

Microwave dielectric properties of M-Type barium, calcium and strontium hexaferrite substituted with Co and Ti

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Suitable ferrite components are designed for use in systems like radar, satellite uplinks, industrial heaters or dryers and nuclear systems which employ high power microwaves. Ferrites are also used as microwave absorbers. Radar absorbing paint made from ferrites can be used to coat military aircraft for stealth operation. In this study, some hexaferrites have been synthesized and characterized for their possible use at high frequencies. Three series of M type hexagonal ferrites having the general formula $M\text{Fe}_{12}\text{O}_{19}$ in which Me was Ba^{2+} , Sr^{2+} or Ca^{2+} and Fe^{3+} ions were replaced partly by $\text{Co}^{2+}\text{Ti}^{4+}$ ions were chosen for synthesis and study. The microwave dielectric constants of these hexaferrites has been measured in the X band of the microwave frequency range after successively increasing the amount of substituted ions in the ferrites. The variation of Complex Permittivity of these hexaferrites with change in composition as well as change in frequency has been measured in this frequency range. Important inferences have been drawn using theoretical concepts.

Keywords: Hexaferrite, Dielectric, M-type Hexaferrites.

Introduction

Ferrimagnetic oxides or Ferrites as they are usually called, are ceramic ferrimagnetic materials which are dark brown or gray in appearance and very hard and brittle in character. They are prepared by heat-treating the various transition metal oxides or alkaline earth oxides with the ferric oxides [1]. The magnetic behavior exhibited by the ferrites is called ferrimagnetism, which is quite different from ferromagnetism that is exhibited by metallic materials. In 1952, a new class of ferrites having permanent magnetic properties was discovered. These were the so-called hexagonal ferrites with formula $M(\text{Fe}_{12}\text{O}_{19})$ where M is usually barium Ba, strontium Sr, Calcium Ca or Lead Pb. The crystal structure is complex but it can be described as hexagonal with a unique c axis, which is the easy axis of magnetization in the basic structure. Hexagonal ferrites are referred to as hard as the direction of magnetization cannot be changed easily to another axis. Workers at Philips laboratory at Eindhoven in the Netherlands made the developments of hexagonal ferrites possible.

Initially, these materials were studied for their use as permanent magnets or as magnetically soft cores at frequencies well into UHF region. Later on it was realized that due to their large “built in” biasing field, these materials have good prospects for application at

microwave frequencies [2-5].

Ferrites are also used as microwave absorbers. Some ferrites absorb microwave by losing interaction of the electric and magnetic field vector of incident waves and in the process transfer microwave energy into thermal energy. These materials possess an imaginary part of the permittivity and permeability that can vary with composition of material and frequency [6]. M type hexaferrite has been reported for applications in microwave devices at mm wave frequencies [7]. Radar absorbing paint made from ferrites can be used to coat military aircraft for stealth operation. The aim of the present work is to synthesize hexaferrites and characterize them for their possible use at high frequencies.

Experimental

Three ferrite series of the composition $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$, $\text{Sr}(\text{CoTi})_y\text{Fe}_{(12-2y)}\text{O}_{19}$ and $[\text{Ca}(\text{CoTi})_z\text{Fe}_{(12-2z)}\text{O}_{19}]_{96.0}[\text{La}_2\text{O}_3]_{4.0}$ where x, y and z vary in the respective series from 0.0 to 1.0 in steps of 0.1 have been synthesized. The ferrites were synthesized from stoichiometric mixtures of BaCO_3 , SrCO_3 , CaCO_3 , CoCO_3 , TiO_2 , Fe_2O_3 and La_2O_3 of 99.9% purity using a normal ceramic method. The reagents were crushed and mixed thoroughly for 6h in acetone in a ball mill. The material was dried and calcined at 1000°C for 12h in air in the case of the barium and strontium hexaferrites series and for 3h in the case of the calcium hexaferrite series. During calcination, the evolution of gases takes place and ferrite is partially formed. This is an important homogenization operation that produces ferrites with reasonably high densities and uniform

