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

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Abstract: The perovskite oxides $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.10, 0.20$) were prepared by chemical method. The dielectric behavior of compositions with $x = 0.10$ and 0.20 in the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ 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 workers¹⁻⁵ 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 applications⁶⁻⁸. 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 $\text{Gd}_{1-x}\text{A}_x\text{CoO}_3$ ($A = \text{Ca}, \text{Ba}, \text{Sr}$) were studied recently by our groups

and published elsewhere⁹⁻¹¹. We had selected the system GdCoO_3 and partially doped with Ni^{3+} 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 $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ (where $x = 0.10, 0.20$).

Experimental

Compositions with $x = 0.10, 0.20$, in the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ were prepared by chemical method using Citric acid. The chemicals used in this method have purity 99.9% or, better. Gadolinium oxide, Cobalt (II) nitrate and Iron nitrate were used as starting materials. Gadolinium oxide was converted into nitrate by adding conc. HNO_3 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 $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.10, 0.20$) 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 $60-70^\circ\text{C}$ and kept the temperature constant till total evaporation of water. The residue was dried at $50^\circ - 60^\circ\text{C}$ 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 ($2\theta = 20 - 80^\circ$) in a X-Ray diffractometer (Philips X-Part) using $\text{Cu-K}\alpha$ 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 (ϵ_r) of the materials were calculated by using the measured capacitance values and dimensions of the pellet by the following equation given below:

$$\epsilon_r = CL / \epsilon_0 A$$

where $\epsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$, 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 m^2 .

Results and Discussion

The recorded peaks were sharp and strong enough to confirm high crystallinity of the synthesized samples. No reflections other than those belonging to orthorhombic structure were observed in the XRD patterns. XRD data for the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ 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 GdCoO_3 , no shift in major peak was observed. From this, we conclude that the basic crystal structure of pure GdCoO_3 has not been affected by doping of Fe^{3+} 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 Fe^{3+} and Co^{3+} ions¹².

Typical SEM micrographs of the fracture surface of the densely sintered $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ 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 $4-5 \mu\text{m}$ for higher values of x. The average grain size varies from $2 \mu\text{m}$ to $3 \mu\text{m}$. The $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ 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 size¹³.

Table 1. XRD data for the system $GdCo_{1-x}Fe_xO_3$

S. No.	x = 0.10			x = 0.20			h k l
	2θ	d(Å)	I/I ₀	2θ	d(Å)	I/I ₀	
1	23.6688	3.7560	21	23.6033	3.7663	22	1 1 0
2	26.4826	3.3630	16	26.3802	3.3758	14	1 1 1
3	33.7648	2.6525	100	33.6364	2.6623	100	1 1 2
4	34.2154	2.6186	27	34.1705	2.6219	21	0 2 0
5	40.0709	2.2484	4	39.9040	2.2574	4	2 1 1
6	43.5281	2.0775	6	43.3719	2.0846	8	1 1 3
7	49.8563	1.8276	12	49.6445	1.8349	12	0 2 3
8	56.6910	1.6224	2	56.5128	1.6271	3	3 1 1
9	59.5086	1.5521	8	59.2331	1.5587	9	0 2 4
10	70.9922	1.3266	9	70.7480	1.3306	10	2 2 4
11	82.3342	1.1702	3	81.9687	1.1745	3	2 4 1
12	87.7423	1.1115	1	87.6018	1.1129	1	3 3 3

Table 2. Lattice parameters and unit cell volume of the system $GdCo_{1-x}Fe_xO_3$

System	Composition	Crystal system	Lattice parameters	Unit Cell volume
			(Å)	(Å ³)
$GdCo_{1-x}Fe_xO_3$	x = 0.10	Orthorhombic	a = 5.2239 ± 0.0128 b = 5.3047 ± 0.0130 c = 7.5902 ± 0.0187	210.3338±1.5546
	x = 0.20	Orthorhombic	a = 5.2278 ± 0.0147 b = 5.3212 ± 0.0150 c = 7.6308 ± 0.0216	212.2706±1.8026

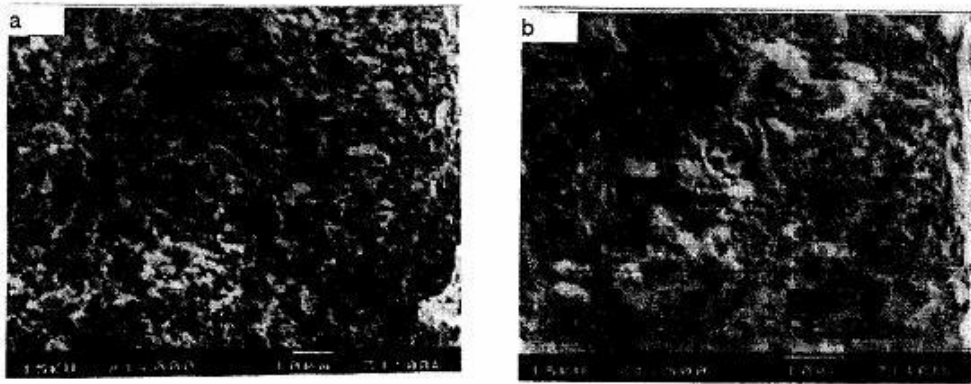


Figure 1. SEM microphotograph for the system $GdCo_{1-x}Fe_xO_3$ (a) x=0.10 (b) x=0.20

