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Laser induced structural and transport properties change in Cu–Zn ferrites

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Abstract The samples were prepared from analar oxides (BDH) using the standard double sintering ceramic technique. X-ray diffraction (XRD) was carried out to assure the formation of the sample in single spinel phase. The effect of Q-switched Nd:YAG laser irradiation with wavelength of 1064 nm on the electrical properties of the prepared samples $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) was discussed. The temperature dependence of the polarization and a.c. conductivity was studied in the range ($300\ K \le T \le 700\ K$) at different applied frequencies ($10\ kHz \le f \le 4\ MHz$). The activation energies were calculated at different temperature regions for the unirradiated and irradiated samples. Their values indicate the semi-conducting like behaviour of the sample. Comparison between the ac electrical conductivity, dielectric constant, dielectric loss, for unirradiated and irradiated samples with different Zn concentrations ($0.1 \le x \le 0.6$) was performed. Seebeck voltage measurements showed that, the n and p-type conduction act in cooperation with each other. The change in a.c. conductivity is attributed to the creation of lattice vacancies after laser irradiation. The decrease of the a.c. conductivity and the dielectric constant after laser irradiation with 18000 shots may be due to formation of traps, which decrease the number of carriers. The lattice mismatch in the grain boundaries causes a planar array of localized states, being able to capture free carriers. The accumulated charge constitutes an electrostatic barrier impeding carriers from free motion. Thus, it is possible to optimize the conductivity of this type of ferrite material to be used in technological applications at room temperature.

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Introduction

Ferrites have many important applications in industry, modern telecommunication and electronic devices and they are still of interest as promising materials for miniature electro-optic modulators, pyroelectric detectors, piezoelectric sensors, high quality filters, transformer cores, ferrite isolators, memory core industry, multilayer chip inductor, rod antennas, radio frequency circuits [1–5], wave guides and electronic memory elements as well as a recording media. For these reasons, engineers and scientists are keenly interested in determining their characterization [6, 7]. The electrical properties of ferrite materials have been found to alter, depending on the substitution of different valance cations as well as the preparation conditions. Moreover, the dielectric constant (ε'), ac electrical conductivity ($\sigma_{a.c.}$) and permeability of semiconductor ferrites are very sensitive to the chemical composition and industrial applications. $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nanocrystallites powder (average size 13 nm) were synthesized from Cu–Zn spent catalyst (fertilizers) industries. The parameters affecting the magnetic properties and crystallite size of the produced ferrites powder were systemically studied by different authors [8, 9]. Spinel copper ferrite shows a remarkable variation in its atomic arrangement depending critically on the thermal history of the preparation and it may be attributed to the distribution of Cu and Fe cations between the two nonequivalent lattice A and B sites [10]. It has been pointed out that the distribution and the valance of metal cations on these sites determine the magnetic and electrical properties.

The major goal of the present work is to investigate the effect of the laser irradiation, temperature and frequency on the ε', ε'', $\sigma_{a.c.}$ and Seebeck coefficient of Cu–Zn ferrite. This will open a new era for using laser irradiation in optimizing the electrical properties of the investigated samples to be more applicable. The real part of the dielectric constant ε' as well as the ac conductivity of the rare earth ferrite $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) was measured at different temperatures (300–800 K) as a function of frequency (10 kHz–4 MHz). More than one hump was obtained due to the presence of different polarization processes and conduction mechanisms.

Experimental techniques

The samples $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) were prepared using the double sintering ceramic technique from pure analar oxides CuO, ZnO and (Fe_2O_3) [11]. Grinding were carried for 3 h after mixing in molar ratios to give the composition $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) and then pressed in pellet form using uniaxial press of pressure 8×10^5 N/m^2. The samples in the form of disks were pre-sintered at 850 °C for 10 h with heating rate of 2 °C min^{-1}. The final sintering was carried out at 1150 °C for 10 h and then cooled to room temperature with the same rate as that of heating. The pre and final sintering were carried out using a UAF 16/5 (UK) furnace with microprocessors to control both heating and cooling rates. The samples were smoothly polished to have uniform parallel surfaces (2 cm in diameter and 0.2 cm in thickness), coated with a thin layer of silver paste as contact electrodes for electrical properties measurements. The samples were placed between two electrodes in an evacuated cell of silica tube supported with a furnace. The temperature of the samples was measured and controlled using Chromel–Alumel thermocouple attached to the samples. X-ray diffraction (XRD) patterns were performed using a Philips PW1730 X-ray unit with CoK$_\alpha$ radiation to assure the good preparations. The real part of the dielectric constant and ac conductivity were recorded at different temperatures as a function of frequency (1 kHz–4 MHz) using RLC bridge model HP (USA) self calibrated. For laser irradiation study, the samples were irradiated by Nd:YAG laser. The laser was operated at a wavelength 1064 nm using repetition rate of 10 Hz. The average power is measured to be of the order 5 W and pulse duration time of 10 ns. The exposure time was 30 min. The resonance frequency and antiresonance were carried out by the method described in previous work [12, 13].

