

Effect of Fe₃O₄ addition on dielectric properties of LaFeO₃ nano-crystalline materials synthesized by sol-gel method

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Abstract. Dielectric properties of nano-crystalline material LaFeO₃.xFe₃O₄ with x = 0, 0.1, 0.2, 0.3, and 0.4 at.% have been studied by impedance spectroscopy method. LaFeO₃ was synthesized by sol-gel method resulting nano-particle. Then, it was mixed with Fe₃O₄ powder. The mixture powder was pressed to form pellet and then sintered at 1300°C for 1 h to form nano-crystalline of LaFeO₃.xFe₃O₄. X-ray diffraction characterization at room temperature for all samples show two phases i.e. perovskite LaFeO₃ (orthorhombic) as a main phase and Fe₃O₄ (cubic) as second phase. It is found that the crystallite size of main phase increases with addition of Fe₃O₄ until 0.3 at.%. The electrical properties as a function of temperature (300-500 K) and frequency (100 Hz - 1 MHz) are presented in Nyquist and Bode plots. It is observed that from equivalent circuit and their parameters, dielectrical properties are contributed by grain and grain boundary. The dielectric constant, ϵ' were calculated by parallel plate method and their values reach up to 10⁷ exhibiting typical colossal dielectric constant (CDC) material like behavior.

1. Introduction

LaFeO₃ is one of the most important multiferroic perovskite materials. It has been wide range in applications, such as electrodes materials for fuel cells and chemical sensors [1]. LaFeO₃ shows electrical and magnetic behaviour with complex correlation. LaFeO₃ is antiferromagnetic with Neel temperature of 740 K [2]. The electrical properties such as dielectric constant and conductivity can be improved by substitution on A and/or B sites [1]. LaFeO₃ ceramics have been reported to exhibit colossal dielectric constant (dielectric constant typically more than 10⁴) with weak temperature-dependence [3]. Chen *et al.* [4] reported colossal dielectric behaviour of LaFeO₃ in the temperature range 80-315K. Bhargav *et al.* [3] reported colossal dielectric behaviour La_{1-x}Pb_xFeO₃ with x = 20 at.% Pb²⁺ with frequency-dependence behavior in the range of 300-500K. Effect perovskite materials composites with Fe₃O₄ have been reported to structural and electrical transport properties. Z. C. Xia *et al.* [5] found that electrical transport properties of La_{0.67}Ca_{0.33}MnO₃/Fe₃O₄ are directly related to the Fe₃O₄ content. In this paper, we have synthesized LaFeO₃ by sol-gel method and added Fe₃O₄ to form composites of LaFeO₃.xFe₃O₄ with x = 0.0, 0.1, 0.2, 0.3, and 0.4 at.%. We focused on the effect of additional Fe₃O₄ on the structural and dielectric properties of composites of LaFeO₃.xFe₃O₄ materials.

2. Materials and methods

In this work, we mainly analyze the effects of Fe₃O₄ compound in nano-crystalline LaFeO₃.xFe₃O₄ on their electrical properties. The samples were prepared by three steps: First, powder samples of LaFeO₃ was synthesized by sol-gel method, and then characterized by XRD to make sure that its phase is formed. The so-obtained LaFeO₃ powders were calcined at 900°C for 6 hours. Second, LaFeO₃ powder were



mixed with Fe_3O_4 powder and grind to form homogeneous powders of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ with $x = 0, 0.1, 0.2, 0.3$, and 0.4 at.%, respectively. Finally, the powders were pressed into pellet with diameter of 10 mm at pressure of 5 kN and sintered at 1300°C for 1 h. The phase identification has done by using X-Ray Diffractometer (XRD) with Cu K ($\lambda = 1.5406 \text{ \AA}$) radiation source in the 2θ range of 10° – 90° with a step size of 0.02° . Rietveld refinement of the diffraction pattern was carried out using the HighScore Plus software. Electrical properties of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ were characterized by *RLC-Meter FLUKE-PM6306* at frequency between 100 Hz until 1 MHz with the temperature range of 300–500 K.