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crystal structure, chemical composition and particle size. The calcined powder was thoroughly ground in a ball mill to produce a grain size distribution that would sinter readily. The grinding of calcined powder is termed black milling. The powder was dried and granulated by adding a few drops of polyvinyl alcohol (PVA) as a binder and sieving it through sieves with mesh sizes 250 and 180 μm respectively. The addition of binder not only imparts strength and good flow properties to the material but also strengthens the compacted part so that it can be handled without damage prior to firing. The granules were compacted to the required size in the shape of rectangular pellets in steel dies under a uniaxial load of 75 N. The pellets were finally sintered in air at a temperature of 1300 °C for 12 hours in an electric furnace in the case of the barium and strontium hexaferrites and for 4h at 1180 °C in the case of the calcium hexaferrites. The heating and cooling rates were maintained at 200 °C per hour. The samples were finally ground to remove any oxide layer formed during sintering. The complex permittivity of the pure hexaferrites series was carried out instead of on the composites. Such studies on composites are largely available in the literature [8-11]. Fewer studies have been done in this field on pure ferrites since these materials are hard and brittle and their machining is quite difficult and it is extremely difficult to prepare pure ferrite samples of very small dimensions to fit exactly in the waveguide or the cavity [12]. So the samples of pure hexaferrites were carefully ground by hand to fit exactly in the waveguide.

Variation of real and imaginary parts of the complex permittivity was measured at microwave frequencies with the help of the Von Hippel method [13]. The microwave power was obtained from a Hewlett Packard (83751A) synthesized sweep generator (2-20 GHz). The leveled output could be continuously varied up to 17 dBm. The frequency could also be continuously varied from (2-20 GHz). A known length of the ferrite sample terminated a short-circuited air filled waveguide transmission line. The terminating impedance was determined experimentally by measurements on the standing wave pattern on the input side of the sample. The following experimental parameters were measured during experiments and substituted in the respective formulae: the wave guide wavelength, λ_g , the length of the sample (which was typically 0.6 cm), the position of the first minima from the air-sample interface, the voltage standing wave ratio (V.S.W.R ≥ 1), the thickness of the sample (d) and the width of the wave guide (a). For measurement of the complex dielectric constant, the complex transcendental equation was used. The complex permittivity of all the samples has been measured in the X band of microwave frequency range and its variation with frequency as well as with composition has been measured for all the three series.

Results and Discussion

In Figs. 1 and 2, the variations of dielectric constants (ϵ') and loss factor (ϵ'') for different values of x in BaCoTi hexaferrites have been depicted. It has been observed from these figures that ϵ' , in general, shows a decreasing trend and ϵ'' shows an increasing trend with increase in frequency for all the compositions. The real part shows dispersion in the X-band. For the unsubstituted barium ferrite, ϵ' decreases continuously from 18 to about 10 as the frequency is increased from 8.5 GHz to 12.4 GHz. The imaginary part of the permittivity ϵ'' increases slowly and then decreases for higher frequencies. For the substituted hexaferrites, ϵ' at 8.5 GHz varies from 14 to 20 depending upon the degree of substitution of $\text{Co}^{2+}\text{Ti}^{4+}$ ions in place of Fe^{3+} ions. At 12 GHz, the value of ϵ' is between 8 to 10 with different amount of substitution. Figure 3 gives the variation of Real and Imaginary parts of the permittivity (Dielectric constant and loss factor) of Barium Cobalt Titanium Hexaferrite $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$ with respect to degree of substitution of Cobalt and Titanium in place of iron in the hexaferrite at three different frequ-