Results and discussion

Effect of laser irradiation on the structure of $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) ferrites

Figure 1 shows the XRD patterns of $Cu_{1-x}Zn_xFe_2O_4$ ($x = 0.5$) as a typical one before and after laser irradiation. From X-ray analysis, it is observed that the samples crystallize in a single-phase spinel structure of cubic symmetry as compared with ICDD card number [25-0283] [14, 15]. After laser irradiation, the diffractogram indicates the formation of a distorted cubic structure. This is because laser interacts with the metal ions on A and B sites, Thus a more contribution towards conductivity by generation of Fe^{2+} and Cu^{1+} from Fe^{3+} and Cu^{2+} takes place. As a result of the

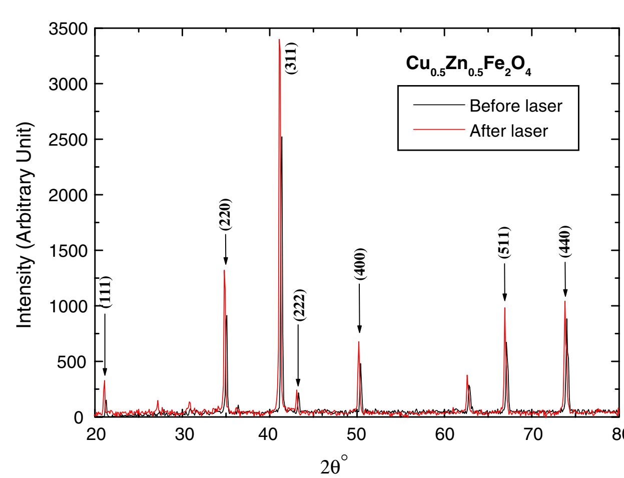


Fig. 1 X-ray diffraction patterns of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ before and after laser irradiation

larger ionic radius of Fe^{2+} and Cu^{1+} than that of Fe^{3+} and Cu^{2+}, respectively a small distortion of the spinel cubic structure is obtained. Moreover, lattice vacancies generated after laser irradiation contribute to the structural deformation.

Effect of laser irradiation on the electrical conductivity of $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) ferrites

The effect of laser irradiation on the investigated samples gives rise to the production of lattice defects as the result of the displacement of atoms from their equilibrium position. The displaced ions are expected to occupy the lattice vacancies and hence reduce oxygen ions diffusion. The laser irradiation of the samples alters the electrical conductivity as the result of absorbing dose in the material.

Figure 2: a–l illustrates the temperature dependence of the a.c. conductivity for unirradiated and irradiated samples of ($Cu_{1-x}Zn_xFe_2O_4$) by using Nd:YAG laser of 15 min exposure time for each face of the samples in the frequency range (1 kHz–4 MHz). It is noticed that the a.c. conductivity for irradiated samples increases exponentially with temperature at fixed frequency range (10–4000 kHz), i.e. $d\sigma_{a.c.}/dT$ is positive. The increase of the a.c. conductivity with temperature is attributed to enhancement of the Verwey hopping mechanism between $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ and hole hopping between $Cu^{2+} + e^- \leftrightarrow Cu^{1+}$ on the B sites, where most of Cu^{2+} ions prefer to occupy B sites together with Fe^{3+} ions. The a.c. conductivity with rising temperature was previously studied [16].

The effect of laser irradiation on the electrical conductivity for the samples $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) is clarified in Fig. 2: a–l. From the figure, it is noticed that the a.c. conductivity increases with increasing both temperature and frequency for the unirradiated and irradiated samples. Comparing the conductivity before and after irradiation, it is clear that the values of the a.c. conductivity decrease after irradiation at all frequencies and temperature. This is due to trapping of charge carriers in the vacancies, which were created as a result of laser irradiation. The increase in a.c. conductivity with increasing frequency is an acceptable result because the frequency acts as a pumping force pushing the charge carriers from one conduction state to another, especially at low frequency. The applied frequency in the present work is low frequency and 4 MHz is the highest of the lowest frequency region. This behaviour is the general trend of Cu substituted ferrites, where the most predominant conduction mechanism is that of Verwey [17] in which the electron hopping takes place between ions of different valences in the equivalent lattice site. This result is in agreement with that published by other authors [18, 19]. It is well known that, the irradiation by laser shock waves is followed by the formation of point defects and some of these vacancies could react with donor impurities, which reduce relatively the concentration of electrically active donors in the sample [19]. At high frequency, 4 MHz, the a.c. conductivity is decreased at high temperature for unirradiated samples as shown in Fig. 2: a–k. From the experimental data, the calculated values of the activation energies are plotted against the frequency in the low temperature range (335–665 K) Fig. 3. It is noted that the decrease in the activation energy with increasing frequency is an acceptable trend as a result of increasing hopping probability as well as conductivity. The increase in the activation energy after laser irradiation at lower frequencies is the result of initiating defects in the samples, which decreases the conductivity. The decrease of activation energy after laser irradiation at higher frequency may be due to either creating of small polarons or initiating holes from varying the valence of Cu ions.

Effect of laser irradiation on the dielectric constant and dielectric loss of $Cu_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.6$) ferrites

The temperature dependence of the dielectric constant ε' and dielectric loss ε'' at different frequencies from 10–4000 kHz for unirradiated and irradiated $Cu_{1-x}Zn_x Fe_2O_4$ ($0.1 \le x \le 0.6$) ferrites by laser with 18,000 laser shots is illustrated in Fig. 4, 5. The increase in ε' with temperature in the range (290–430 K) can be ascribed to the thermal excitation of charge carriers. Above 450 K, the dielectric constant decreases sharply as the result of high thermal energy and the increase of lattice vibrations resulting in scattering of charge carriers. The peak position and height were varied depending on both frequency and Zn content. The shift in the position towards higher temperature with increasing the applied frequency may be due to the strong effect of the field where the dipoles can't orient themselves in the field direction. The decrease of ε' with increasing frequency is ascribed to the increase of the jumping frequency of the charge carriers, which gives a remarkable dispersion as in Fig. 4. The value of

