Dielectric Properties of the System GdCo$_{1-x}$Fe$_x$O$_3$
Synthesized by Chemical Route (x = 0.10, 0.20)

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Abstract: The perovskite oxides GdCo$_{1-x}$Fe$_x$O$_3$ (x = 0.10, 0.20) were prepared by chemical method. The dielectric behavior of compositions with x = 0.10 and 0.20 in the system GdCo$_{1-x}$Fe$_x$O$_3$ was studied in the temperature range 300-500 K. It is observed that dielectric constant increases with increasing Fe$^{2+}$ ions concentration. The frequency dependence of dielectric constant in these materials indicates that space charge polarization contributes significantly to their observed dielectric parameters. A uniform distribution of grains is observed from the microstructure by Scanning electron microscopy.

Keywords: Chemical method, Dielectric Constant, Gadolinium Cobaltate, SEM

Introduction

Extensive research is being carried out on oxide of transition metals like Cu, Co, Ni, Fe, Cr, V and Mn in the simple as well as complex forms including perovskite oxide. The perovskite oxide are represented by the general formula ABO$_3$, where A cation may be rare earth, alkaline earth, alkali or large ion and B cation may be transition metals. Perovskite oxide of the rare earth transition metals have been studied by various groups of workers because of their technological applications. The reason for broad application includes their stability over wide temperature ranges and their low cost. The composition and microstructure of ABO$_3$ may be optimized by doping in A site or B site or by simultaneous doping and tailored to specific applications. Traditionally perovskite oxides were prepared by conventional ceramic method at high temperature. This leads to poor compositional homogeneity and high sintering temperature. The electrical and dielectric properties of the system Gd$_{1-x}$A$_x$CoO$_3$ (A = Ca, Ba, Sr) were studied recently by our groups...
and published elsewhere 9-11. We had selected the system GdCoO₃ and partially doped with Ni³⁺ ions in place of Co- ions proportionally by using chemical method. In this paper we report the preparation, characterization the dielectric behaviors of the system GdCo₁₋ₓFeₓO₃ (where x = 0.10, 0.20).

**Experimental**

Compositions with x = 0.10, 0.20, in the system GdCo₁₋ₓFeₓO₃ were prepared by chemical method using Citric acid. The chemicals used in this method have purity 99.9% or, betters. Gadolinium oxide, Cobalt (II) nitrate and Iron nitrate were used as starting materials. Gadolinium oxide was converted into nitrate by adding conc. HNO₃ and evaporated to dryness. Standard solution of metal nitrate was prepared in distilled water. Solution having stoichiometric amount of these metallic ions in the system GdCo₁₋ₓFeₓO₃ (x = 0.10, 0.20) were mixed in a beaker. Calculated amount of citric acid equivalent to the metals ions was added to the solution. The solution was mixed on a hot plate magnetic stirrer and warmed up to 60-70°C and kept the temperature constant till total evaporation of water. The residue was dried at 50°C – 60°C in a hot air oven for 12hrs. Dry powder was calcined at 700°C for 8hrs. The calcined powder was grounded into fine powder and made cylindrical pellets. The pellets were sintered at 750°C for 6 hrs.

Sintered pellets were grounded into fine powder and X-ray diffraction patterns were recorded (2θ = 20 – 80°) in a X-Ray diffractometer (Philips X-Part) using Cu-Kα radiation with a Ni-filter. The capacitance (C) and AC conductance (G) were measured by HIOKI 3532 LCR HiTESTER (Japan) with variation of frequencies and temperature. The relative dielectric constant (εᵣ) of the materials were calculated by using the measured capacitance values and dimensions of the pellet by the following equation given below:

$$εᵣ = \frac{CL}{ε₀A}$$

where $ε₀ = 8.854 \times 10^{-12} \text{ Fm}^{-1}$, is permittivity of free space, C is the capacitance, L is the thickness of the pellet in meter and A is the cross section area of the cylindrical pellet in m².

**Results and Discussion**

The recorded peaks were sharp and strong enough to confirm high crystallinity of the synthesized samples. No reflections other then those belonging to orthorhombic structure were observed in the XRD patterns. XRD data for the system GdCo₁₋ₓFeₓO₃ having compositions x = 0.10, 0.20 is given in Table 1. All the reflection peaks were indexed on the basis of orthorhombic structure. The lattice parameter and unit cell volume were determined using least squares refinement method with the help of computer software package which are shown in Table 2. Compared to pure GdCoO₃, no shift in major peak was observed. From this, we conclude that the basic crystal structure of pure GdCoO₃ has not been affected by doping of Fe³⁺ ions in small amount. However, a minor shift is observed in the peak positions indicating a small change in the lattice parameters. The orthorhombic unit cell volume increase slightly due to difference in ionic radius of Fe³⁺ and Co³⁺ ions 12.