3. Results and discussion

3.1. Structure analysis

Figure 1 shows XRD pattern of nano-crystalline $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ with $x = 0.1, 0.2, 0.3$, and 0.4 at.% at room temperature. HighScore Plus software was used to analyze all of XRD pattern. All samples exhibit two phases i.e. LaFeO_3 orthorhombic structure as a main phase and Fe_3O_4 cubic structure as a second phase. The Bragg angle, 2θ were observed shifted insignificantly for addition of Fe_3O_4 but the crystal structure of LaFeO_3 is still remain. The refined structural parameters are tabulated in table 1.

Table 1. Refined lattice parameters and crystallite size of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ bulks sintered at 1300°C for 1 h in air.

Samples	$\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$				
	$x=0$	$x=0.1$	$x=0.2$	$x=0.3$	$x=0.4$
Lattice parameters of LaFeO_3					
a	5.5578	5.5686	5.5621	5.5660	5.5770
b	7.8500	7.8515	7.8649	7.8572	7.8713
c	5.5467	5.5538	5.5469	5.5574	5.5540
Crystallite size of LaFeO_3 (nm)	25.0	30.1	33.1	34.3	23.8

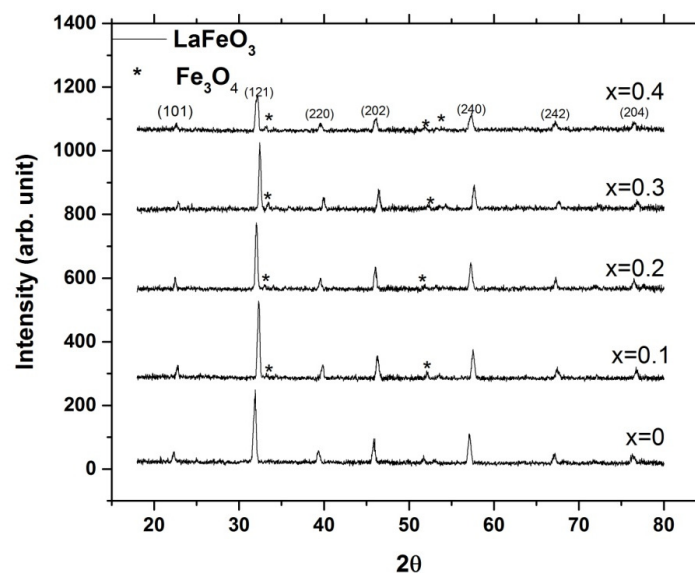


Figure 1. The XRD patterns of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ bulks sintered at 1300°C for 1 h in air.

