Preparation and characterization of $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ filled PP composites

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Abstract. Phase pure U type hexaferrites having molecular formula $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ is synthesized through solid state route as filler for the fabrication of magneto-dielectric (MD) composite. Being a MD material the U type hexaferrite has a promising future in information and communication sector as a base substrate for electronic circuits. Since they exhibit both electric and magnetic properties, they can contribute effectively to circuit miniaturization and bandwidth enhancement compared to an antenna printed on a dielectric substrate. The filler material is then blended with PP (Poly Propylene) matrix and Magneto dielectric substrates are produced via hot pressing technique. Filler concentration has been varied from 70 to 90 wt. % in PP matrix and ascertained amount of optimum filler fraction for dimensionally stable substrate having acceptable properties. Dielectric and magnetic characterizations have been done using Impedance analyzer. It is found that the density of the composite and the dielectric constant is increasing with the increase in filler loading up to an optimum level and further filler loading reduces the density as well as the dielectric constant due to increased porosity. For optimum filler loading a maximum density of 2.96 g/cm$^3$ is achieved. Relative permeability values are found increasing with filler loading even beyond the optimum filler loading. The optimum loaded poly Propylene/ $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ composite has an effective dielectric constant of 9.21, loss tangent of 0.083, relative permeability of 3.6 and a magnetic loss of 0.060 at 1MHz. Coefficient of thermal expansion (CTE) of the composite has been investigated using thermo mechanical analyzer. Moisture absorption rate of the optimum filler loaded composite is studied and found to be less than 0.1%. Relatively good dielectric constant, low loss tangent together with better relative permeability make the $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ filled PP composites an excellent choice as Microwave substrate.

1. Introduction

A wide range of uses and applications in various technological and commercial grounds along with promising results in microwave region [1-3] has made hexaferrites an interesting material in microwave research. Hexaferrites are magneto dielectric materials which possess both magnetic and dielectric properties. Being a magneto dielectric substance hexaferrites can contribute to miniaturization of circuits. Miniaturization factor is proportional to square root of product of permeability and permittivity. High values of magnetic and dielectric properties exhibited by MD
substances help them to achieve better miniaturization [4-5]. Hexaferrites are classified into M, W, X, Y, Z and U type phases. Among hexaferrites U type hexaferrites with composition $\text{Ba}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$ where Me is divalent metal ion like Co, Zn etc. Possess a very complex structure, Uniaxial Magnetic Crystallography [1-2], Unique electromagnetic properties and very high magnetic crystalline anisotropy [3]. These Properties make UHF a suitable material in microwave applications [6-10]. U type hexaferrites have a stacking sequence of RSR*S*TS* [11] is combination of M & Y hexaferrites and are less studied [7-8] compared with other hexaferrites. Present Work focuses on preparation of $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ (Co2U) filled Polypropylene (PP) composites. Even though different polymer matrices like Polytetrafluoroethylene (PTFE), Polyetheretherketone (PEEK), Polypropylene (PP) etc., are available, PP is chosen as the polymer matrix because of its ease of processing, good electrical properties and low cost [12]. Preparation of $\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$ filled PP composite is carried out by fine mixing followed by compression moulding technique. The proposed study consists of crystallography of the filler, Magnetic and dielectric properties, microstructure analysis, thermo mechanical analysis and moisture absorption analysis of the composites.

2. Experimental Analysis

2.1 Materials Used

$\text{BaCO}_3 \geq 98\%$, M/s Sigma Aldrich: $\text{Fe}_2\text{O}_3 \geq 99\%$, M/s Golcha Pigments: $\text{Co}_3\text{O}_4 \geq 99\%$, M/s Sigma Aldrich: PP granules M/s Reliance.

2.2 Solid state Synthesis of Phase pure U-Type hexaferrite ($\text{UHF-Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$) filler

The filler materials are prepared via conventional solid state route. Stoichiometric amount of precursor materials comprises of $\text{BaCO}_3$, $\text{Fe}_2\text{O}_3$, $\text{Co}_3\text{O}_4$ are weighed out to an agate mortar and uniformly mixed to the form of paste with DI water as the media. It is then dried in an oven and grinded to a fine powder. This ensures the uniformity of the mixture. The powder is calcined at a temperature of 1100°C for 5 h initially. The calcined powder is grinded again and further calcined at a temperature of 1250°C for 10 hours. This is done to obtain the phase pure UHF filler.

2.3 Preparation of U-Type hexaferrite ($\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$) filled PP composites

PP based composites are prepared by compression moulding technique. The phase pure ceramic filler and polymer matrix are weighed for preparing composites of different filler weight percentage from 70-90 (volume % 27.8 to 59.8). This range of filler loading is chosen because the under filled composites have little influence over the electrical and magnetic properties and overfilled composites have inferior mechanical property and are difficult to handle. The weighed constituents of the composite are transferred into a high speed mixer for mixing thoroughly. Two different sets of dies have been used for making disc shaped samples having a diameter of 8mm and the other one for toroid samples of OD 19.8 mm and ID 5.01mm. These are loaded with the composite material and hot pressed under 160°C and a pressure of 10 kg/cm$^2$ for obtaining the required MD composite samples. Density of the composites are measured and tested for electrical and magnetic properties.

