# Effect of sintering temperature and frequency on the electrical properties of $Co_{0.22}Zn_{0.78}Fe_2O_4$ ferrite

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**Abstract** : The ac resistivity of $Co_{0.22}Zn_{0.78}Fe_2O_4$, sintered at different temperatures was measured at different frequencies The Curie temperature was decreased with increasing frequencies from 10 kHz to 1 MHz. The suggested hopping model for the conduction mechanism was found to be suitable due to electrons generated by transformation of $Fe^{2+}$ to $Fe^{3+}$ and jumping from one localized state to another. The real part of relative permittivity $\varepsilon'_r$ was measured at the above mentioned frequencies. The values of $\varepsilon'_r$ increased 20 times by varying the sintering temperature from 1200°C to 1400°C due to distribution of anions and cations in $A$ and $B$ sites.

## 1. Introduction

In the past few years, several researchers have studied the electric and magnetic properties of ferrite materials in view of their importance in the application within the range of frequencies up to few GHz. This is due to low eddy currents and dielectric loss as well as their wide applications in microwave devices, computer memories and magnetic recording [1–3]. The order of magnitude of the conductivity greatly influences the dielectric and magnetic behaviour of ferrites.

The spinel Co-Zn ferrite contains reducible iron ions and Co ions and therefore, one may expect that this material exhibits both electron and hole hopping conductivities.

Most ferrites have a spinel type [4,5] structure of general formula $MFe_2O_4$, where M is a divalent metal ions with ionic radius between 0.6 and 1 Å. In a simple ferrite, M is one of the divalent ions of the transition elements Co, Ni, Zn and Fe, while in the mixed ferrite more than one divalent ion is introduced during preparation, where M (in this case)

represents the combination of the two divalent ions and trivalent iron ions in the ratio 1 : 2 respectively. The smallest cell of the spinel lattice has a cubic closed packed arrangement of anions with one-half of the octahedral interstices in $B$-sites and cation filled one-eighth of the tetrahedral interstices in $A$-sites.

In simple $CoFe_2O_4$ [6], the charge carriers are not free to move through the crystal lattice but jump from one ion to another leading to a decrease in the resistivity with increasing temperature. In case of Zn and Co mixed ferrite, the Zn ions prefer to occupy tetrahedral sites in the spinel lattice with the following distribution $Zn_x^{2+} Fe^{3+} [Co^{2+}_{1-x} Fe^{3+}]O_4$, where the square bracket represents the $B$-site.

The investigation of electric and magnetic properties of almost all ferrite materials takes place in the neighbourhood of their Curie-temperature. Few studies are available such as ac conductivity and dielectric properties at different frequencies as a function of composition beyond the Curie-temperature. Beside the technical importance of Co-Zn ferrite, it can be considered as one of the nonmagnetic-magnetic ferrite solid solution series, confirming the theory of ferromagnetism developed by Neel [7].

By this way ferrite can be considered as a polycrystalline dielectric material [8–11] in which the relative permittivity depends on many factors such as sintering temperature, the preparation conditions and the range of frequency in which the measurements were carried out.

The object of this work depends mainly on studying the effect of the above factors on the electrical properties of $Co_{0.22}Zn_{0.78}Fe_2O_4$ samples.

## 2. Experimental

The $Co_xZn_{1-x}Fe_2O_4$ ferrite (where $x = 0.22$) sample under investigation was prepared by using the double sintering standered ceramic technique in which a molar ratio of analar CoO, ZnO and $Fe_2O_3$ (BDH) were mixed and then ground to a very fine powder by using agate mortar for about two hours. The sample was transferred to an electric shaker. Pre sintering was carried out at 800°C and the final sintering was done at 1200°C for compressed pellet form of diameter 10 mm and thickness of about 1.8 mm under a pressure of $15 \times 10^7$ N/m$^2$. Lenton Furnace UAF 16/5 (England) with microprocessor 818P was used for preparing the samples. Different sintering temperatures of (1200, 1250, 1300, 1350 and 1400°C) were used. The heating rate of 6°C/min was adjusted by the microprocessor of the furnace. Same rate was used to cool the samples to room temperature.

The X-ray analysis were carried out to show that the spinel structure was formed. The two surface of each pellet were polished (to remove the layer in which the $Zn^{2+}$ ions evaporated during sintering and to obtain a uniform thickness) and coated with silver paste and checked for ohmic contact. The electrode effects are confirmed to be minimum by repeating the measurements on samples of different thickness.

