5}O_4$ ferrite have been prepared by conventional double sintering ceramic method. The samples were palletized and irradiated by Nd:YAG laser with different laser fluencies and characterized by infrared spectroscopy and DC electrical resistivity in order to obtain phase, crystal structure and conduction mechanism in pristine and irradiated samples. The infrared spectroscopy is employed to study the local symmetry and conduction mechanism in crystalline solids before and after irradiation. The DC electrical resistivity measured by two-probe technique from room temperature to beyond Curie temperature with steps of 10 K increases after laser irradiation. Variation of dielectric properties like dielectric constant and dielectric loss tangent is also measured as a function of temperature. A significant reduction in the values of dielectric constant and dielectric loss tangent has been observed with the increase of laser dose.

1. Introduction

Spinel ferrites have potential applications in electrical components, memory and microwave devices over a wide range of frequencies because of their high resistivity and loss behaviour. Spinel structured ferrites MFe_2O_4, where M is often a transition metal atom, is kind of most important magnetic materials and have been widely used in technologies. Lithium and substituted lithium ferrites have attracted considerable interest for their potential microwave applications such as circulators, isolators, phase shifters, etc., which are due to their high resistivity, low eddy current losses and reasonably low costs involved [1–5]. Recently, irradiation techniques have emerged as an attractive tool for the modification in the physical properties of spinel powders for commercial applications. A number of studies have shown that materials modifications can be produced after irradiation [6–10]. The photochemical reaction based on the photoexcitation of metal oxides has been intensively investigated. The fundamental photophysics of the metal oxides followed by the photoexcitation of the plasmon band has been explored by fast laser spectroscopy. Photoirradiation of the metal oxides induces modifications in crystalline phase and modifications in the magnetic properties. Pulsed laser excitation has also induced some morphological changes of the spinel ferrite. The properties of lithium ferrites can be tailor made by irradiating them with different laser fluencies for device applications.

Effect of swift heavy ion (SHI) irradiation on the hyperfine interactions of $Cr_{0.5}Li_{0.5}Fe_2O_4$ has been reported by Parmar et al. [11] and also on structural and magnetic properties of Ti^{4+} substituted Li–Al and Li–Cr ferrite by Chhantbar et al. [12]. Effect of γ-irradiation on the polarization and resistance of Li–Co–Yb ferrite was reported by Ahmed et al. [13]. Ahmed and Bishay have reported that the electrical properties of Li–Co spinel ferrite are affected by irradiation with LIMO–IR laser diode [14]. However, to our knowledge, no reports are available in the literature on the effect of Nd:YAG laser irradiation on the electrical properties of Li–ferrite prepared by ceramic technique.

In this work, the attempt has been made to contribute to the understanding of the conduction mechanism in Nd:YAG laser irradiated lithium ferrite. IR spectroscopic results shows the change in the band frequencies which results in the redistribution of metal ions over the tetrahedral (A) and octahedral [B] sites in the spinel lattice on incorporation of laser dose and is responsible for the modification in properties. The principal requirements which have to be considered for the conduction mechanism of pristine and unirradiated lithium ferrite are introduced together with a justification from the experimental point of view.

2. Experimental techniques

Samples of polycrystalline $Li_{0.5}Fe_{2.5}O_4$ spinel ferrite was prepared by conventional double sintering ceramic method. The details of method of preparation and laser irradiation parameters were discussed in our previous reports [15,16].

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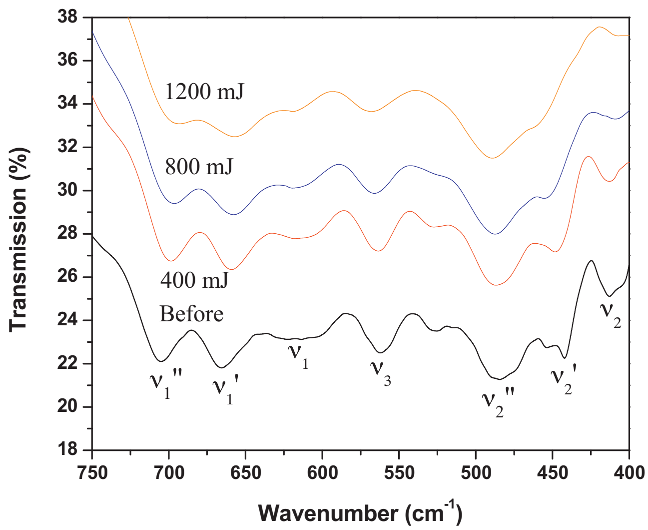

Fig. 1. The Infrared absorption spectra for $Li_{0.5}Fe_{2.5}O_4$ before and after laser irradiation.