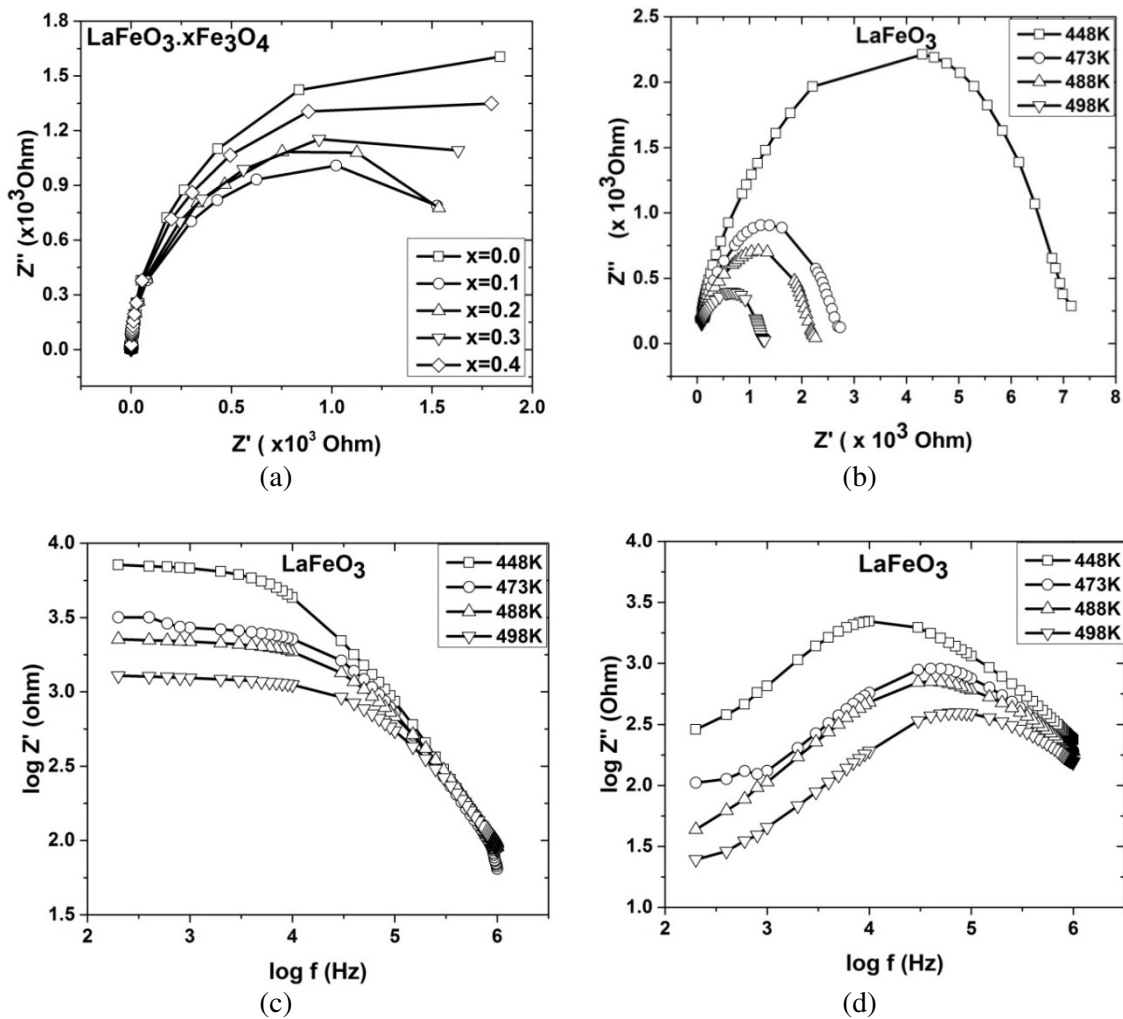


Figure 2. Nyquist plots of (a) $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ at room temperature and (b) LaFeO_3 as a function of temperature; and (c) real and (d) imaginary parts of impedance with frequency at different temperatures for LaFeO_3 compounds.

As shown in the table 1, the crystallite size of LaFeO_3 is significantly increased with the increasing of Fe_3O_4 content until $x = 0.3$ (at.%). The similar phenomenon is found by Xia *et al.* [5] for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ composited with Fe_3O_4 . This behavior is due to the Fe_3O_4 composition on composite $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ (x) that exceeds 0.3, which is able to cause the slowing on the crystal growth process. With the higher composition of Fe_3O_4 to the composite, it would increase the blockade of crystal growth of LaFeO_3 , lead to decrease of crystallite size [5].

3.2 Electrical properties

The Nyquist plots of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ are shown in figure 2. The impedance spectrum is showed by the semicircular arcs, whose changes with increasing of temperature. Nyquist plot in figure 2a and 2b show similar equivalent circuit. The high frequency semicircle can be attributed to the bulk (grain) property, and the low frequency semicircle can be attributed to the grain boundary property of the material that arising due to equivalent circuits of two parallel resistance-capacitance (RC)(RC) elements similar as reported by Triyono *et al.* [6] for $\text{Sr}_2(\text{Fe,Ti})\text{O}_6$ compounds. Figure 2c and 2d show the bode plots of the LaFeO_3 ceramics at different temperatures. Figure 2c shows the Z' value of Z' (f) decrease in increasing