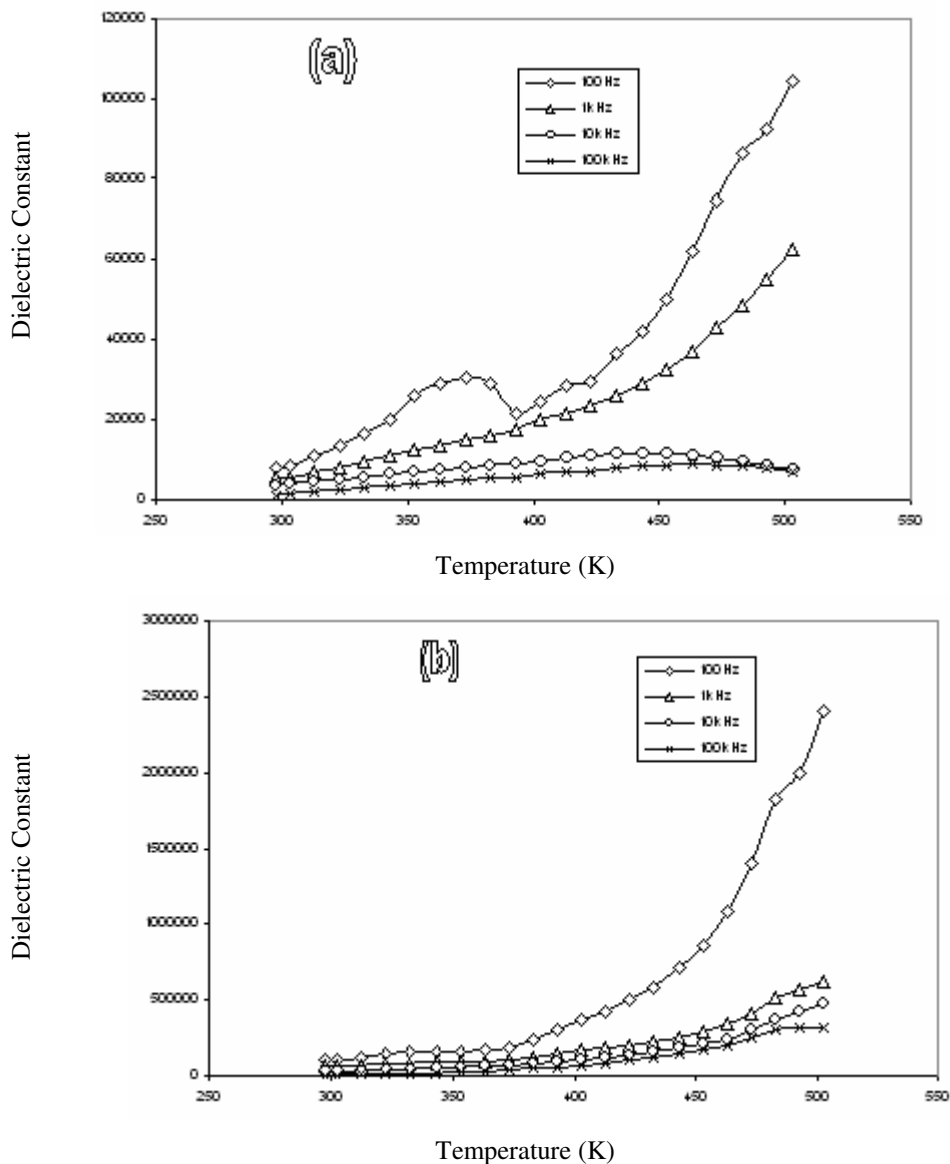


Figure 2. Plots of dielectric constant versus temperature (a) $x = 0.10$ (b) $x = 0.20$ for the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$

Plots of dielectric constant (ϵ_r) versus temperature for compositions $x = 0.10$ and 0.20 of the systems $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ at four frequencies (0.1 kHz, 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 ϵ_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 $x = 0.20$ 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 ϵ_r value as compared to $x = 0.10$. The amount of doping of Fe in place of Co, in the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$, enhanced the dielectric constant of the oxide perovskite.

The high value of ϵ_r observed in $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ system shows the ferroelectric 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.