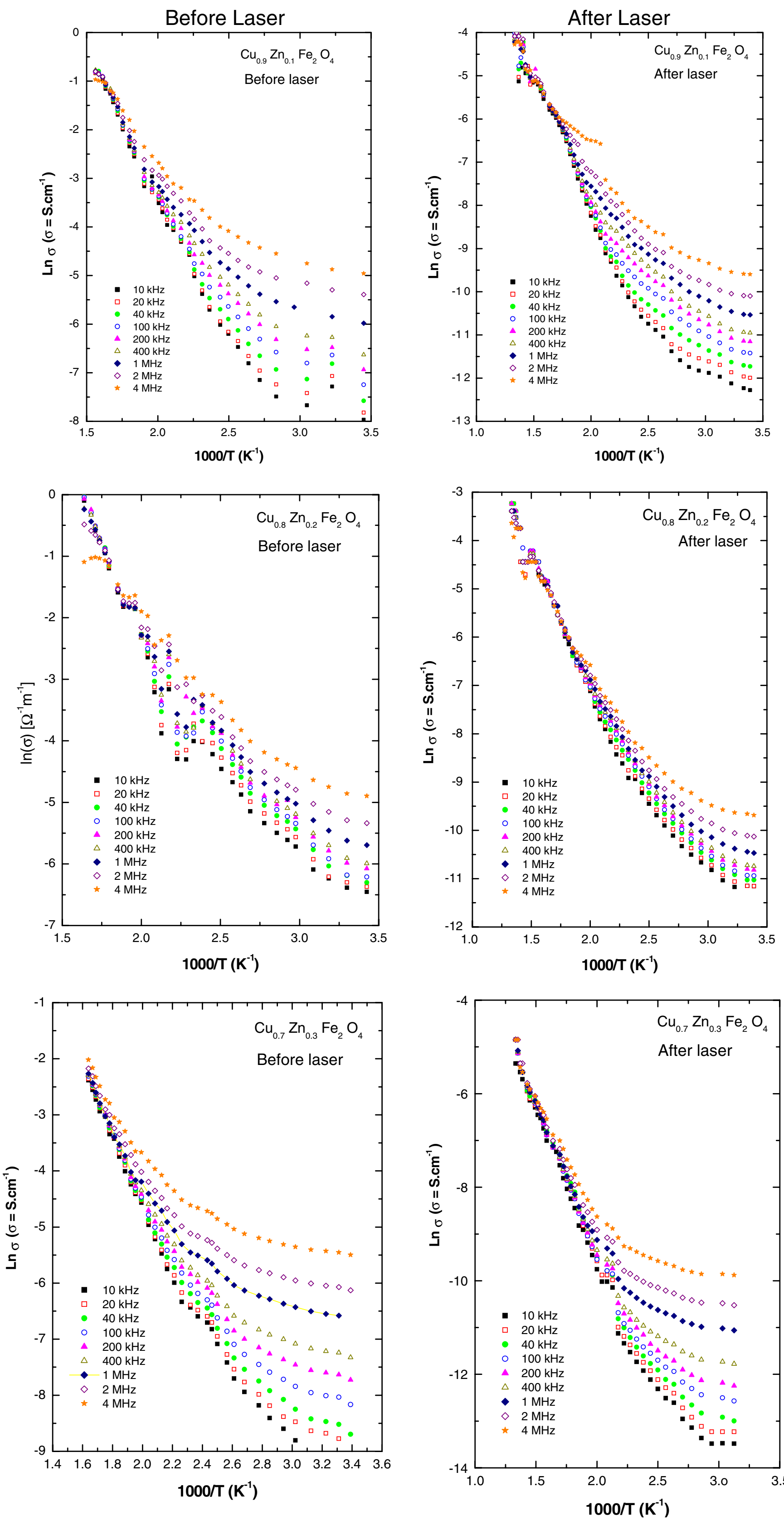
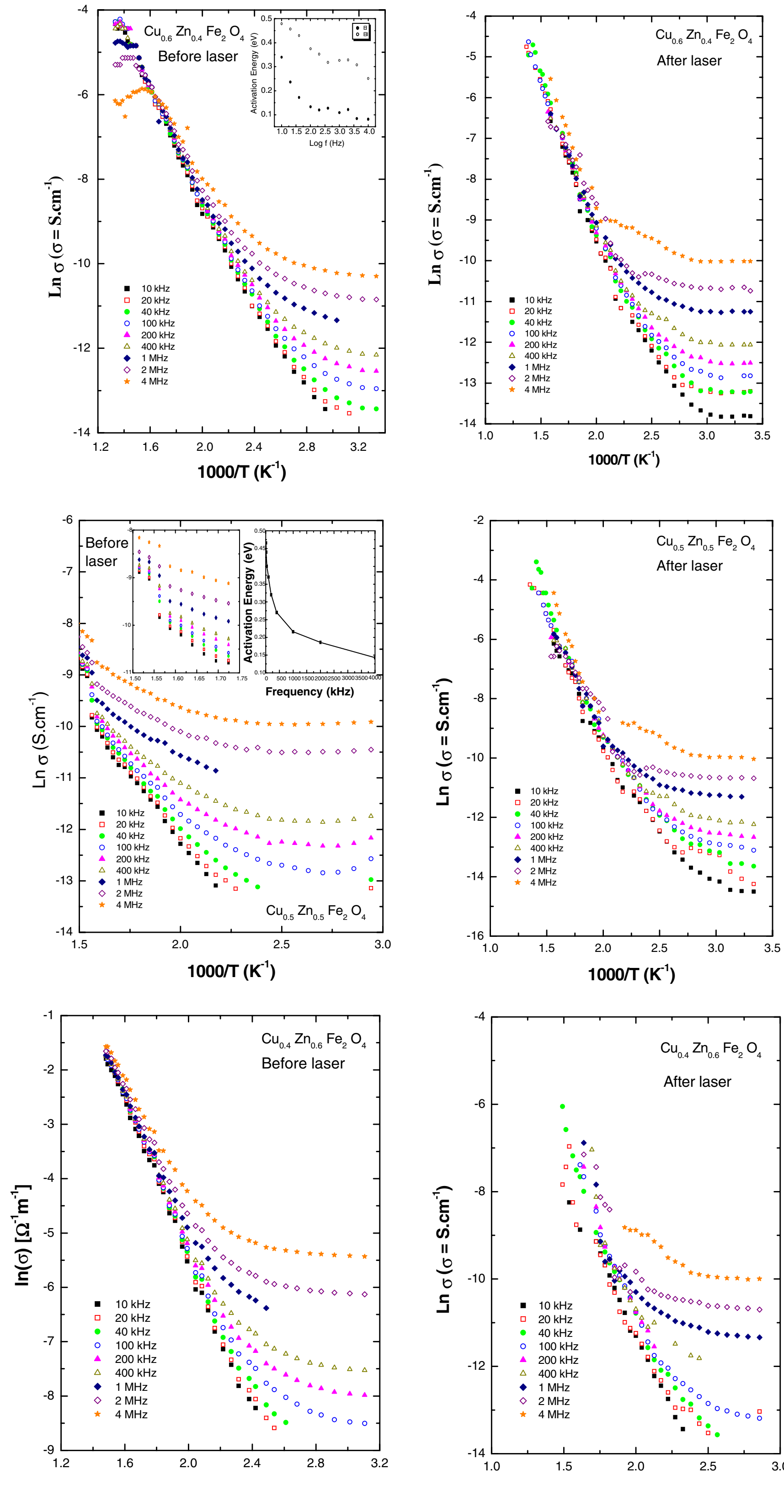