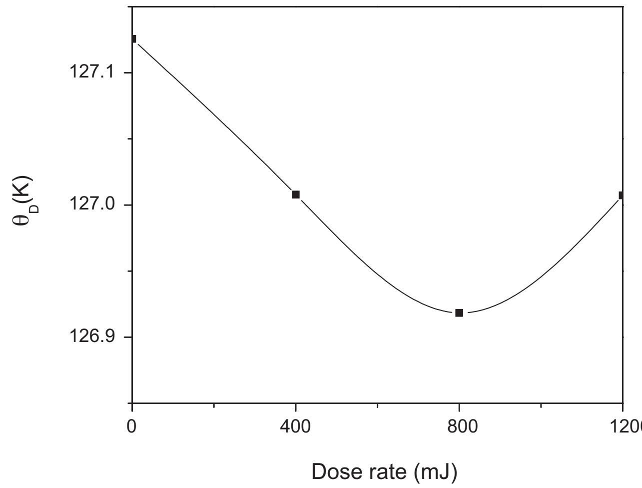

Fig. 2. Variation of Debye temperature with laser dose.

Infrared (IR) spectra were recorded in the range of 400–750 cm^{-1} at room temperature by using Perkin-Elmer spectrometer. The DC electrical resistivity of the samples was measured using the two-probe method in which silver paste was used as a contact material. The samples were firmly fixed between two electrodes to produce good surface contact. An auxiliary heater was used for heating all of the investigated samples. The temperature was measured using a chromel–alumel thermocouple. The dielectric constant (ε') and dielectric loss tangent ($\tan\delta$) were measured as a function of temperature by using an LCR-Q meter (Model HP 4284 A).

3. Results and discussion

3.1. Infrared spectroscopy

The results of room temperature IR spectra in the range of 400–750 cm^{-1} for irradiated and unirradiated $Li_{0.5}Fe_{2.5}O_4$ powders are shown in Fig. 1. The IR absorption bands of solids are usually attributed to vibrations of ions in the crystal lattice [17]. Waldron proposed that the ferrites structure can be considered as continuously bonded crystals [18]. The IR spectra of unirradiated $Li_{0.5}Fe_{2.5}O_4$ powders show three absorption bands and small change was observed after irradiation with laser. Lithium ferrites behave as an n-type semiconductor based on the inverse spinel [19].

The Debye temperature (θ_D) for laser irradiated and unirradiated $Li_{0.5}Fe_{2.5}O4$ ferrite sample was calculated by using the following relation [20] and variation with dose rate is shown in Fig. 2.

$$\text{Debye temperature } (\theta_D) = \lambda C \nu_{av} = 1.438\nu_{av} \quad (1)$$

where

$$\nu_{av} = \frac{\nu_A + \nu_B}{2} \quad (2)$$

ν_A is the frequency of primary band at A-site, ν_B is the frequency of primary band at B-site, it can be seen that Debye temperature (θ_D) initially decreases and then increases for samples irradiated at higher laser dose. This behaviour can be explained on the basis of specific heat theory. According to this theory, electrons absorbed part of the heat and θ_D may decrease, this confirms that the conduction for these samples due to electrons (i.e. n-type). After that the samples irradiated at 1200 mJ changes to p-type and the absorption part of heat by electrons transfer to increase Debye temperature (θ_D). This means that the electrons should make significant contribution to the specific heat and consequently to Debye temperature.

Table 1
Force constants (K_o and K_t), activation energy in paramagnetic region (E_p), and activation energy in ferrimagnetic region (E_f) for irradiated and unirradiated $Li_{0.5}Fe_{2.5}O_4$.