2.4 Characterization Techniques

Phase purity and crystal structure of the Co2U filler is verified by powder XRD technique. Density of Composite samples are determined by measuring their mass and volume. Topography, Surface morphology, microstructure and distribution of filler in the composite samples are studied using a Scanning Electron Microscope (Carl Zeiss, EVO 18 Research, UK). An Agilent make, model: E4293A Impedance Analyzer, is used to measure Relative permeability, Dielectric constant and loss tangent of the MD composites. Dielectric constant and loss tangent of the samples are determined by employing parallel plate capacitance method and relative permeability of the samples are obtained by measuring inductance of the samples. EXSTAR 6000 model thermo mechanical analyzer (SII Nano technology
INC, (Japan) is employed to measure the coefficient of thermal expansion of the composite samples. IPC–TM-650 2.6.2 is carried out to conduct moisture absorption studies of the optimum filler loaded composite. The samples are initially kept at a temperature of 105°C for 1 h in oven. Weight of the Samples are taken and immersed in de-ionized water at 23°C for 24 hours. After 24 hours substrate specimen is taken from water and surface water is removed using a dry cloth and immediate weighing is incorporated. By determining the weight gained by the specimen, moisture absorption is obtained.

3. Results and Discussion

3.1 Powder X Ray diffraction Analysis

Figure 1 shows the X-ray diffraction pattern of the MD filler Ba$_4$Co$_2$Fe$_{36}$O$_{60}$ prepared by conventional solid state route by calcination under 1100°C for 3 h which is then followed by another round of calcination under 1250°C for 10 h. Since there is no ICDD data available, previously reported X-ray diffraction patterns [1,2,6-10] are collected and the peaks are matched with those of reported ones, the peaks in the X-ray diffraction pattern is also indexed with help of these reports [1-2]. No extra peaks are detected which confirms the phase purity of the filler.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + hl}{a^2} \right) + \frac{l^2}{c^2}
\]  

Value of interplanar distance d can be obtained from the X-ray diffraction pattern. CO$_2$U is rhombohedral with R3m space group [6-8] with hexagonal unit cell. By choosing appropriate h, k, l values the lattice parameters a and c are calculated, using the equation 3.1. Value of lattice parameter a is obtained as 5.94 Å and value of c as 112.2 Å which matches with the early reports of a = 5.88 Å and c = 113 Å [3, 6].

![Figure 1. XRD pattern of Ba$_4$Co$_2$Fe$_{36}$O$_{60}$](image)

Knowing a and c theoretical density of the filler is calculated using the known formula [1, 2].

\[
D = \frac{2nm}{(\sqrt{3}Na a^2 c)}
\]  

(2)
Where,  
\( n \) is the number of molecules per unit 
\( M \) is the molecular weight of the sample 
\( N_A \) is Avogadro’s number per gram mole.

‘a’ and ‘c’ are the lattice constants obtained from X-ray diffraction analysis.

U-type phase has \( n \) value of 3 [2, 7]. The molecular weight \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) is 3622 g. Hence the obtained density is 5.26 g/cc which is nearly equal to the density 5.44 g/cc [13] indicated for phase pure filler.

3.2 Density measurement of composite.

Theoretical density of the composite with varying filler fractions from 70-90 wt % are calculated using the principles of rule of mixtures [14]. During calculations density of \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) is taken as 5.44 g/cc and that of poly propylene as 0.90 g/cm\(^3\). The theoretical density values are compared with the experimentally obtained values. Variation of both theoretical and experimental densities alone with wt. percentage of filler is shown in figure 2.

![Figure 2](image.png)

**Figure 2.** Variation of density with filler loading.

The figure 2 shows that experimental density increases with filler loading up to 85 wt % and a clear fall of density is observed on further filler loading. This is the point of optimum filler loading, a maximum density of 2.95 g/cm\(^3\) is obtained at this point. When filler loading exceeds the optimum value, density of the composite shows a decreasing trend. The decrease in density after 85 wt % is due to the increase in porosity in the composite. A porosity of 4.5 % is obtained at 85 wt % which increases up to 20% with subsequent filler loading. Porosity arises because of the lack of polymer material to encapsulate the filler particles. So with increase in filler loading availability of polymer to encapsulate the filler material decreases and this results in increase in porosity. Porosity has an adverse effect over the mechanical, electrical and magnetic properties of the composite, hence the optimum filler loading point is chosen such that the porosity is minimum and the density is maximum for
obtaining a dimensional stable substrate. Those compositions exceeding optimum filler loading can’t be considered for substrate applications [15].

3.3 Morphological study of the composite
Scanning Electron Micrograph is used to study the surface morphology, microstructure and the distribution of filler in the PP matrix. Results are shown in figure 3.