The elemental analysis using atomic absorption spectrophotometer type PYE UNICAM SP 1900.

The real $\varepsilon_r'$ and imagenary $\varepsilon_r''$ parts of relative permittivity and ac resistivity were measured using Hioki 3530 LCR Bridge (Japan). Non-inductive furnace with temperature controller was used to heat the samples during experiment. The temperature of the samples was measured using $K$-type thermocouple connected to Digi-Sense thermometer (USA) with junction in contact with the sample to obtain the exact temperature with accuracy better than ± 1%.

## 3. Results and discussion

Figures (1a, b) correlate the ac resistivity (ln $\rho$) and the reciprocal of the absolute temperature at two different frequencies (10 and 500 kHz) on samples prepared by sintering at the indicated temperature. The general feature of the figure is the appearance of the phase transition at about 360 K and shifted to 454 K for samples sintered at 1200°C and 1400°C respectively. The figures also show that the resistivity of the samples is decreased by increasing both applied frequency and measuring temperature. This peculiar behaviour is mainly due to the variation of sintering temperature.
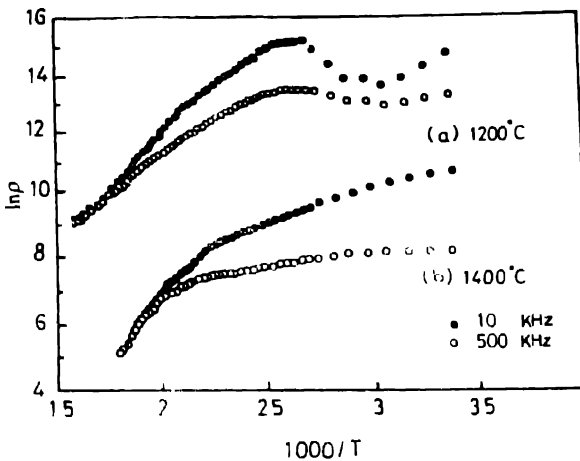


**Figure 1.** The ac resistivity (ln $\rho$) of $Co_{0.22}Zn_{0.78}Fe_2O_4$ as a function of the reciprocal of the absolute temperature at two different frequencies 10, 500 kHz and different sintering temperatures (a) 1200°C, (b) 1400°C

Figure 2 shows a typical resistivity curve for sample sintered at 1300°C as a function of temperature and frequencies. From the Figure it is clear that the behaviour is similar to that known in case of similar ferrites with a change in the slope of graphs at a certain temperature called Curie-temperature. A small but noticeable shift of the Curie-temperature towards lower value was obtained by increasing frequency from 10 kHz to 1 MHz. The values of the activation energy as calculated from the experimental data at different frequencies below and above Curie-point were reported in Table 1, using Arrhenius relation,
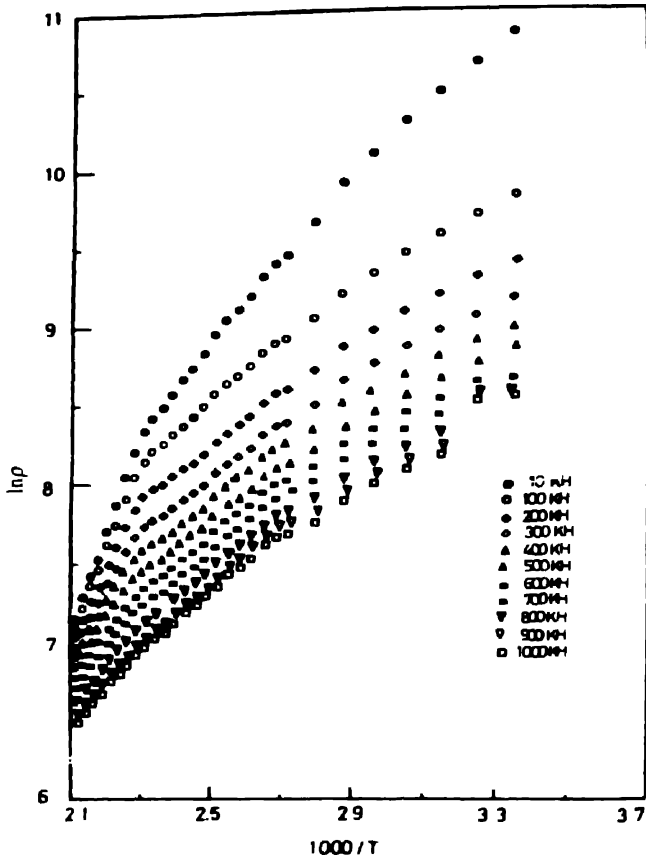
**Figure 2.** Dependence of the ac resistivity (ln $\rho$) of $Co_{0.22}Zn_{0.78}Fe_2O_4$ on temperature and applied frequency for a sample sintered at 1300°C

