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Role of Mo substitution on electric modulus and electrical conductivity of cobalt-zinc spinel ferrite

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Abstract: Cobalt- Zinc ferrites are presently utilized as a significant component material for fabricating multiferroic composite. Conventional ceramic technique was utilized to synthesize the bulk cobalt-zinc ferrite with Mo substitution (CZFMO). In this present article, we accounted for the study of detail electric modulus and electrical conductivity of $Co_{0.65}Zn_{0.35}Fe_{2-x}Mo_xO_4$ (x=0.0, 0.1 and 0.2) spinel ferrites. The production of the inverse spinel nature of the material structure has been affirmed by the high resolution XRD pattern. The frequency reliance of real and imaginary part of electric modulus have been studied in detail. In the present framework the behavior of electric modulus could be communicated by the modified Kohlrausch-Williums-Watts (KWW) equation. The variation of the imaginary part of electric modulus (M″) with frequency indicates the existence of non-Debye relaxation process in the current samples. The curves showing the variation of ac conductivity with frequency follow the Jonscher's single power equation. This suggest that the conduction in the material is due to correlated barrier hopping (CBH) mechanism. Additionally, the conduction procedure can be best clarified based on Verwey-de Boer method. The activation energy in both ferromagnetic and paramagnetic area is assessed from the ln σ_{ac} vs. 1/T curves. The temperature reliance of dc conductivity obeys the Arrhenius expression. Also the semiconducting nature of material has confirmed from the conductivity plot.

Keywords: Ferrite, spinel, multiferroic, electric modulus, AC conductivity.

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1. Introduction: As of late, spinel ferrite materials have developed their enthusiasm for the advanced innovation because of their intriguing electrical and magnetic properties such as high resistivity, high dielectric constant, very low dielectric loss, moderate saturation magnetization etc. Thus, ferrite have adaptable applications in various region of present day innovation, e.g., magnetic sensors, microwave electronics, high density memory device, waveguides spintronics and transducer and so on **[1]**. Also ferrites are currently used as a major part of a multiferroic composite **[2]**. The multiferroic materials involves the presence of both ferromagnetic (FM) and ferroelectric (FE) behavior in a solitary substance. In light of this promising nature of the materials, they are utilized to develop high density memory gadget in which, the information can be composed electrically and read magnetically and the other way around **[3]**.

Especially, cobalt ferrite exhibit very small multiferroic property because of its feeble ferroelectric ordering [4]. The doping of nonmagnetic Zn^{2+} cation at the octahedral A-site of the cobalt ferrite unusually increment the saturation magnetization. The general chemical formula of inverse spinel structured cobalt-zinc ferrite is $Co_xZn_{1-x}Fe_2O_4$. It has some outstanding properties like high dielectric constant, high resistivity, chemical stability, low eddy current, low dielectric and magnetic loss, moderate saturation magnetization and low cost of manufacturing and so on. This makes the material intensely valuable in various applications such as magnetic recording, transducer, microwave electronics, resonator, waveguides, magnetic switches, satellite communication, magnetic coolant, ferrofluids, control drug delivery, cancer thermotherapy, MRI (magnetic resonance imaging) and so on [5, 6]. Also the ferrites are high T_C magnetic semiconductors with moderate magnetic moment and spin reliant band gap which could be utilized in spin-caloritronics and spintronics [7].

The impact of different substitution on the electrical and magnetic properties of ferrite have been studied by various research groups throughout the world. Arjumanara *et al.* [8] researched the electric modulus variations in Cobalt-Copper-Zinc ferrite elaborately. The ac conductivity, impedance spectroscopy and dielectric behavior in Nickel-Zinc ferrite was accounted by Mandal *et al*. [9]. The connection of electrical and magnetic behavior close to Curie point was displayed by Pradhan et al. [7]. Meaz et al. [10] considered the impact of Ti substitution on Co-Zn ferrite and shown the decline of conductivity. The conduction procedure was clarified based on small polaron conduction process.