![Figure 3. Scanning Electron Micrograph (SEM) image of the 85 wt % Co2U filled PP composite.](image)

From the figure 3 it is seen that the filler is uniformly distributed in the polymer matrix and the particle size has wide range from 4-20 µm. Since it is the optimum filler loading it can be seen that the distribution of the filler is uniform throughout the matrix with good density as seen in the figure 2 with acceptable porosity.

3.4 Dielectric Properties of the composite
The dielectric properties of Polypropylene/ Ba₄Co₂Fe₃₆O₆₀ composites are studied in the microwave frequency region using Agilent E4294A Impedance analyser. The variation of dielectric constant and loss tangent with respect to filler loading at 1 MHz is shown in figure 4.

![Figure 4. Variation of dielectric constant and loss tangent with UHF filler loading in PP matrix.](image)
A dielectric constant of 21 is shown by \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) at 8 GHz [1] and dielectric constant of PP is 2.2 [16]. From the graph it is clear that dielectric constant of the composite keeps on increasing till the optimum filler loading (till 85 wt. %) and above which a fall in dielectric constant is observed. The increase in filler loading enhances the ceramic to ceramic connectivity resulting in increased dipole-dipole interaction leading to increased dielectric constant. The decrease in dielectric constant after optimum filler loading is due to formation of the micro voids in the composite. Loss tangent shows an increasing behaviour with filler loading. Compared to matrix, the filler has high loss tangent and that corresponds to the increase in dielectric loss. When an electromagnetic signal passes through the composite it passes through matrix, filler and the matrix-filler interface. Interface volume increases with the increase in filler loading thus, the signal passing through the composite has to face more heterogeneous phases which results in more loss due to anharmonicity [17].

### 3.5 Magnetic Properties

The magnetic properties of \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) filled Polypropylene composites are studied in the low frequency region using an Agilent E4294A Impedance analyzer. The variation of relative permeability with filler loading at 1 MHz is given in figure 5.

![Figure 5. Variation of relative permeability with filler loading at 1 MHz](image)

Increase in filler content have significant effect over the magnetic properties of composite samples. As expected the value of effective permeability increases with filler loading. Since the polymer matrix PP is nonmagnetic (\( \mu = 1 \)), the magnetic properties of the composites is from the contribution of filler \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) only. At low concentrations, the magnetic interaction between ferrite particles is weekend and hence the value of permeability is low. At higher loading percentages, the filler concentration increases giving rise to an enhanced magnetic permeability. This enhancement in permeability can be attributed to different factors such as improved magnetic interaction between ferrite particles, decrease in volume fraction of the polymer which is non-magnetic etc.
3.6 Thermo mechanical analysis of composites
Linear thermal expansion of composite is determined both by the filler and the matrix. In mechanical designing of substrate, coefficient of thermal expansion of the dielectric coating is a crucial element. For fabricating microcircuits, a metal conductor layer has to be constructed over the top and bottom surfaces of MD composites. CTE of the filled substrate should matches with that of metal conductor layer for efficient circuit fabrication as slight mismatching between CTE values will result in delamination of layer [17]. Since polymers have high CTE values and inorganic filler have low CTE value, overall thermal expansion of the composite is controlled by filler loading.

![Figure 6. Variation of CTE with filler loading in PP Matrix](image)

CTE values are recorded for the composites having various filler fraction ranging from 80% to 90% using TMA. Overall CTE of the composite is found decreasing with the increase in filler loading [15]. Optimum loaded sample with 85 wt % filler showed a CTE of 99.03 ppm/°C. This decrease in CTE value with increase in filler loading is a result of increased interaction between the filler and the polymer matrix.

3.7 Moisture absorption Studies
Moisture absorption is an important parameter in determining the mechanical and electrical properties of a composite [17]. Dielectric properties of the composite are very much depended on the amount of moisture that contained in the composite. Mechanical strength of composite reduces with increase moisture absorption. Water has high dielectric constant and loss tangent, so with increase in moisture absorption dielectric loss of the composite increases [18]. The percentage of moisture absorption of the optimum filler loaded composite is calculated as 0.06%, which is well within the limit (< 0.1%) for substrate applications.
4. Conclusion
The present work discussed the preparation and characterization of \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) filled PP composite for microwave substrate applications. The dielectric constant, relative permeability, dielectric loss of the composite has been studied using Agilent E4294A Impedance analyzer. Coefficient of thermal expansion of optimum filler loaded composite is determined using Thermo mechanical analyzer and moisture absorption rate of the composite are measured. Density and dielectric constant of the Polypropylene/ \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) composite increased linearly with respect to filler loading up to 85 wt.

% and then showed a decreasing trend due to porosity. But the magnetic permeability showed an increasing trend with filler loading. The prepared \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) filled PP composite have an effective dielectric constant of 9.21, loss tangent of 0.083, relative permeability of 3.65 and a magnetic loss of 0.060 at 1MHz. Present study shows that the \( \text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60} \) filled PP composite exhibits relatively good dielectric constant, better relative permeability acceptable low loss tangent, and good permeability and hence can be used as substrate material for microwave applications.

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