**Table 1.** The values of the activation energy below and above the Curie point at different frequencies for $Co_{0.22}Zn_{0.78}Fe_2O_4$ sintering at 1300°C

| Freq (kHz) | $E_1 < T_c$ (eV) | $E_{11} > T_c$ (eV) |
|---|---|---|
| 10 | 0.249 | 0.558 |
| 100 | 0.164 | 0.472 |
| 200 | 0.142 | 0.406 |
| 300 | 0.137 | 0.354 |
| 400 | 0.141 | 0.332 |
| 500 | 0.148 | 0.289 |
| 600 | 0.134 | 0.267 |
| 700 | 0.146 | 0.228 |
| 800 | 0.150 | 0.251 |
| 900 | 0.144 | 0.215 |
| 1000 | 0.134 | 0.195 |

$$\rho = \rho_o \exp (E/kT),$$

where $E$ is the activation energy in eV, which according to Verwey and De Boer [12] is the energy needed to release an electron from the ion for jumping to the neighbouring ion and participate in conduction processes, $\rho_o$ is a constant, $k$ is the Boltzmann's constant.

An extensive investigation into the origin of the electrical conductivity of spinels has been carried out by many authors [13,14,1,11].

In ferrite samples under investigation, the surface resistivity is lower than that of the bulk of the material due to the following :

The Zn ions have been evaporated from the surface layer at high sintering temperature and as a result, ferrous ions have been formed and occupy the $B$-sites. During heating, some of $Fe^{2+}$ ions have been transformed to $Fe^{3+}$ ions and generate electrons which participate in conduction mechanism [15]. The simultaneous presence of $Fe^{2+}$ and $Fe^{3+}$ ions on equivalent lattice sites (octahedral sites), may cause the low surface resistivity. The large number of electrons that are generated during the transformation process of valencies of both of $Fe^{2+}$ and $Co^{2+}$ to $Fe^{3+}$ and $Co^{3+}$ respectively, will raise the conduction state of the system. This means that the resistivity of the system will decrease with increasing temperature due to generation of such electrons. A closer look to Figures (1a, b) and, by increasing sintering temperature, the resistivity of the sample decreases. This may be due to the increase of the ratio of $Fe^{2+}/Fe^{3+}$ ($Fe^{3+} \Leftrightarrow Fe^{2+}$) in the system. The grain size was found to change with varying the sintering temperature. This can be detected by scanning electron micrographs carried out for a fracture surface sample sintered at 1200°C. A typical one has been shown in Figure 3. The micrograph indicates a relatively uniform microstructure. From the images, one can say that :
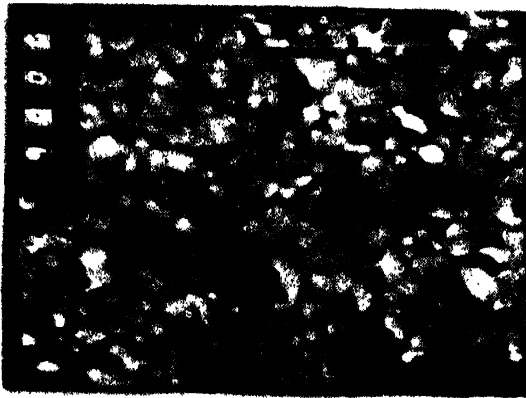


**Figure 3.** Scanning electron micrograph for $Co_{0.22}Zn_{0.78}Fe_2O_4$ at sintering temperature 1200°C.

Large grain size is appeared by increasing the sintering temperature due to removal of the boundaries between the grains.

2.      The bridging between the different grain size is increased with sintering temperature which may be due to the diffusion of $Zn^{2+}$ ions filling the pores.