Fig. 2 Variation of the electrical conductivity with the reciprocal of the absolute temperature as a function of the applied frequency for $Cu_{1-x}Zn_xFe_2O_4$; $(0.1 \le x \le 0.6)$ before and after laser irradiation

Fig. 2 continued



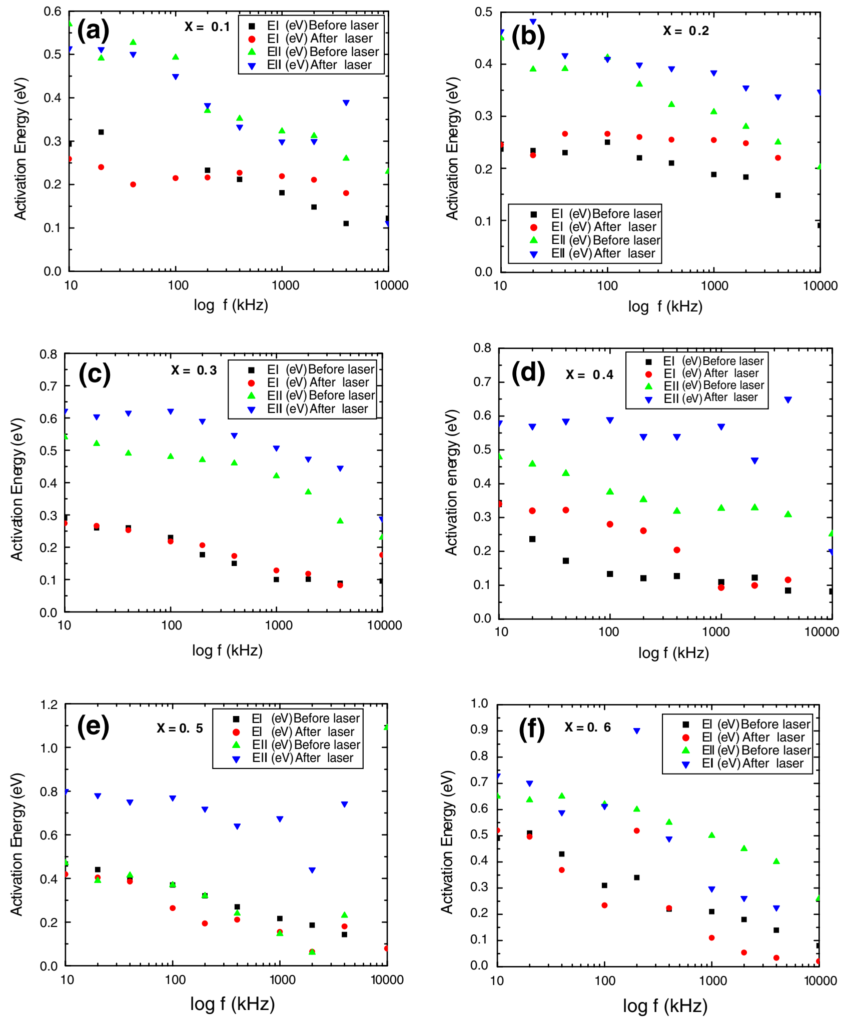


Fig. 3 Dependence of the activation energy on the applied frequency in the low (E_I) and in the high (E_{II}) for $Cu_{1-x}Zn_xFe_2O_4$; ($0.1 \le x \le 0.6$) before and after laser irradiation

ε' decreases after laser irradiation at all temperatures. This behavior may be due to formation of point defects, which act as trapping centers for the charge carriers. Accordingly, the conductivity as well as ε' decreased because they are of the same origin. Though, the investigated samples obey the model [20] [$\varepsilon' \propto \sigma$]. From a closer look to the obtained data one can observe the decrease of ε' with increasing Zn content before and after laser irradiation. This agrees well with the data of the conductivity Fig. 2. The electrons produced from the valence exchange $Fe^{2+} \leftarrow \rightarrow Fe^{3+} + e^-$ are captured by the Cu ions existing on the octahedral site as follows $Cu^{2+} + e^- \leftarrow \rightarrow Cu^{1+}$. This in turns decreases the conductivity as well as ε'. Consequently, one can say that the conduction in the investigated samples is a collective contribution of two types of carriers; p and n-type carriers. Therefore, the position of the peak depends on whether the majority is in p-type or n-type carriers in the sample. It can be noticed that as the iron content is increased resulting in more $Fe^{2+} \leftarrow \rightarrow Fe^{3+} + e^-$ transitions. Furthermore, the increase in n-type carrier with increasing Fe content results in a shift of peak temperature towards higher temperature side with increase in frequency.