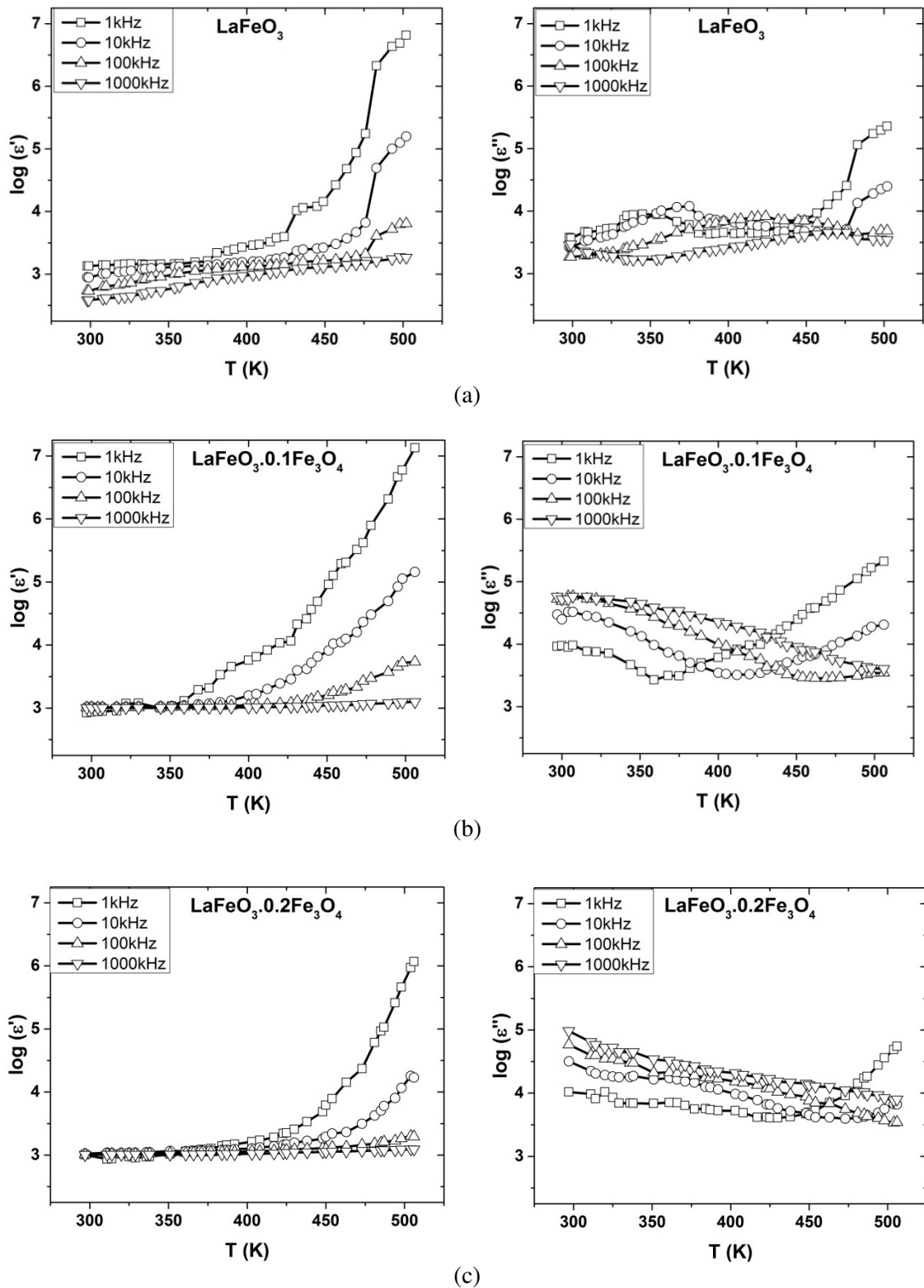


Figure 3. Variation of real ϵ' and imaginary ϵ'' part of dielectric constant with temperature at different frequencies for $\text{LaFeO}_3 \cdot x\text{Fe}_3\text{O}_4$ composites (a) $x = 0$, (b) $x = 0.1$ and (c) $x = 0.2$.

of temperature. This directly related to the increasing of ac conductivity. Figure 2d shows the value of Z'' increased with increasing of frequency until exhibited a maximum value before starts to decrease rapidly. The maximum values shift to higher frequency with increase of temperature indicate there is occurring temperature dependent electrical relaxation phenomenon [7].