As it was stated by Jonker and Van Santen [16], one expect the existance of two conductivity regions (with different activation energies); one of them contains $Co^{2+}$ and $Co^{3+}$ and having high resistivity, while the other contains $Fe^{2+}$ and $Fe^{3+}$ with low resistivity.

In normal semiconductors, the electron concentration may reach $\sim 10^{19}-10^{20}$ $cm^{-3}$, while in ferrites, the electron concentration can reach a value of $10^{22}$ $cm^{-3}$ [17]. The concentration of charge carriers in ferrites will lead to low mobility for electrons and holes. The effect of temperature on the generation of conduction carriers is relatively small. Its effect appears only as an increase in their mobility.

The electrical conductivity in the system under investigation can be explained on the basis of the presence of $Co^{2+}$ on the octahedral sites which favour the mechanism [18]

$$Co^{2+} + Fe^{3+} \leftrightarrow Co^{3+} + Fe^{2+}.$$

The hopping mechanism in this case may be due to electron hopping between $Fe^{2+}$ and $Fe^{3+}$ in the octahedral sites [19] and/or hole hopping between $Co^{3+}$ and $Co^{2+}$. The last one is expected to take place with a minor value in $ZnFe_2O_4$ and becomes major in the system $Co_xZn_{1-x}Fe_2O_4$, if $x$ is higher than 0.4. This was clear from the measurements of Seebeck voltage coefficient which will be published latter. In other words and from the orbital consideration, the hopping mechanism in Co-Zn ferrite takes place between ions of different metals which is likely to be more highly activated than that for ions of the same metal.

The hole hopping is reported in other ferrites containing cobalt ions [18,20,21]. The maximum value of activation energy for the ferrimagnetic and paramagnetic regions are 0.249 eV and 0.558 eV respectively at a frequency of 10 kHz. These energy values agree well with those sufficient for electron to hop between $Fe^{2+}$ and $Fe^{3+}$ ions in the octahedral sites. When comparing the values of $E_I$ and $E_{II}$ in Table 1 and at all frequencies, one can find that $E_{II}$ is always greater than $E_I$. This may be attributed to the participation of divalent and trivalent metal ions in conduction process which needs more energy to activate them. This participation occurs at the same time with the hopping that takes place in region I (ferrimagnetic region). It is expected that, if some Co ions diffuse with increasing temperature forming cation vacancies, the number of $Fe^{3+}$ that transform to $Fe^{2+}$ ions are equal to the cation vacancies. This will maintain the high bulk electronic conductivity. Also in ferrimagnetic region, one can attribute the increase in conductivity to the increase in charge carrier mobility due to expectation of constant charge carrier concentration [2]. This will enhance the use of hopping model to the samples under investigation. In this model, the charges are not completely free but are localized in an energy state and jump from one state to another in order to participate in conduction process. The localization of charge carriers comes from polaron formation (electron-phonon interactions).

In the system under investigation, the divalent iron ions which are expected to be formed, during sintering process in the bulk materials under slightly reducing conditions,

will lead to the formation of high conductivity grains [8]. These grains were separated by low conductivity layers (grain boundary), so they behave as inhomogeneous dielectrics. Accordingly, the space charge (interfacial) polarization can be taken into consideration. The space charge polarization which is produced from the accumulation of charges within the sample will vary the net internal field and in turn, it will alter both conductivity and relative permittivity of the samples. The obtained data of dielectric loss factor $\varepsilon_r''$ (Figure 5) give a strong indication that the space charge polarization plays a significant role. The limits of conduction in this case, depend on the applied field. This result agrees well with the observation of other workers [22].

Bady and Collins [23] stated that the dielectric constant of commercial ferrites and garnets are independent of measuring frequencies from 1 MHz to 10 GHz. So we choose the range from 1 kHz to 1 MHz in which the values of relative permittivity $\varepsilon_r'$ is very sensitive and gives drastic variation.