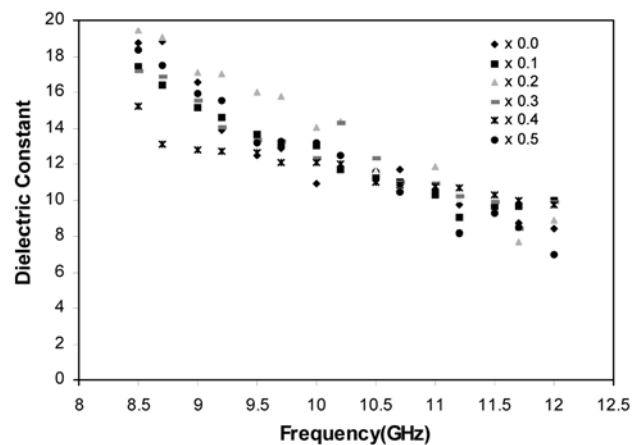


Fig. 1. Variation of loss factor (ϵ'') for different values of x in $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$)

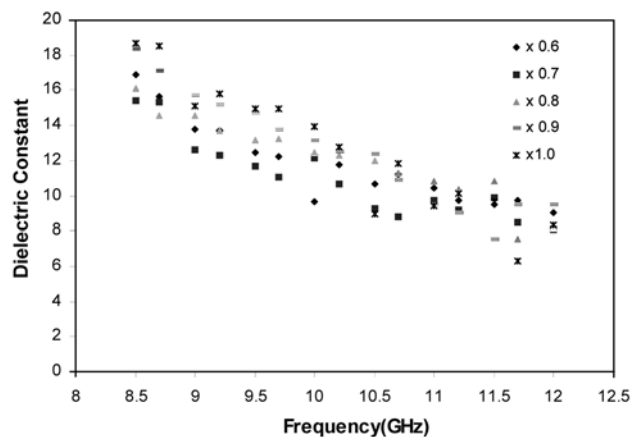


Fig. 2. Variation of loss factor (ϵ'') for different values of x in $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$ ($x = 0.6, 0.7, 0.8, 0.9, 1.0$)

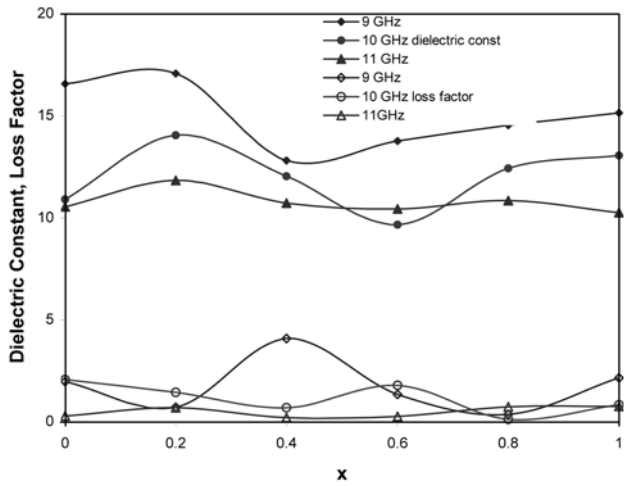


Fig. 3. Variation of Real and Imaginary part of Permittivity (Dielectric constant and loss factor) of Barium Cobalt Titanium Hexaferrite $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$ with respect to degree of substitution of Cobalt and Titanium in place of iron in the hexaferrite at three different frequencies in the X-band.

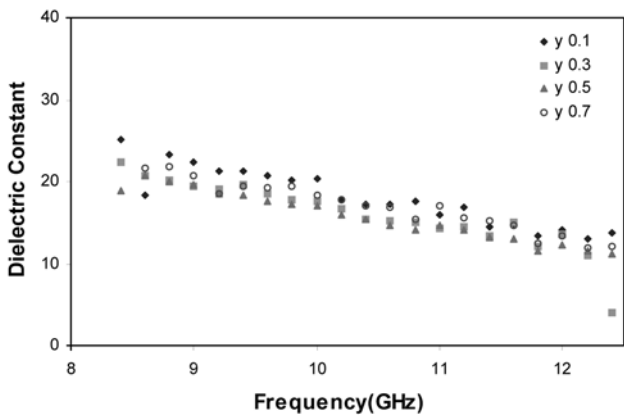


Fig. 4. Variation of dielectric constant (ϵ') for different values of y in $\text{Sr}(\text{CoTi})_y\text{Fe}_{(12-2y)}\text{O}_{19}$ ($y = 0.1, 0.3, 0.5, 0.7$)