Figure 3 shows the temperature dependent real (ϵ') and imaginary (ϵ'') part of dielectric constant at different frequencies for $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ from 300 K to 500 K. We have identified that the dielectric constant is decreasing with decreasing of temperature, which is exhibited in all materials. At higher temperatures, the real part of dielectric constant of $\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ shows increasing order of 10^4 and it decreased at low temperature with relatively weak temperature dependence. Interestingly, the temperature-dependent behavior of dielectric observed on all samples is indicated as an observed behavior of typical colossal dielectric constant (CDC) ceramics [3]. The highest dielectric constant at high temperature is achieved for the sample with $x = 0.1$ i.e. until 10^7 . In the high temperature region, higher value of dielectric constant may be related polarization which comes from mobility of ions, Fe^{3+} - Fe^{3+} and imperfections from this material [8]. This combined effects cause a sharp increase in the dielectric constant when temperature increases. We have measured the frequency dependence of dielectric constant especially for $x = 0.1$ in the temperature range of 300-500 K as presented in figure 4. Figure 4 shows the frequency dependence of dielectric constant of $\text{LaFeO}_{3.0.1}\text{Fe}_3\text{O}_4$. The dielectric spectra as a function of temperature of all samples are similar. At low frequency, the increasing of dielectric constant at $x = 0.1$ is observed, where the dielectric constant reaches 10^4 . At high temperature, the dielectric constant increases significantly as the frequency decreases. And the dielectric constant changes very little with the frequency at room temperature. The larger dielectric constant at low frequencies is related to stronger polarization at low frequencies of this material [9].

The dielectric constant (real and imaginary parts) decrease when increase in frequency and become independent in higher frequency. This phenomenon can be explained by space charge polarization which is related by presence of fairly conducting grains in poorly conducting grain boundaries [10]. From figure 4, we observe that increase of dielectric constant with temperature may be due to thermal fluctuation [11]. The similar phenomenon is found by Kumari *et al.* [10] for Cr^{3+} substituted Fe_3O_4 and El-Mallah [11] for $(\text{Pb,Ca})\text{TiO}_3$ ceramics. However, in our samples show much higher in the values of dielectric constant.

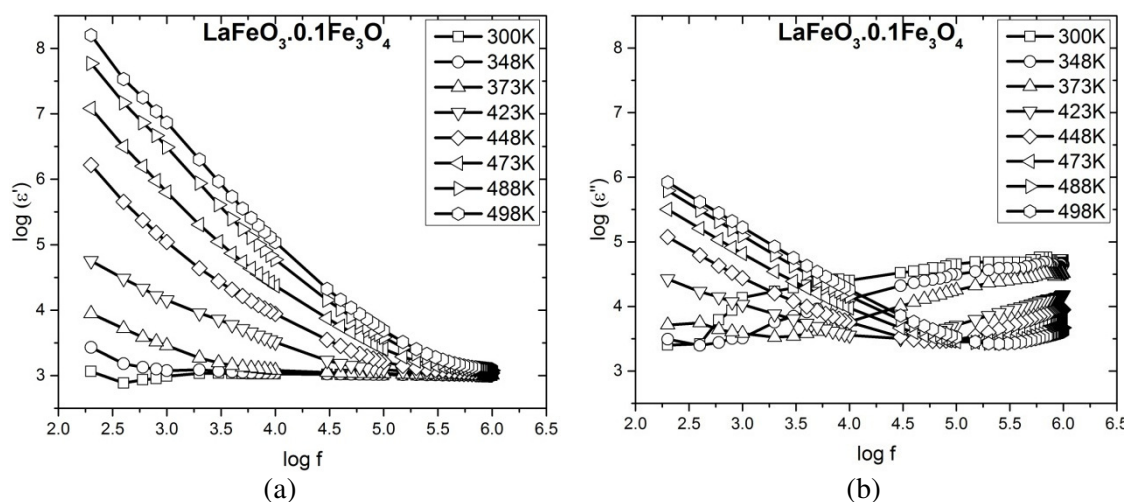


Figure 4. Real (ϵ') and imaginary (ϵ'') part of dielectric constant as a function of frequencies at 300-500K for $\text{LaFeO}_{3.0.1}\text{Fe}_3\text{O}_4$ composites.

4. Conclusions

$\text{LaFeO}_{3-x}\text{Fe}_3\text{O}_4$ with $x = 0.0, 0.1, 0.2, 0.3$, and 0.4 at.% compounds has been successfully synthesized by sol-gel method. XRD characterization for all samples show two phases i.e. LaFeO_3 orthorhombic structure as a main phase and Fe_3O_4 cubic structure as a second phase. The electrical properties are

indicated by grain and grain boundary contribution. The dielectric constant, ϵ' values reach up to 10^7 exhibiting typical colossal dielectric constant (CDC) material like behaviour.

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