Figure 4a is a typical curve which correlates the real part of relative permittivity $\varepsilon_r'$ and absolute temperature at different frequencies for the compound $Co_{0.22}Zn_{0.78}Fe_2O_4$



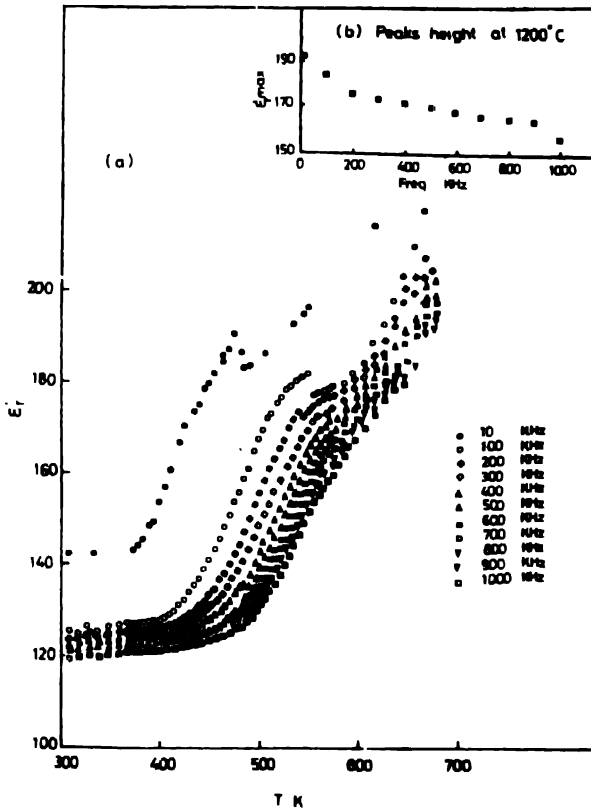**Figure 4.** (a) Typical curve, $\varepsilon_r'$ *versus* absolute temperature for $Co_{0.22}Zn_{0.78}Fe_2O_4$ sintered at 1200°C. (b) The inset shows the variation of the maximum value of $\varepsilon_r'$ with frequency.

sintered at 1200°C. The general feature of this curve is the increase of $\varepsilon'_r$ with increasing temperature. Sharp increase in $\varepsilon'_r$ at ~450 K (Curie-temperature $T_c$) is observed and shifted to higher temperature with increasing frequencies from 10 kHz to 1 MHz. A hump begins at 470 K and shifted to higher temperature with increasing frequencies. This can be explained by the presence of predominant dipole moment, indicating an effective small charge separation. The small separation is expected to be due to the assymmetry in the fields experienced by either the anions or the cations which occur through the distortion of oxygen neighbours forming the tetrahedron. The variation of the maximum value of $\varepsilon'_r$ as a function of frequencies is shown in the inset (Figure 4b). At higher frequencies, the relative permittivity is decreased due to the decrease in polarization of the system. This is because the dipoles cannot follow-up the fast variation of the field accompanied with the applied frequency. When comparing the room temperature values of $\varepsilon'_r$ for sintering temperature 1200°C and 1400°C, one can find that it is increased from 120 to 2200 units respectively This is because the sintering temperature will affect the distribution of cations between tetrahedral ($A$) and octahedral ($B$) sites in the system ($Zn_x^{2+} Fe^{3+}$) [$Co^{2+}_{1-x} Fe^{3+}$], where ( ) and [ ] represent the $A$ and $B$ sites respectively. Also it is observed that $\varepsilon'_r$ decreases sharply after $T_t$ with increasing sintering temperature to 1400°C. This behaviour is due to the high thermal energy given to the system in the paramagnetic region which is sufficient to overcome the effect of the field orienting the dipoles.

The values of $T_c$ and $\varepsilon'_r$ at the peak for the samples sintered at different temperatures (1200°C–1400°C) as a function of frequencies, were reported in Table 2. From the reported data, it is observed that varying sintering temperature will vary the grain size and in turn affects the polarizability and shifts the Curie temperature of the sample.

**Table 2.** Values of $T_c$ and $\varepsilon'_r$ at the peak as a function of frequencies of samples sintered at different temperature

