Synthesis and Characterization of B_2O_3 Additive on Ni-Cu-Zn ferrites by Solid State Reaction Method

Abdul Gofur, Alamgir. Hossain, Shibendra S. Sikder, and Dilip K. Saha

Abstract—Ni-Cu-Zn ferrites are well-known technological magnetic materials used for manufacturing of multilayer chip inductor and applications in various electrical devices. The work is focused on the persuade of substitutions and sintering additive B2O3 on structural, transport and electromagnetic properties of Ni-Cu-Zn ferrites. The composition Ni0.28Cu0.10Zn0.62Fe2O4 + x wt. % where x = 0.2 to 0.8 for V2O5 was prepared by using the solid state reaction technique sintered at 1200oC with 6 hours holding time. Lattice parameters of Ni0.28Cu0.10Zn0.62Fe2O4 + x wt. % B2O3 are slightly decrease with increase x content. The grain growth by increasing the additives B2O3 content inter diffusion as results after > 0.4wt. % B2O3 content abnormal grain growth. Curie temperature (Tc) decreases continuously with increase of doped B2O3 additives in ferrite samples. The magnetization process all the samples are soft magnetic behavior of magnetic materials. Initial permeability (µi) decreases with increasing doped B2O3 content in ferrite samples and hence the highest value of quality factor is found for x = 0.4 within the range 20 kHz to 2MHz. The µi shows the flat profile from 1 kHz to 4MHz indicating frequency stability for all the ferrite samples. The visible grain growth indicates the improved electromagnetic properties. DC resistivity decreases with increasing temperature shows the semiconducting nature of the sample. With increasing the frequency, the dielectric constant is found to decrease continuously and remain almost frequency independent at higher frequency range.

Index Terms—Solid State Reaction Method, Grain Size, Saturation Magnetization, Curie temperature, Dielectric Constant.

I. INTRODUCTION

Ni-Cu-Zn ferrite materials with V2O5 and Bi2O3 additives are prepared by the conventional ceramic technique. The use of sintering additives was found to be an effective method in practical manufacturing to lower the sintering temperature with degrading the electromagnetic properties [11]. To obtain materials with high permeability as well as high quality factor, a key step is to tailor the additives composition to produce densification with limited grain growth. During the grain growth, the dislocation of the additives into the ceramic is assisted by solution re-precipitation process, which reduces the volume fraction of intergranular phases. The compositions of additives, melting temperature, reactions between the additives and ferrites, and microstructural evolution during the liquid-phase sintering are all very important parameters to characterize and understand any attempt to precisely control the magnetic properties [2]-[3]. Many researchers used Bi2O3 [4]-[5], V2O5 [6]-[7], MoO3 [8]-[9], Glass [10], PbO [11] and WO3 [12] as sintering aids in Ni-Cu-Zn ferrite.

These additive liquid phase are which either due to the melting of additives or eutectic liquid phase formation between the additives and ferrites. Amount of liquid phase increases with increasing amount of sintering aids which results in increased densification. However, excessive amount of sintering additives will deteriorate electromagnetic properties of ferrites. In addition, deriving as a liquid phase to promote the densification, it is important to recognize that the additives components may also play an important role in the contribution to the magnetic properties of the sintered ferrites. Hsu et. al. [13] stated that 0.5mol.% (~0.20wt.%) V2O5 addition had better densification in Ni-Cu-Zn ferrites.

In these study of the present work are to synthesize Ni-Cu-Zn ferrites of composition Ni0.28Cu0.10Zn0.62Fe2O4 + x wt.% the concentration sintering additives were varied 0.2wt.% to 0.8wt.% for Bi2O3. The green samples containing different additives were sintered at temperatures 1150oC with 6 hours holding time. Effects of those sintering additives on the densification behavior were investigated. The X-ray diffraction analysis proves that the additives do not affect the final crystal phase of the Ni-Cu-Zn ferrite in our testing range. These characteristics evidently affect the electrical and magnetic properties such as Scanning Electron Microscope (SEM), magnetic phase transition were determined by permeability versus temperature, structural, transport and magnetic properties of sintered specimens were also measured.

