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Extraordinary role of rare-earth elements on the transport properties of barium W-type hexaferrite

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ABSTRACT

The influence of R_2O_3 substitution on the electrical properties and the thermoelectric power on the W-type hexaferrite $Ba_{0.95}R_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27}; $R = Y^{3+}$, Er^{3+}, Ho^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}, and Ce^{3+} ions as a function of the absolute temperature and frequency in the ranges 300–750 K and 100 kHz–4 MHz, respectively have been studied. The results obtained reveal that, by introducing a relatively small amount of R_2O_3 instead of Fe_2O_3, an important modification of both structure and physical properties can be obtained. The dielectric constant ε', the dielectric loss factor ε'' and AC conductivity σ of the investigating samples have highest values in the case of Sm^{3+}. The values of the calculated activation energy varied between (0.335 and 0.553 eV) and (0.106 and 0.232 eV), above and below the transition temperature, respectively which indicate the semiconducting properties of the prepared samples. The conduction mechanism for Ho^{3+} sample is associated with the small polaron whereas the hopping conduction mechanism is predominant mechanism for the samples doped with the rest of rare-earth ions. The thermoelectric power measurements indicated that the samples are n-type semiconductors except Er^{3+} and Y^{3+} samples, where the thermoelectric power of them is positive at low temperature but nearly above 480 and 375 K, respectively transits to negative. The charge carriers concentration n increases with slightly increasing RE ionic radius to critical value (≈1.04 Å), after that n becomes nearly constant.

1. Introduction

Hexaferrite powders with a narrow size distribution are promising materials for industrial applications due to their high coercivity and saturation magnetization [1]. Polycrystalline hexagonal ferrites are very useful for microwave applications due to its very low dielectric loss. Also these ferrites can be used for permanent magnets, recording media and microwave devices [2], such applications depend on the type of the hexaferrite and the dopants materials. Other interesting applications are the presence of the electromagnetic properties (conductivity, permittivity and permeability) suitable for electromagnetic interference suppression and radar absorbing material (RAM) coatings from centimeter to submillimeter wavelengths of the electromagnetic spectrum [3]. The hexagonal ferrites with W-type structure, having compositional formula $Ba(Sr)Me_2{}^{2+}Fe_{16}{}^{3+}O_{27}$, continues to be very attractive materials for home appliance, electronic products, communication equipment and data processing devices due to its unique electrical and magnetic properties [4]. So one can obtain more valuable information on the behavior of free and localized charge carriers by measuring the electrical, magnetic and thermal properties of these ferrites. Moreover, the measurement of thermoelectric power is simple and its sign gives vital information about the type of conduction mechanism in semiconductors; n- or p-type [5,6]. The magnetic and dielectric behavior of W-type hexaferrite depends on many factors, such as preparation method, calcining temperature, amount and type of substitution. Extensive studies have been made for the frequency and temperature dependence of the dielectric constant and permeability of W-type hexaferrite [7–9]. They showed that, the dielectric constant gives a peak at certain frequencies and their results were discussed on the basis of Rezlescu and Rezlescu [10] assumption. The relation between magnetic properties and substitutions of various kinds of metal ions, the effects of rare-earth elements on the magnetic properties and microstructure, were studied [12,11]. The effects of composition on complex permeability and complex dielectric constants of $Ba_2Zn_ZCo_{2-Z}Fe_{16}O_{27}$ compound were investigated [13]. Effects of rare-earth elements (RE) substitution on microstructural and electromagnetic properties were studied for the compound $Ba(MnZn)_{0.3}Co_{1.4}R_{0.01}Fe_{15.99}O_{27}$ with R = Dy, Nd and Pr [14].

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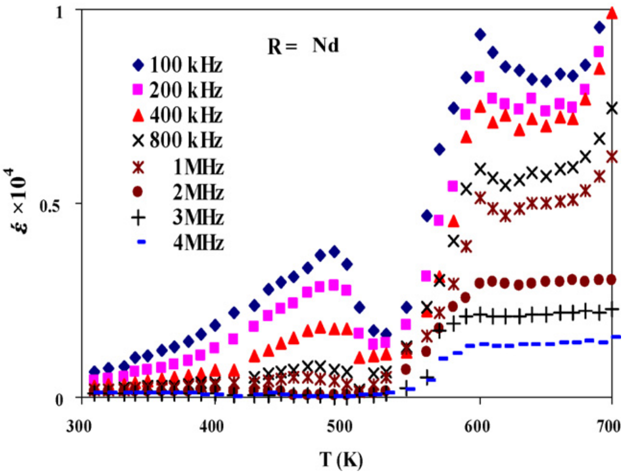

Fig. 1. Dependence of the dielectric constant (ε') on the absolute temperature at different frequencies for the sample $Ba_{0.95}Nd_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27}.

The aim of the present work was to the investigated the AC conductivity and dielectric constant as a function of the temperature and frequency for $Ba_{0.95}R_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27} hexagonal ferrite system, where R = Y^{3+}, Er^{3+}, Ho^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}, and Ce^{3+} ions. However, the presence of R^{3+} ions distributed among various sublattices makes the W-type very interesting for basic studies and different technical applications.