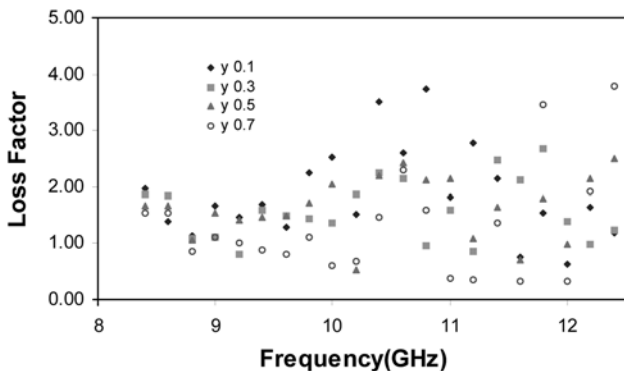


Fig. 5. Variation of loss factor (ϵ'') for different values of y in $\text{Sr}(\text{CoTi})_y\text{Fe}_{(12-2y)}\text{O}_{19}$ ($y = 0.1, 0.3, 0.5, 0.7$)

encies (9, 10 and 11 GHz) in the X-band.

The variation of the dielectric constant and loss factor for $\text{Sr}(\text{CoTi})_y\text{Fe}_{(12-2y)}\text{O}_{19}$ series with respect to frequency from 8.4 GHz to 12.4 GHz is reported in

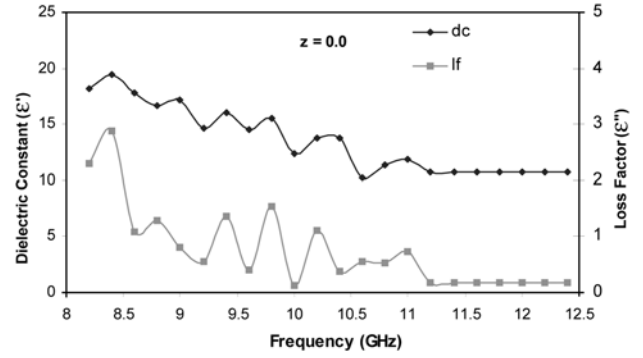


Fig. 6. (a) Frequency dependence of dielectric constant and loss factor of Calcium Cobalt Titanium Hexaferrite $[\text{Ca}(\text{CoTi})_z\text{Fe}_{(12-2z)}\text{O}_{19}]_{96.0}[\text{La}_2\text{O}_3]_{4.0}$ ($z = 0.0$)

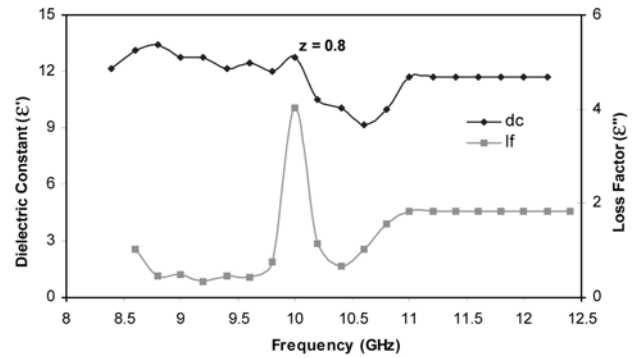


Fig. 6. (b) Frequency dependence of dielectric constant and loss factor of Calcium Cobalt Titanium Hexaferrite $[\text{Ca}(\text{CoTi})_z\text{Fe}_{(12-2z)}\text{O}_{19}]_{96.0}[\text{La}_2\text{O}_3]_{4.0}$ ($z = 0.8$)