	$K_t \times 10^2$ (N/m)	$K_o \times 10^2$ (N/m)	E_p (eV)	E_f (eV)
Before	1.83	0.93	0.856	0.209
400 mJ	1.68	0.98	0.461	0.206
800 mJ	1.63	1.01	0.334	0.169
1200 mJ	1.53	1.05	0.228	0.095

The force constant is a second derivative of potential energy with respect to the site radius, the other independent parameters being kept constant. The force constants, for tetrahedral site (K_t) and octahedral site (K_o), were calculated by employing the method suggested by Waldron [18]. According to Waldron, the force constants, K_t and K_o, for respective sites are given by

$$K_t(\text{N/m}) = 7.62 \times M_1 \times \nu_1^2 \times 10^{27} \quad (3)$$

$$K_o(\text{N/m}) = 10.62 \times \frac{M_2}{2} \times \nu_2^2 \times 10^{27} \quad (4)$$

where M_1 and M_2 are the molecular weights of cations on A- and B-sites, respectively, calculated from cation distribution. The variation of force constants with laser dose for $Li_{0.5}Fe_{2.5}O_4$ ferrite is shown in Table 1. It is observed from Table 1 that force constant K_t decreases and K_o increases after irradiation with Nd:YAG laser.

3.2. DC electrical resistivity

Fig. 3 shows the temperature dependent variation in direct current (DC) electrical resistivity measured by two-probe method. The DC electrical resistivity increases as the laser irradiation dose increases, which can be due to the conduction mechanism in ferrite which takes place mainly through the hopping of electrons between Fe^{2+} and Fe^{3+} at B-sites. In general, the conductivity of spinel ferrites is due to the presence of Fe^{2+} ions. The conductivity arises due to the mobility of the extra electron, which comes from Fe^{2+} through the crystal lattice [21]. The hopping probability depends upon the separation of ions involved and the activation energy. As the distance between two metals ions at B-sites is smaller than the distance between two metal ions, one at A-site and another at B-site, therefore the electron hopping between A- and B-sites have a less probability as compared to hopping between B-B sites. Hopping between A- and B-sites does not limit for the simple reason that there are only Fe^{3+} at A-site and only Fe^{2+} preferentially occupy B-site during processing.

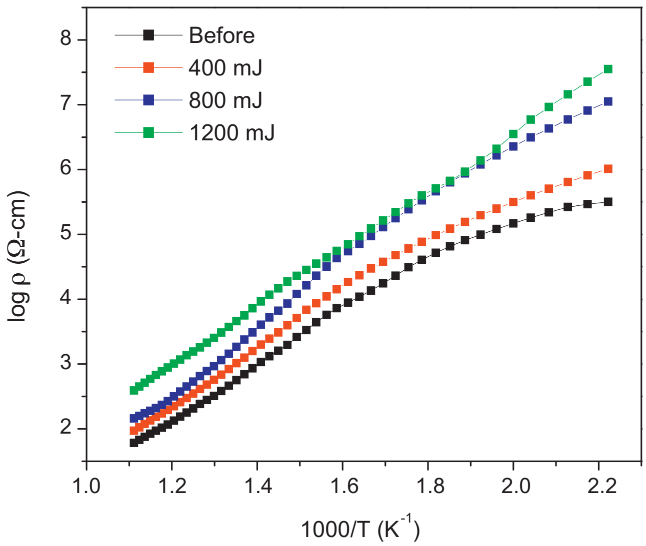

Fig. 3. . Variation of DC electrical resistivity with temperature for $Li_{0.5}Fe_{2.5}O_4$ before and after laser irradiation.