2. Experimental techniques

A series of polycrystalline W-type hexagonal ferrites with compositions $Ba_{0.95}R_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27}, R = Y^{3+}, Er^{3+}, Ho^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}, and Ce^{3+} ions, were prepared by the solid-state reaction technique. The pre-sintering and final sintering were carried out at 1000 and 1300 °C, respectively for 10 h followed by cooling in furnace to room temperature with the same heating and cooling rate of 4 °C min^{-1}. The details of the preparation method have been given in our earlier publications [15]. Identification of hexagonal phase was carried out using X-ray technique with Co Kα radiation. It is clear that, in all cases RE^{3+} ions partially entered the W structure, while, at higher concentration a secondary phase of orthoferrites ($RFeO_3$) was formed. The samples were good polished to obtain uniform parallel surfaces. Contacts on the sample surface were made by silver paste. The real part of dielectric constant (ε') and the AC conductivity (σ) were measured by the two probe method using LCR bridge model Hioki type 3531 (Japan) as a function of the temperature from 300 to 750 K at different frequencies ranging from 100 kHz to 4 MHz. The sample was inserted between the two cell electrodes. A non-inductive and calibrated furnace was used for heating the samples with constant rate. The temperature of the samples was measured using a T-type thermocouple connected to a digit-sense thermometer (USA) with junction in contact with the sample. The thermoelectric power for the samples was measured at different temperature ranging from 300 to 650 K to know the type and behavior of charge carriers in the investigated samples.

3. Results and discussion

3.1. Dielectric constant

The dielectric constant (ε') as a function of temperature at different frequencies ranging from 100 kHz to 4 MHz is shown in Fig. 1 as a typical curve corresponding to the sample with Nd^{3+} ions. It can be seen from the figure that, the relation between the dielectric constant and the absolute temperature can be divided to three regions as follows: in the first region, the dielectric constant of the samples increases with increasing temperature, until reaching a maximum value (first relaxation peak) at a certain temperature after which ε' decreases with increasing temperature, in the second region ε' return to increasing to a maximum value (a second relaxation peak), after that ε' decreases again, in the last one ε' increases continuously. It is known that, the dielectric constant in general is due to orientational, electronic, ionic and interfacial polarization [16]. In the first region the orientational polarizability is predominant, by increasing temperature the vibration of ions increases, and the number of dipoles which aligned with applied field increases. This leads to an increase in the dielectric constant, and reaches maximum value when the hopping frequency of dipoles nearly equal to the frequency of applied field. After that the orientational polarizability decreases (above the transition temperature) $\alpha_d = p^2/3k_BT$ [17]. This attributed to the effect of the thermal energy on the dipoles becomes higher than that of electric field. This in turns leads to increasing the randomization, with the result of decreasing ε'. In the second region the increase in the temperature liberates more localized dipoles from the atomic bonds so the number of charge carriers increases and under the applied field, the contribution of them in the polarizability increases, hence ε' increases and reaches the second peak as a result of contribution of negative and positive charge carriers. After that, ε' decreases with increasing temperature which may be due to the interaction of charge carriers with the thermal phonons. With further increasing of temperature ε' increases continuously (third region), this behavior may be attributed to the increase in the distances between ions. Therefore, the mean relaxation time between two successive electron–phonon collisions increases, which leads to the increase of the drift mobilities, consequently increasing (ε').

Fig. 2a is a typical curve for the sample doped with Er^{3+} illustrating the dielectric constant ε' of the sample as a function of frequency from 100 kHz up to 4 MHz at different temperatures. It is clear that the dielectric constant decreases with increasing frequency [18,19]. This normal behavior in ferrite can be attributed to the electron exchange between ferrous and ferric ions follow the alternating electric field but it cannot be done that beyond a critical frequency [20,21]. It can be also seen that the dielectric constant is larger at low frequencies than at high frequencies. This is due to the fact that the amplitude of vibration of the ions is much greater at the lower frequencies (lower than the natural frequency of vibration of the ions), therefore most of the dipoles get the chance to be aligned

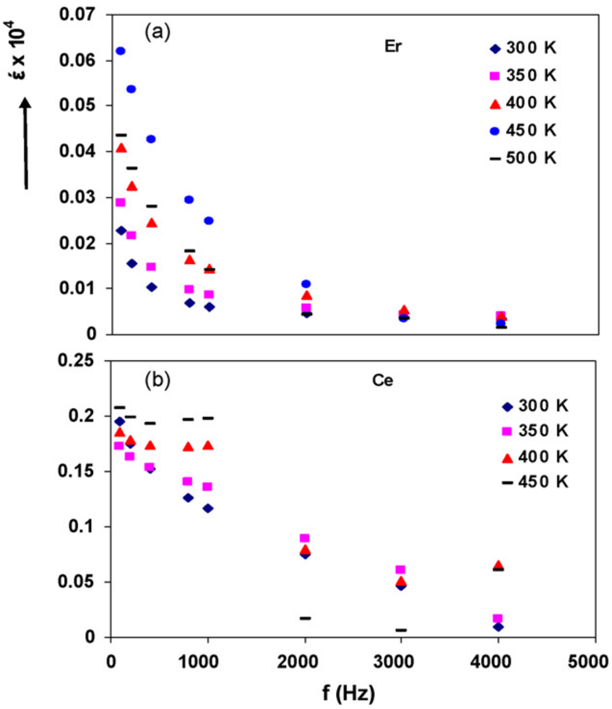

Fig. 2. Relation between the dielectric constant and the applied frequency as a function of the absolute temperature for the samples: (a) $Ba_{0.95}Er_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27} and (b) $Ba_{0.95}Ce_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27}.