Figure 5 a–l shows the temperature dependence of the dielectric loss factor ε'' at different frequencies ($10\ \text{kHz} \le f \le 4\ \text{MHz}$) before and after laser irradiation with 18,000 laser shots. The data clarify that the value of dielectric loss increases with increasing temperature at frequencies 10–4000 kHz, for different Zn concentrations ($0.1 \le x \le 0.6$), but at $x = 0.2$ and 0.4, the peaks will be observed at 440, 600 K respectively. The sharp decrease of ε'' with increasing frequency may be due to the fact that the activation energy is not sufficient to create dipoles, where the peaks are disappeared after laser irradiation. The data correlate the variation of $\ln\sigma_{a.c.}$, ε', ε'' versus Zn content are shown in Figs. 6–8.

The Seebeck coefficient was carried out for the investigated samples Fig. 9 a–f. The positive and negative values of Seebeck coefficient, for all samples, over the investigated temperature range denote the presence of p and n-type charge carriers. The presence of the two types of charge carriers defines the two regions of temperature dependence of conductivity in which the sample is changed from p-type to n-type and vice versa. Part of the energy of the applied field frequency consumed in the orientation of the dipoles and other part of this energy enhances the electrical conductivity of the samples.

Conclusion

Cu–Zn ferrites induced in wide range of industrial applications, due to their unique properties. The XRD patterns of irradiated samples by laser show a distorted cubic structure. Drop in the values of electrical conductivity; dielectric constant ε' and dielectric loss ε'' at range of frequencies from 10 to 4000 kHz for irradiated ferrites samples by laser with 18,000 laser shots were detected. Response of these materials to laser irradiation showed different effects on the conductivity depending on the temperature of the samples. Three regions of conductions (300–350 K), (350–500 K) and (500–670 K) were obtained. Both electrons and holes participate in conduction mechanism.

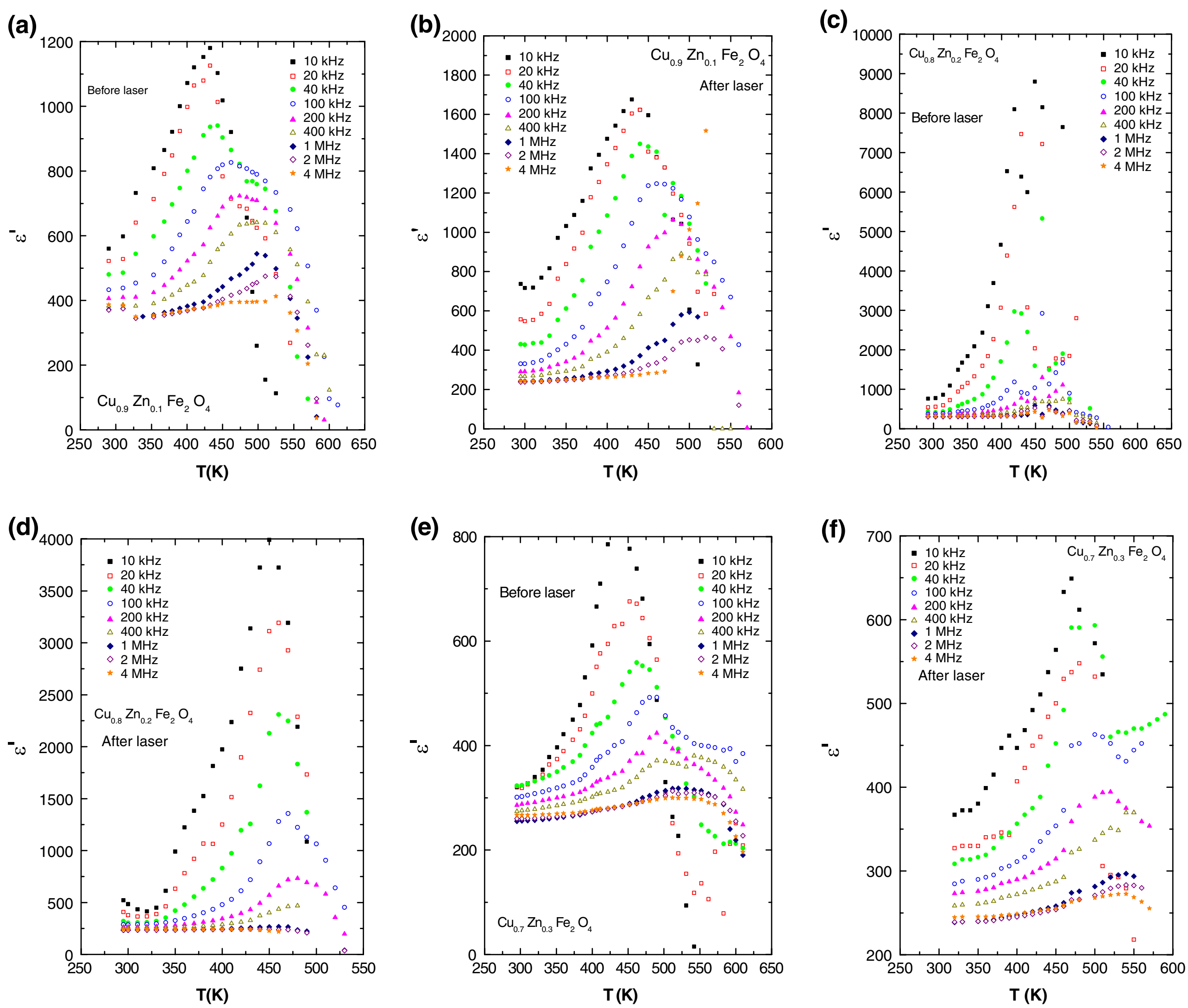


Fig. 4 (**a–l**) Dependence of the dielectric constant on the absolute temperature as a function of the applied frequency for $Cu_{1-x}Zn_xFe_2O_4$; ($0.1 \le x \le 0.6$); before and after laser irradiation