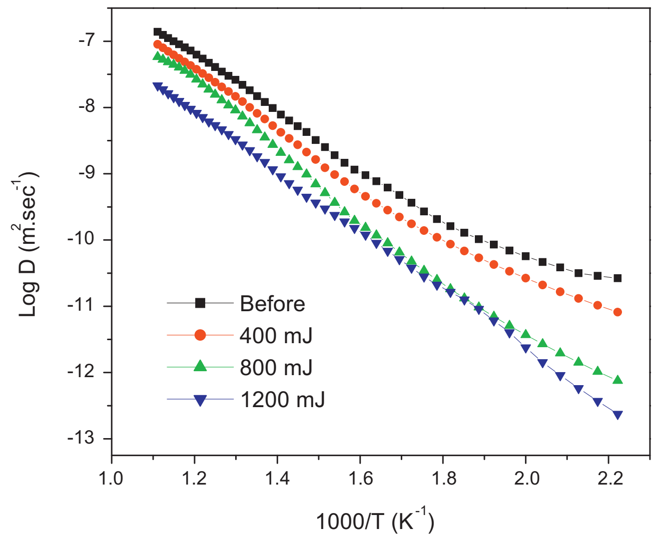

Fig. 4. Variation of diffusion coefficient with temperature for $Li_{0.5}Fe_{2.5}O_4$ before and after laser irradiation.

The activation energy was calculated by according to following relation [22]:

$$\rho = \rho_o \exp\left(\frac{\Delta E}{k_B T}\right) \quad (5)$$

where ΔE is the activation energy, ρ_o is the temperature dependent constant and k_B is Boltzmann constant. The activation energy calculated from above relation in paramagnetic (E_p) and ferrimagnetic (E_f) region is given in Table 1. It is observed from Table 1 that the values of activation energy in paramagnetic region are found to be greater than those observed in ferrimagnetic region, this suggest that the process of conduction is affected by the change in magnetic ordering.

The irradiated spinel ferrite samples maintain the same trend as those for unirradiated ones. It is shown that the values of resistivity increases as compared with unirradiated sample. One can understand from the obtained results that after laser irradiation electronic rearrangements occur, leading to formation of voids and clusters which impede the conduction process and increase the resistance of the samples. Fast electron exchange is considered to occur among the Fe^{2+} and Fe^{3+} ions on the octahedral sites. This causes a decrease in the rate of electron exchange between Fe^{2+} and Fe^{3+} by the hopping mechanism, which also causes a decrease in the conductivity.

The diffusion coefficient (D) of oxygen vacancies was estimated from the relation [23]

$$D = \frac{\sigma k_B T}{Ne^2} \quad (6)$$

where σ is the DC electrical conductivity, N the number of atoms/m^3 equal to $4 \times 10^{28}\ m^{-3}$, e is the electronic charge, and k_B the Boltzmann constant. The diffusion coefficient of oxygen vacancies for $Li_{0.5}Fe_{2.5}O_4$ ferrite before and after irradiation is illustrated in Fig. 4 as a function of temperature. The diffusion of oxygen ions occurs when defects or structural vacancies are present in the lattice. It is clear that the diffusion coefficient decreases with laser irradiation this could be explained on the basis of migration of Li^{1+} ions from A- to B-site. The diffusion coefficient decreases because of the mobility of electrons is affected after irradiation with Nd:YAG laser.

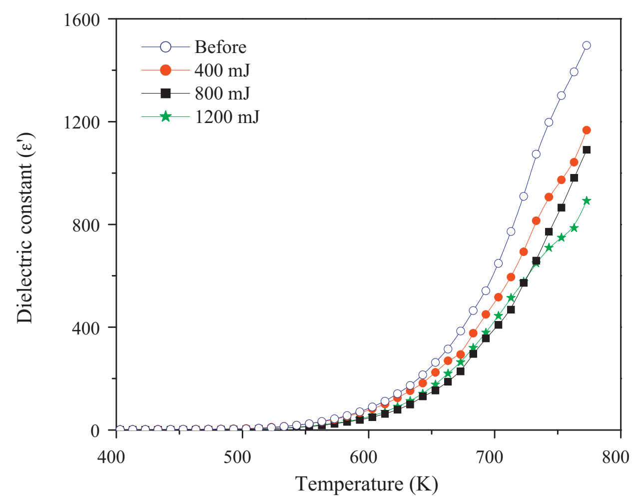

Fig. 5. Variation of dielectric constant with temperature for $Li_{0.5}Fe_{2.5}O_4$ before and after laser irradiation.