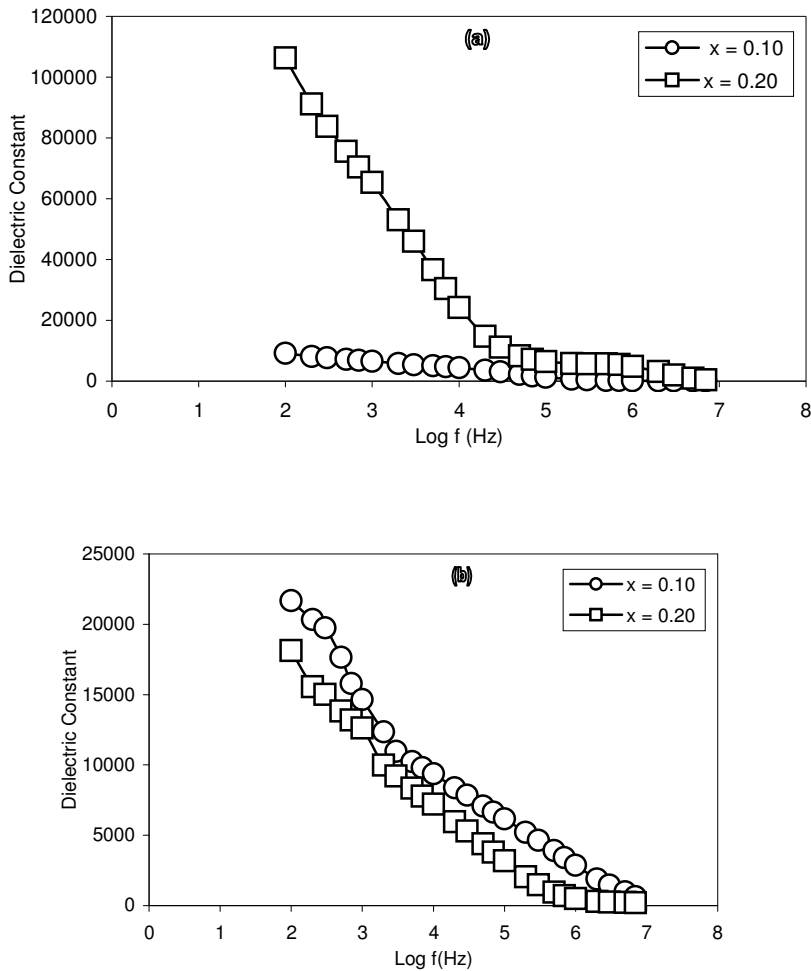


Figure 3. Plots of dielectric constant versus frequency for the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ at (a) 300 K and (b) 400 K

The plots of dielectric constant with frequency for the system $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ at 300 and 400K for the samples having compositions $x = 0.10$ and 0.20 are shown in Figure 3. The dielectric constant (ϵ_r) decreases sharply up to $\sim 1\text{kHz}$ and then shows slow decrease and becomes almost constant at $\sim 1\text{MHz}$. The dielectric constant depends strongly on frequency. The ϵ_r decreases with increasing frequency. This shows that space charge polarization contributes more significantly to the observed dielectric parameters in these compositions. Interfacial polarization¹⁴ 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-level¹⁵.

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References

1. Buchanan R C , Ceramic Material for Electronics ,Marcell Deker, New York, 1986
2. Halliyal A, Kumar U, Newnham and Cross L E, *J. Am. Chem. Soc.*, 1989, **70**, 119.
3. Parkash Om, Mandal K D and Sastry M S, *J. Alloys and compounds*, 1995, **228**, 177.
4. Rivas-Vazquez L P, Rendon-angles J C, Rodriguez-Galicia J L, Gutierrez-Chavarria C A, Zhu K J and Yanagisawa K, *J. European Cer. Soc.* 2006, **26**, 81.
5. Sharma P K and Raman A, *J. Mater. Sci.*, 1996, **31**, 773.
6. Bhide V G, Rajoria D S, Rama Rao G and Rao C N, *Phys. Rev.* 1972, **B6**, 1021.
7. Raccah P and Goodenough J B, *Phys. Rev.* 1967, **155**, 932.
8. Ganguli P, and Rao C N R, *Mater. Res. Bull.* 1973, **8**, 405.
9. Mandal K D, Behera L and Ismail K, *J. Alloys and Compounds*, 2003, **352**, 309.
10. Mandal K D, Behera L, Prasad R L and Behera R C, *Cryst. Res. & Technol.*, 2003, **38**, 465.
11. Mandal K D, Behera L and Behera R C, *J. Mater. Sci. & Technology*, 2002, **10**, 21.
12. Shannon R D and Prewitt C T, *Acta. Cryst.* 1969, **B25**, 925.
13. Rout D, Subramanian V and Hariharan K, *Materials Science and Engineering*, 2005, **B123**, 107.
14. Iwauchi K, *Japan J. Appl. Phys.*, 1971, **10**, 1520.
15. Koops C G , *Phys. Rev.*, 1951, **83** , 121.