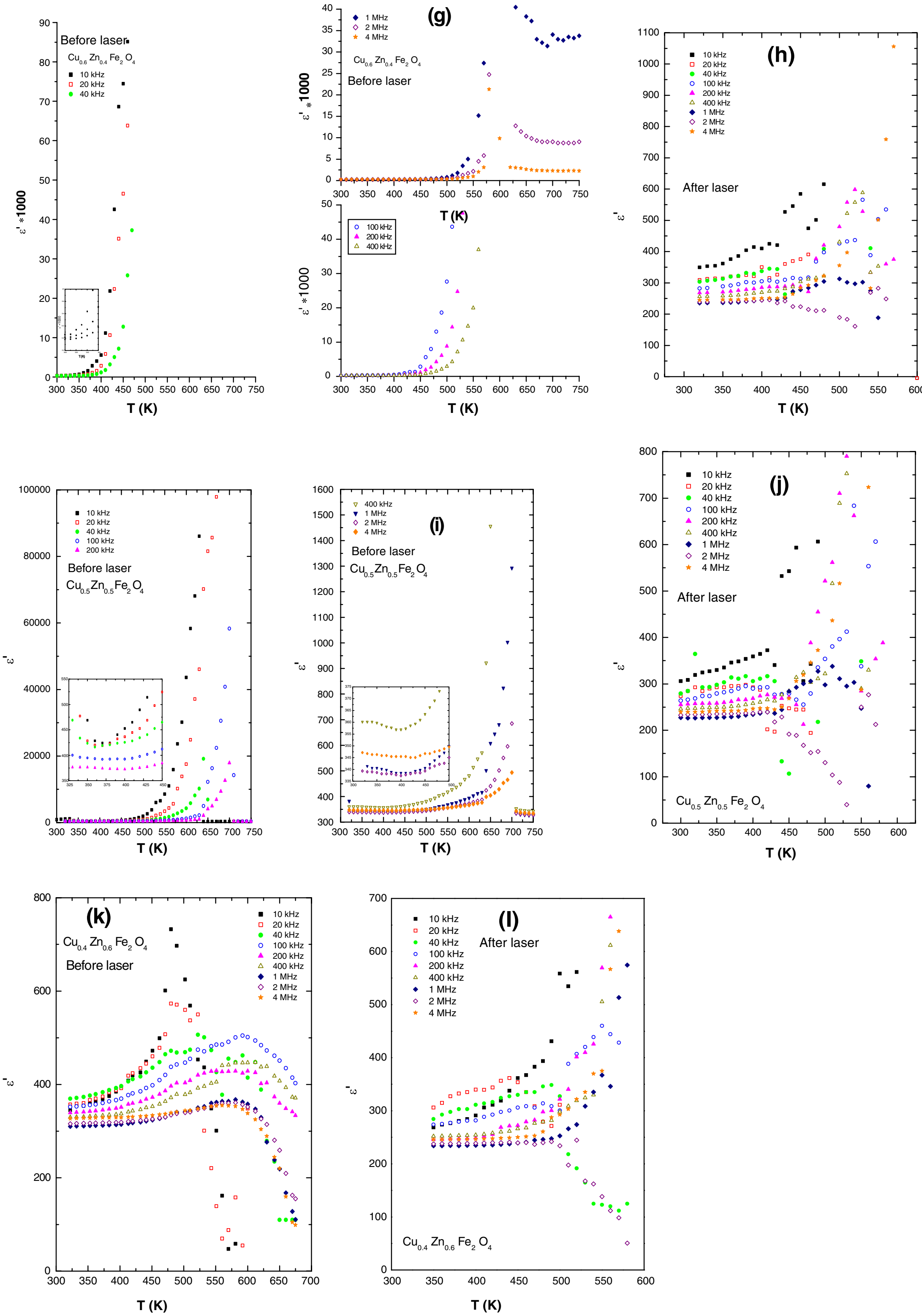


Fig. 4 continued

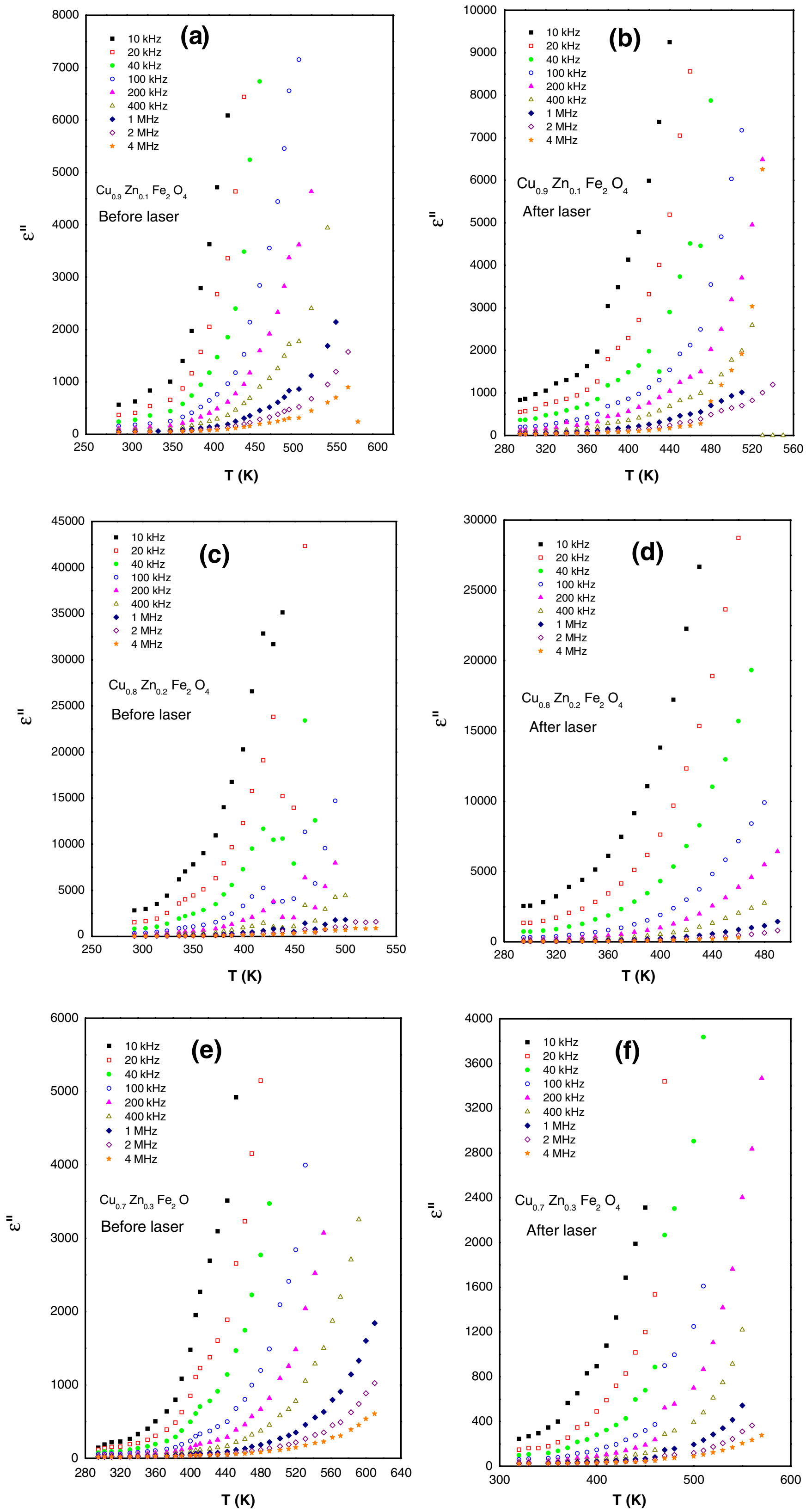


Fig. 5 (**a–l**)Dependence of the dielectric loss factor on the absolute temperature of $Cu_{1-x}Zn_xFe_2O_4$; ($0.1 \le x \le 0.6$) at different frequency and Zn content before and after laser irradiation