3.3. Dielectric properties

The real part i.e. dielectric constant (ε'), the imaginary part i.e. the dielectric loss tangent ($\tan\delta$) of $Li_{0.5}Fe_{2.5}O_4$ were computed according to Smit and Wijn [24] as a function of temperature. The measurements were carried out in the temperature range of 403–773 K. Fig. 5 shows the variation of the dielectric constant with temperature at a fixed frequency of 1 kHz and different doses. It is clear from Fig. 5 that the dielectric constant increases with increasing temperature for all samples. This temperature dependence of the dielectric constant and dielectric loss tangent for $Li_{0.5}Fe_{2.5}O_4$ is in very good agreement with other spinel ferrites [25,26], for which the dielectric constant increases with increasing temperature. The variation of the dielectric loss tangent with temperature is given in Fig. 6, in which it is observed that the dielectric loss tangent increases with increasing temperature. According to Rabkin and Novikova [27], the process of dielectric polarization in ferrite occurs through a mechanism similar to the conduction process. From the electronic exchange of $Fe^{3+} \leftrightarrow Fe^{2+}$ one obtains the local displacement of the electron in the direction of the applied electrical field. This displacement determines the polarization of both types of charge carrier, n and p, which contributes to the

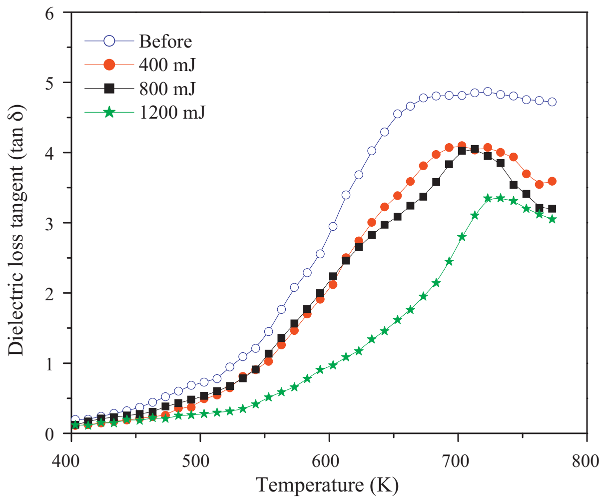

Fig. 6. Variation of dielectric loss tangent with temperature for $Li_{0.5}Fe_{2.5}O_4$ before and after laser irradiation.

polarization and depends on temperature. The laser irradiated $Li_{0.5}Fe_{2.5}O_4$ spinel ferrite shows collective contribution of both p- and n- type conduction due to formation of defects [16]. The temperature dependence of the dielectric constant and dielectric loss tangent can be explained by the polarization effect. As temperature increases, the electrical conductivity increases due to the thermal activity and mobility of the electrical charge carriers according to the hopping mechanism. Thus, the dielectric polarization increases, increasing the dielectric constant and the dielectric-loss tangent.

A maximum in the dielectric-loss tangent versus temperature appears when the frequency of the hopping charge carriers coincides with the frequency of the applied alternating field. A broad peak of the dielectric-loss tangent indicates the existence of a distribution of relaxation times rather than a single relaxation time [28]. The condition for observing maxima in dielectric-loss tangent of a material is $\omega\tau = 1$, where $\omega = 2\pi f_{max}$ and τ is the relaxation time. The relaxation time is related to the jumping probability per unit time P by the relation

$$f_{max} \alpha P \quad \text{or} \quad \tau = \frac{1}{2}P \tag{7}$$

Further, as the radiation dose increases, the position of maximum dielectric loss is shifted towards higher temperatures. This results indicate that irradiation of the sample increases the cross-linking density of macromolecule. This in turn, decreases segmental mobility and increases the relaxation time of dipole segmental loss.

4. Conclusions

On the basis of experimental results and discussions mentioned above, we can infer the following conclusions:

- The infrared spectrum of irradiated samples shows disordered structure from that of unirradiated samples.
- The Debye temperature shows change in conduction mechanism from n-type to p-type.
- The experimental data on dc electrical resistivity shows two regions of different activation energies. It may be due to a change of conduction mechanism.
- Dielectric constant and dielectric loss tangent increases with increasing temperature.
- The high dc resistivity and low dielectric losses are the desired characteristics of Li–ferrites used to prepare microwave devices.

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