In this literature, our intension to find out the role of Mo substitution on the electric modulus and electrical conductivity of Co-Zn spinel ferrite. All the samples are synthesized utilizing the conventional solid state reaction technique and described by X-ray diffraction method. The frequency reliance of real and imaginary part of electric modulus have been studied. Also both frequency and temperature reliance of ac and dc conductivity has also accounted for.

2. Experimental

Mo substituted Co-Zn ferrite having chemical equation $Co_{0.65}Zn_{0.35}Fe_{2-x}Mo_xO_4$ (x = 0.0, 0.1, 0.2) was prepared by employing the solid state reaction method. The stoichiometric quantity of highly pure (99.9 %) Co_3O_4, ZnO, Fe_2O_3 and MoO_3 oxides were taken and ground using agate mortar and pestle for few hours in a wet media. The resultant powder was then calcined at 1100 ^oC for one day. Finally 5 % PVA (polyvinyl alcohol) binder is added to the powder to make pellets. The pellets were then sintered at 1200 ^oC for approximately 36 h.

The high resolution X-ray diffractometer (HRXRD) was utilized to describe structure of all the samples by the Cu-Kα (λ ~ 1.542 Å) radiation at RT. The impedance, dielectric constant, tangent loss and so forth are estimated by utilizing Impedance analyzer PSM1735 (Newtons4th Ltd, UK) with a heater of varying temperature (0 – 400 ^oC).

3. Results and discussion

3.1 Structural characterization: The XRD pattern of all CZFMO samples is illustrated in Fig.1. The XRD pattern clearly shows the development of well crystalline ferrite samples without impurity. It additionally uncovers that the samples are cubic inverse spinel structured having space group *Fd3m* [11]. The maximum intensity is found corresponding to (311) plane. The lattice constant are determined utilizing the equation [12]

$$a = \frac{\lambda}{2}\sqrt{\left[\frac{h^2+k^2+l^2}{sin^2\theta}\right]} \qquad (1)$$

where λ express the wavelength of X-ray and the Miller indices are (*hkl*). The assessed lattice constant for pure Co-Zn ferrite is 8.38 Å and does not change significantly with Mo substitution.

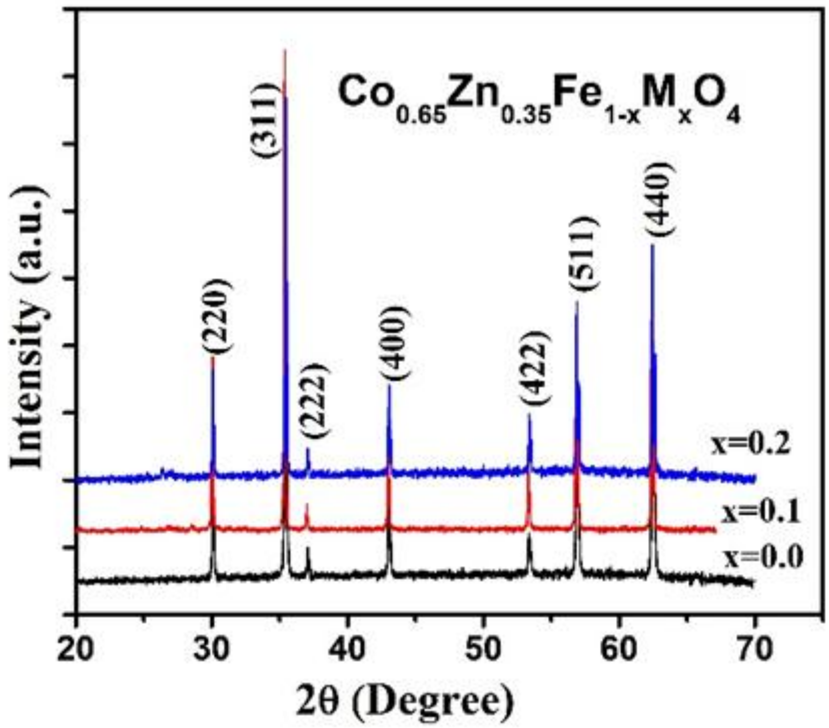

Figure (1): XRD pattern of CZMO (x = 0.0, 0.1, 0.2).