Typical SEM micrographs of the fracture surface of the densely sintered GdCo₁₋ₓFeₓO₃ samples are shown in Figure 1. The micrographs suggest that materials comprise of polycrystalline microstructure and the percentage of doping affect the microstructure. The sample shows well developed and relatively equal-axe-shaped grains as the Fe content increases. The size of the grains grows with the increase in Fe concentration and the micrographs indicate the presence of grains with 4-5 µm for higher values of x. The average grain size varies from 2 µm to 3 µm. The GdCo₁₋ₓFeₓO₃ sample shows a fairly uniform
distribution of grain size through out the surface but becomes non-uniform as the Fe concentration increases. Dielectric constant, saturated polarizations are all dependent on grain size of the materials. The number of domain variants will increase with the increase of the grain size. This is because increase in grain size reduces the volume fraction of grain boundaries. As a result, the coupling effect between the grain boundaries and the domain wall will decrease. Thus the domain wall mobility will increase, leading to an increase in dielectric constant, with increase in grain size\textsuperscript{13}.

Table 1. XRD data for the system GdCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3}

<table>
<thead>
<tr>
<th>S. No.</th>
<th>θ (°)</th>
<th>d(Å)</th>
<th>I / I\textsubscript{o}</th>
<th>θ (°)</th>
<th>d(Å)</th>
<th>I / I\textsubscript{o}</th>
<th>h k l</th>
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Table 2. Lattice parameters and unit cell volume of the system GdCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3}

<table>
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<tr>
<th>System</th>
<th>Composition</th>
<th>Crystal system</th>
<th>Lattice parameters (Å)</th>
<th>Unit Cell volume (Å\textsuperscript{3})</th>
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<tr>
<td>GdCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} x = 0.10</td>
<td>Orthorhombic</td>
<td>a = 5.2239 ± 0.0128</td>
<td>b = 5.3047 ± 0.0130</td>
<td>c = 7.5902 ± 0.0187</td>
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<tr>
<td>GdCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} x = 0.20</td>
<td>Orthorhombic</td>
<td>a = 5.2278 ± 0.0147</td>
<td>b = 5.3212 ± 0.0150</td>
<td>c = 7.6308 ± 0.0216</td>
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Figure 1. SEM microphotograph for the system GdCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} (a) x=0.10 (b) x=0.20
Figure 2. Plots of dielectric constant versus temperature (a) $x = 0.10$  (b) $x = 0.20$ for the system GdCo$_{1-x}$Fe$_x$O$_3$

Plots of dielectric constant ($\varepsilon_r$) versus temperature for compositions $x = 0.10$ and 0.20 of the systems GdCo$_{1-x}$Fe$_x$O$_3$ at four frequencies (0.1kHz, 1 kHz, 10 kHz and 100 kHz) are shown in Figure 2. The dielectric constant for the composition $x = 0.10$ at frequencies 0.1 kHz and 1 kHz increases with increase in temperature. But the dielectric constant remains almost constant with temperature up to 500 K at higher frequencies i.e. at 10 kHz and 100 kHz. The variation of $\varepsilon_r$ for the composition $x = 0.20$ is shown in Figure 2(b). It is observed that the nature of variation of this composition is different as compared to the composition $x = 0.10$. 


The dielectric constant of the composition \( x = 0.20 \) is remains constant up to 375 K at all four frequencies and then increases slowly except at 0.1 kHz frequency. Dielectric constant for \( x = 0.20 \) at 0.1 kHz increases rapidly after 400 K temperature. It is also observed that the composition \( x = 0.20 \) shows high \( \varepsilon_r \) value as compared to \( x = 0.10 \). The amount of doping of Fe in place of Co in the system GdCo\(_{1-x}\)Fe\(_x\)O\(_3\), enhanced the dielectric constant of the oxide perovskite.

The high value of \( \varepsilon_r \) observed in GdCo\(_{1-x}\)Fe\(_x\)O\(_3\) system shows the ferroelectrics nature of the system. This may be due to distortion of the octahedral on temperature variation. The distorted octahedra couple together and a very large spontaneous polarization can be achieved at the transition temperature. This large spontaneous polarization leads to a large dielectric constant.

![Dielectric Constant vs Frequency Plot](image)

**Figure 3.** Plots of dielectric constant versus frequency for the system GdCo\(_{1-x}\)Fe\(_x\)O\(_3\) at (a) 300 K and (b) 400 K
The plots of dielectric constant with frequency for the system GdCo$_{1-x}$Fe$_x$O$_3$ at 300 and 400K for the samples having compositions $x = 0.10$ and 0.20 are shown in Figure 3. The dielectric constant ($\varepsilon_r$) decreases sharply up to ~1kHz and then shows slow decrease and becomes almost constant at ~1MHz. The dielectric constant depends strongly on frequency. The $\varepsilon_r$ decreases with increasing frequency. This shows that space charge polarization contributes more significantly to the observed dielectric parameters in these compositions. Interfacial polarization arises due to random occupation of equivalent octahedral sites by Ni and Co ions. This gives rise to micro-regions with different compositions, having different conductivities responsible for interfacial polarization. The space-charge polarization in these materials also arises due to the chemical heterogeneities present in them at the micro-level.

Acknowledgements

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References