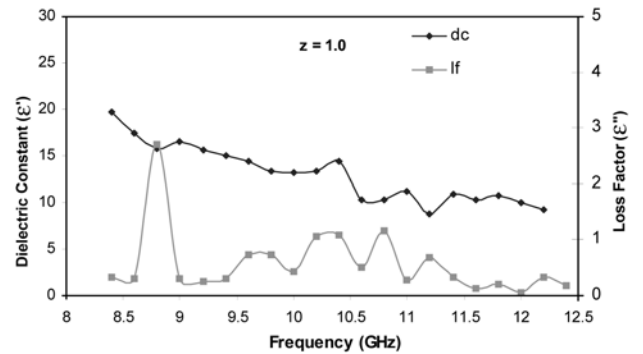


Fig. 6. (c) Frequency dependence of dielectric constant and loss factor of Calcium Cobalt Titanium Hexaferrite $[\text{Ca}(\text{CoTi})_z\text{Fe}_{(12-2z)}\text{O}_{19}]_{96.0}[\text{La}_2\text{O}_3]_{4.0}$ ($z = 1.0$)

Figs. 4 and 5. Here also, the dielectric constant decreases with frequency for all the compositions. The variation in the dielectric constant with composition of ions is also there. At 9 GHz, the dielectric constant varies between 18 and 22 for different compositions whereas at 12 GHz it is about 12 to 14 for different compositions. It is concluded that we can have a wide variation of the real part of the permittivity by varying the degree of substitution of cobalt titanium ions in this series as well. On the other hand, the imaginary part of the permittivity (loss factor) increases with an increase

in frequency. We can observe a variation in the loss factor of the strontium ferrites with $\text{Co}^{2+}\text{Ti}^{4+}$ content as well. Figure 6 shows the variation of dielectric constant and loss factor of one of the compositions of the calcium hexaferrite series. Here also a decreasing trend of the real part of the permittivity is observed with an increase in frequency

If we compare the three series, all of them depict similar types of variation in dielectric constant and loss factor with an increase in frequency and increase in cobalt titanium content. This type of similarity is expected as Ba, Ca and Sr belong to the same group of the periodic table and moreover the substitution done is the same. The dielectric properties of ferrites are mainly due to interfacial polarizations at interfaces of grains and grain boundaries caused by a non-uniform distribution of oxygen ions during sintering [14, 15]. An oxygen ion possesses two extra loosely bound electrons. Therefore, polarization can be produced even by a small applied electric field and hence the observed high values of dielectric constant can be explained due to this reason.

To explain the dispersion in dielectric constant in ferrites, Koops [16] has proposed a general model for heterogeneous dielectrics consisting of well-conducting grains separated by poorly conducting grain boundaries as found in polycrystalline ferrites. Based on this model, certain relations have been derived by Koops which depict that an increase in frequency causes a decrease in dielectric constant as is observed in the present system of synthesized hexaferrites. A physical interpretation of dispersion can be done on the basis of hopping of electrons between Fe^{2+} and Fe^{3+} ions and between Co^{2+} and Co^{3+} ions. The electrons are displaced slightly by the applied electric field and polarization is produced. But the electrons can respond to the changes in applied electric field as long as the time required for hopping is less than half the period of the alternating field. This is the reason for the dispersion in the dielectric constant observed in the present systems of ferrites. A similar type of variation in the dielectric properties of strontium ferrites has been observed at still higher frequencies [17].

Conclusions

Complex ferrite series of the composition $\text{Ba}(\text{CoTi})_x\text{Fe}_{(12-2x)}\text{O}_{19}$, $\text{Sr}(\text{CoTi})_y\text{Fe}_{(12-2y)}\text{O}_{19}$ and $[\text{Ca}(\text{CoTi})_z\text{Fe}_{(12-2z)}\text{O}_{19}]_{96.0}[\text{La}_2\text{O}_3]_{4.0}$ where x, y and z vary from 0.0 to 1.0 in steps of 0.1 for the three series which have been synthesized. All of them depict similar types of variation in dielectric constant and loss factor with an increase in frequency and increase in cobalt titanium content. The microwave dielectric constant of these hexaferrites has been measured in the X band of microwave frequency range after successively increasing the amount of substituted ions in the ferrites. The variation of the complex permittivity of these hexaferrites with a change in composition as well as a change in frequency has been measured in this frequency range.

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