3.2 Electric modulus behavior: The complex modulus formalism was first adopted by P. B. Macedo et. al. **[13]** to determine the space charge relaxation process, rate of hopping and so on. The electric modulus can be assessed by utilizing the equation communicated as **[14]**

$$M^* = M' + iM'' = i\omega C_0 Z^* \quad (2)$$

$$C_0 = \frac{\varepsilon_0 A}{d}$$

where ε_0 represents the permittivity of free space, A is the area of sample and d is the thickness of sample.

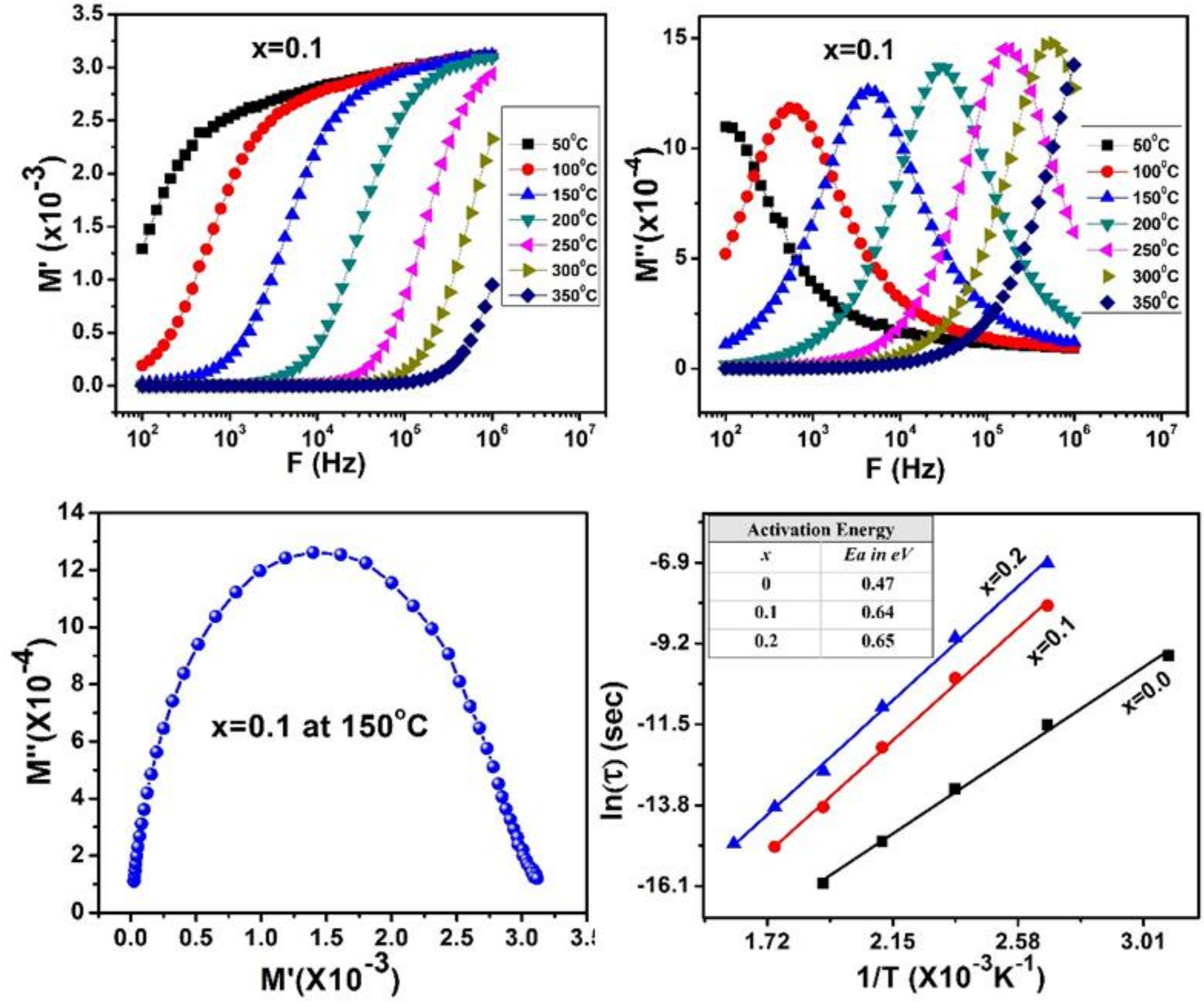

Figure (2): Frequency variation of (a) M′ and (b) M″ at different temperature; (c) Nyquist plot for x=0.1 at 150°C. (d) $\ln \tau$ vs. 1/T plot and inset shows the activation energy.