| Freq. (kHz) | 1200°C | | 1250°C | | 1300°C | | 1350°C | | 1400°C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\varepsilon'_{max}$ | $T_c(k)$ | $\varepsilon'_{max}$ | $T_c(k)$ | $\varepsilon'_{max}$ | $T_c(k)$ | $\varepsilon'_{max}$ | $T_c(k)$ | $\varepsilon'_{max}$ | $T_c(k)$ |
| 10 | 184 | 536 | 229 | 454 | 4460 | 431 | 5371 | 428 | 7030 | 412 |
| 100 | 176 | 548 | 192 | 508 | 3680 | 435 | 4114 | 432 | 5333 | 422 |
| 200 | 169 | 550 | 186 | 510 | 3340 | 437 | 3600 | 442 | 5030 | 426 |
| 300 | 166 | 553 | 178 | 513 | 3100 | 469 | 3257 | 450 | 4969 | 430 |
| 400 | 164 | 555 | 175 | 519 | 2880 | 471 | 3143 | 452 | 4720 | 436 |
| 500 | 162 | 558 | 173 | 524 | 2860 | 472 | 2972 | 454 | 4545 | 440 |
| 600 | 158 | 560 | 172 | 538 | 2720 | 473 | 2800 | 458 | 4500 | 446 |
| 700 | 157 | 561 | 171 | 546 | 2680 | 473 | 2572 | 459 | 4424 | 452 |
| 800 | 156 | 562 | 169 | 548 | 2580 | 474 | 2229 | 460 | 4398 | 454 |
| 900 | 154 | 563 | 167 | 550 | 2540 | 474 | 2172 | 462 | 4354 | 458 |
| 1000 | 153 | 564 | 165 | 552 | 2460 | 475 | 2114 | 467 | 4303 | 460 |

The temperature and frequency dependence of the dissipation of charges in ferrite materials is represented as the imaginary part of the relative permittivity $\varepsilon''_r$ for a

sample sintered at 1200°C (Figure 5) which is similar to other Co-Zn ferrite samples sintered at different temperature. From the Figure, it is clear that $\varepsilon_r''$ is relatively small when compared with other dielectric materials. This means that the eddy currents which can be produced in $Co_{0.22}Zn_{0.78}Fe_2O_4$, is very small and so it can be used in many electronic applications.
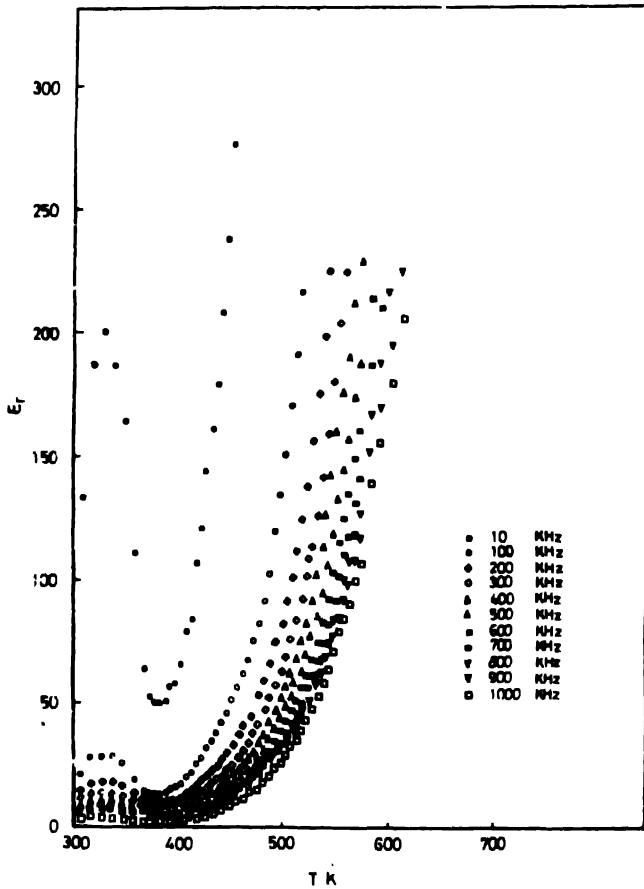


**Figure 5.** The imaginary part of the relative permittivity $\varepsilon_r''$ as a function of absolute temperature for $Co_{0.22}Zn_{0.78}Fe_2O_4$ sintered at 1200°C.

As an exceptional case, the sample sintered at 1400°C gives no relaxation peaks than that sintered at 1200°C and the values of $\varepsilon_r''$ becomes 100 times larger at room temperature. This may be due to the increase in the distortion that occurs in the tetrahedron formed from metal cation and the four neighbouring oxygen anions. The assymmetry produced from the distortion due to sintering at 1400°C is expected to increase the polarizability of the sample; so a very small energy is needed to obtain the relaxation peak, which may be shifted to lower temperature and disappeared as in Figure 5.

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