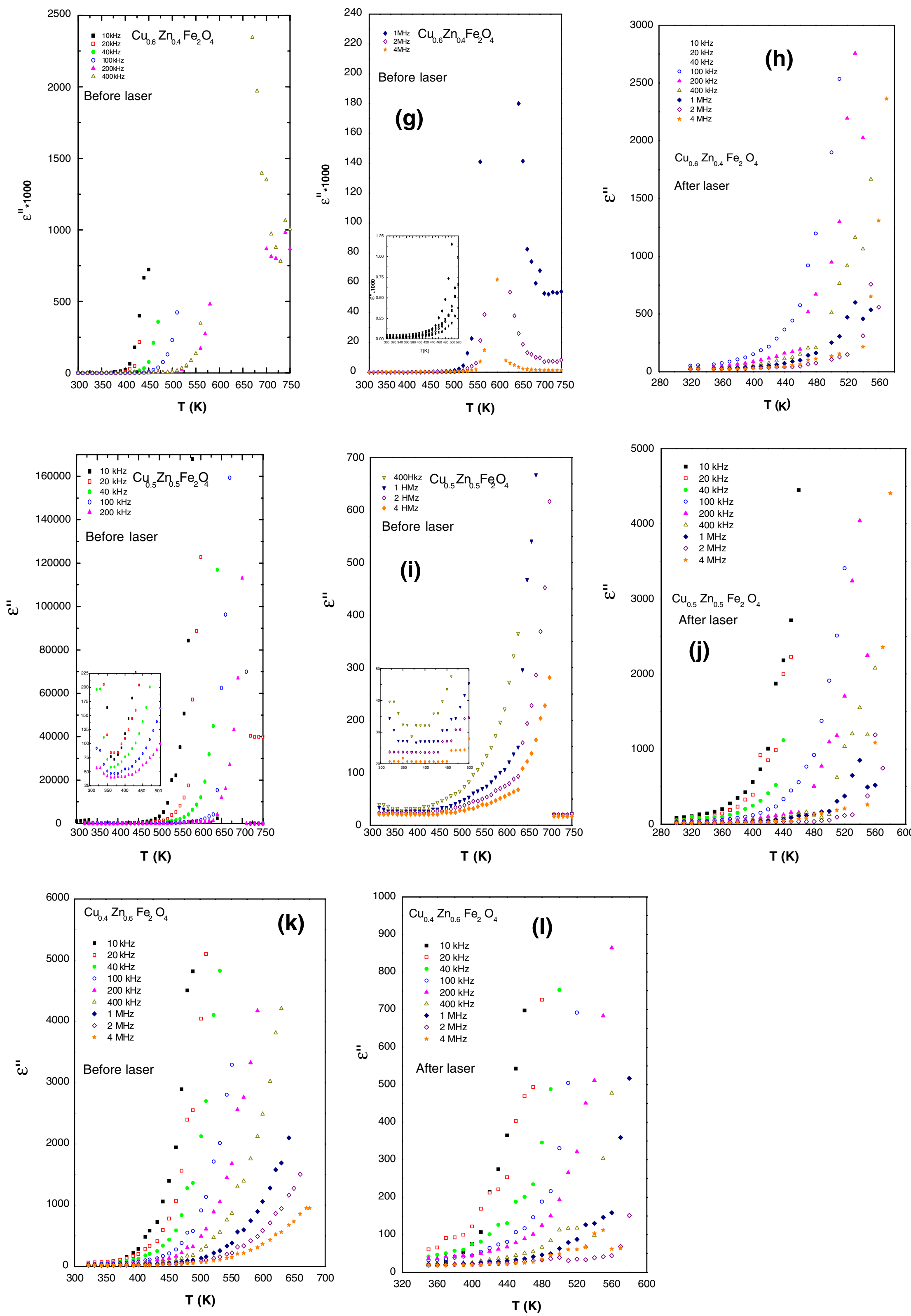


Fig. 5 continued

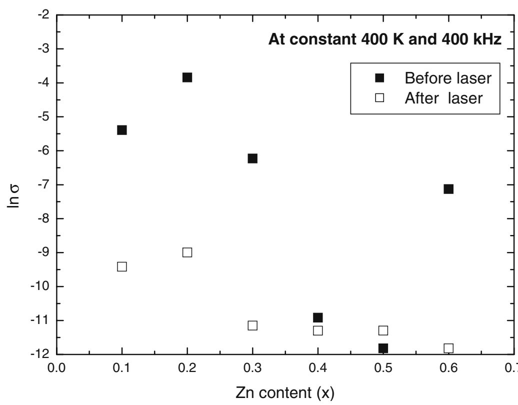


Fig. 6 Variation of ln $\sigma_{a.c.}$ as a function of Zn content for the samples $Cu_{1-x}Zn_xFe_2O_4$; $(0.1 \le x \le 0.6)$ at 400 K and 400 kHz before and after laser irradiation

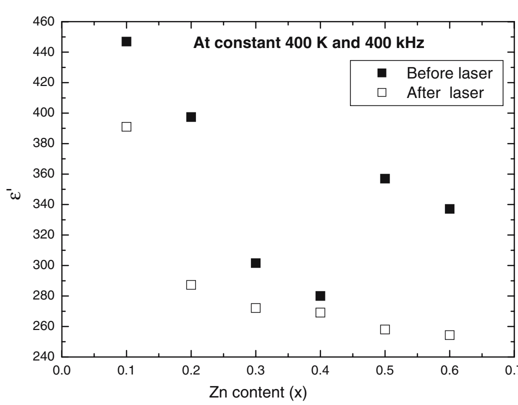


Fig. 7 Variation of ε' as a function of Zn content for the samples $Cu_{1-x}Zn_xFe_2O_4$; $(0.1 \le x \le 0.6)$ at 400 K and 400 kHz before and after laser irradiation