Figure (2a) demonstrates the frequency reliance of real part of electric modulus *M´* at various temperatures. It recommend that very little value of *M´* at lower frequency and a constant scattering with the expansion of frequency and tending to saturate at an asymptotic maxima in the higher frequency site for every sample.

The change imaginary part of the electric modulus *M´´* with frequency is illustrated in Figure (2b) for x=0.1 at various temperatures. *M´´* is associated with the energy dissipated in the irreversible conduction mechanism. In the latest framework the electric modulus properties can be communicated by the altered Kohlrausch-Williums-Watts (KWW) function proposed by Bergman **[15]**. The imaginary part of modulus *M´´* is characterized as **[16]**

$$M'' = \frac{M''_{max}}{(1-\beta)+\frac{\beta}{1+\beta}\left[\beta\left(\frac{f_{max}}{f}\right)+\left(\frac{f_{max}}{f}\right)^{\beta}\right]} \qquad (3)$$

Where β represent the stretched exponent parameter and f_{max} is the frequency in connection to M''_{max}. The estimation of *β* lies in the scope of $0< \beta \leq 1$.

Figure (2c) illustrate the complex spectrum *M´ vs. M´´* of CZMO. One semi-circular arc at low frequency propose that the relaxation is because of the grain boundary only and the grain effect is stifled. The relaxation time is determined from the *M´´* vs. *f* plot at various temperatures and ln τ vs. 1/T as depicted in Figure (2d). From the incline of the straight line the activation energy is assessed.

3.3 Electrical conductivity:

The ac conductivity of a ferrite material of a ferrite material can be evaluated from the condition as **[17]**

$$\sigma_{ac} = \varepsilon_0 \varepsilon' \omega tan\delta \qquad (4)$$

where ε_o represents the permittivity of free space, ε′ represents the real part of dielectric constant and the angular frequency is ω.

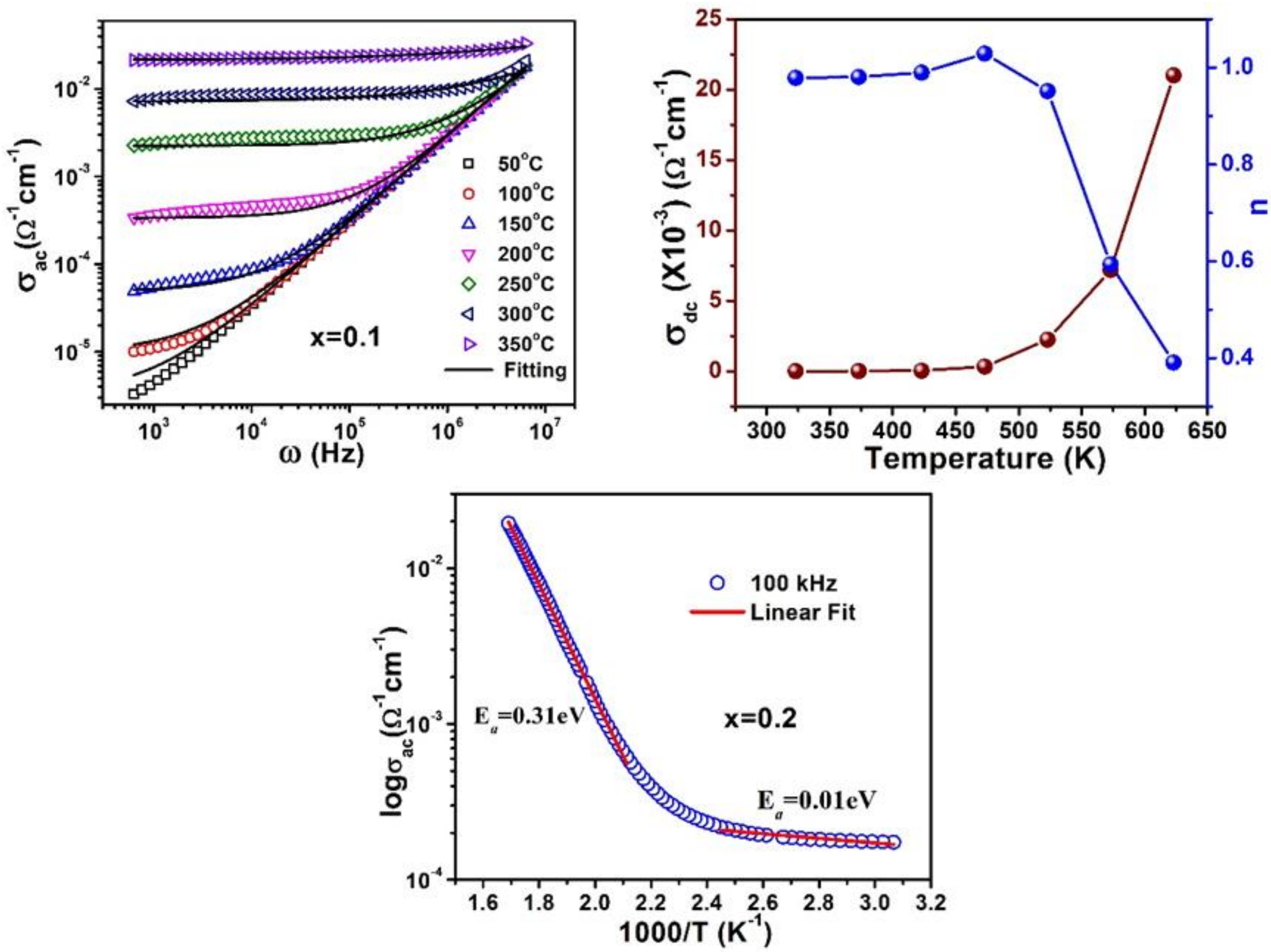

Figure (3): (a) Frequency dependence of ac conductivity at various temperature. (b) Temperature reliance of dc conductivity and the exponent n for x = 0.1; (c) $\ln \sigma_{ac}$ vs. $1/T$ plot for x = 0.2.

The reliance of ac conductivity on frequency for x = 0.1 is illustrated in Figure (3a). Every plots satisfy the Jonscher's single power law **[18]**, is communicated as

$$\sigma_{ac} = \sigma_{dc} + A(T)\omega^n \qquad (5)$$

where σ_{dc} is the dc conductivity which is frequency independent, the temperature subordinate pre-factor is A(T) and n represents the frequency exponent. The variety of n and σ_{dc} with temperature is exhibited in Figure (3b). The curve demonstrates that dc conductivity increases exponentially with temperature while n diminishes. In the current system, change of n with temperature uncovers that the conduction is because of correlated barrier hopping (CBH) process **[19].** Likewise the conduction procedure can be best clarified based on Verwey-de Boer method.

The variety of ln σ_{ac} with 1/T for x = 0.2 is appeared in Figure (4). It has been observed that the conductivity increments with temperature which demonstrate the semiconducting behavior of the material. It is observed that the slope of the straight line changes at the Curie temperature. The activation energies in paramagnetic and ferrimagnetic region has been evaluated.

4. Conclusions: In synopsis, Mo doped Co-Zn ferrites are effectively prepared utilizing the solid state reaction technique. The XRD pattern affirms the creation of inverse spinel structure. The modulus spectroscopy investigation confirms that the conduction procedure is for the most part connected with grain boundary at lower frequency. The ac conductivity pursues the correlated barrier hopping (CBH) process. The frequency variation of ac conductivity satisfy Jonscher's power law. The temperature reliance ac conductivity affirms the semiconducting behaviour of the sample.

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