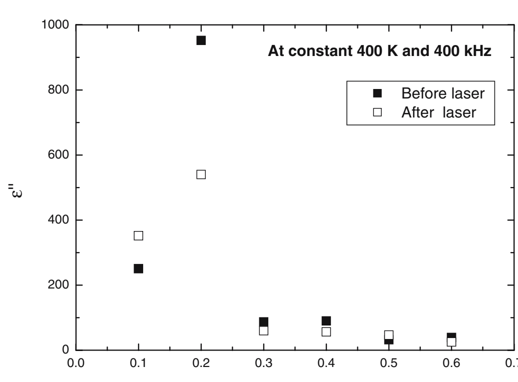


Fig. 8 Variation of ε'' as a function of Zn content for the samples $Cu_{1-x}Zn_xFe_2O_4$; $(0.1 \le x \le 0.6)$ at 400 K and 400 kHz before and after laser irradiation

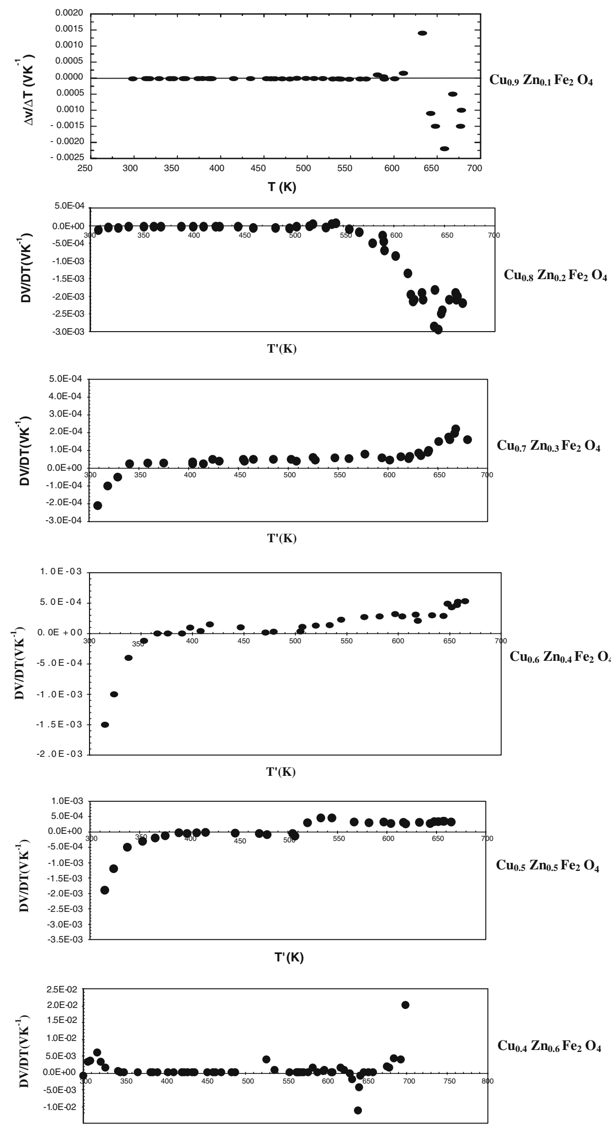


Fig. 9 Seebeck coefficient for $Cu_{1-x}Zn_xFe_2O_4$ at different Zn content before laser irradiation

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