II. MATERIALS AND METHODS

Solid State Reaction Technique devised for a series composition of Ni-Cu-Zn ferrites are synthesized, characterized and investigated. The powder preparation process and sintering facility available at the Material Science Division, Atomic Energy Centre, Dhaka has been utilized for the preparation of samples. General formula for sample is objectives of the present research work are to synthesize Ni-Cu-Zn ferrites of composition Ni0.28Cu0.10Zn0.62Fe2O4+ x wt.% B2O3[x = 0.2, 0.4, 0.6 and 0.8] additives. The properties of Ni-Cu-Zn with addition of additives like B2O3 sample is influenced considerably by sintering temperature and compositions. The ease preparation technique of ferrites comprises of the following operation as shown in block diagram:
III. RESULTS AND DISCUSSION

The phase formation behavior of Ni0.28Cu0.10Zn0.62Fe2O4+ x wt% Bi2O3 (x = 0.2, 0.4, 0.6 and 0.8) sintered at 1150°C for 6 hours were studied by XRD. All the samples show crystallization with well defined diffraction lines. The powder XRD patterns exhibited that all the samples were identified as a single phase of spinel structure. The XRD patterns for all the samples were indexed for fcc spinel structure and the Bragg planes are shown in the patterns. The XRD patterns are shown in Fig. 2. The peaks (111), (220), (311), (222), (400), (422), (511) and (440) corresponds to phase which are characteristics of spinel structures with a single phase. The lattice parameter ‘a’ corresponding to each plane was calculated by using the X-ray data.

Table I shows the results of lattice parameter, theoretical density, bulk density calculated porosity. The porosity which is intrinsic for any oxide materials plays an important role in deciding the magnetic and electrical properties.

<table>
<thead>
<tr>
<th>Bi2O3 content (x%)</th>
<th>a (Å)</th>
<th>(ρx) (g/cm³)</th>
<th>(ρB) (g/cm³)</th>
<th>P%</th>
<th>M (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>8.4120</td>
<td>5.337</td>
<td>4.07</td>
<td>23.63</td>
<td>239.019</td>
</tr>
<tr>
<td>0.04</td>
<td>8.4085</td>
<td>5.345</td>
<td>4.03</td>
<td>24.53</td>
<td>239.021</td>
</tr>
<tr>
<td>0.06</td>
<td>8.4050</td>
<td>5.344</td>
<td>4.02</td>
<td>24.32</td>
<td>239.023</td>
</tr>
<tr>
<td>0.08</td>
<td>8.4035</td>
<td>5.350</td>
<td>4.01</td>
<td>25.04</td>
<td>239.025</td>
</tr>
</tbody>
</table>

The bulk density (ρB) is lower than the X-ray density (ρx). This may be due to the existence of pore, which are inevitable during ceramic processing and formed and developed during the sample preparation or the sintering process.

This enhancement of bulk density is due to activated diffusion process triggered by the excess vacancies created by Bi2O3 additives.
migrating and larger crystal grains swallowing the small ones. During the growth the more different in size of the crystal grains, the more beneficial for longer crystal grains to swallow smaller up to 0.4 wt.% doped Bi2O3. After > 0.4 wt.% Bi2O3 additive contents abnormal grain growth occurs if this driving force is inhomogeneous. Moreover, the strength of the driving force depends upon the diffusivity of individual grains, sintering temperature and porosity.

Fig. 3(a - d) shows the SEM microstructure of Ni0.28Cu0.10Zn0.62Fe2O4 + x wt% Bi2O3 (x = 0.2, 0.4, 0.6 and 0.8) sintered at 1150°C for 6 hr.

During the liquid phase sintering grain growth occurs via a dissolving/solution-precipitation process. Energetically, small grains are less stable than large grains due to their higher specific surface areas. As consequences small grains would be dissolved in the liquid-phase layers. Once the concentration of the dissolved phase reached a critical level, precipitation would take place. It seems that small grains have to “Swim” through a barrier (liquid phase layer) to combine with large grain. A gradual increase in grain size distribution is observed with increased doped Bi2O3 additive contents.

The crystal grain growth depends on grain boundaries
Figure 4(a - d) shows the temperature dependence of initial permeability for Ni0.28Cu0.10Zn0.62Fe2O4 + x wt.% Bi2O3 (x = 0.2, 0.4, 0.6 and 0.8%) sintered at 1150°C for 6 hrs.

Figure 4(a - d) shows the temperature dependence of initial permeability for toroid shaped samples of Ni0.28Cu0.10Zn0.62Fe2O4+ x wt.% Bi2O3 (x = 0.2, 0.4, 0.6 and 0.8) ferrites sintered temperature at 1150°C at 6 hours, which is measured at constant frequency 100kHz of an ac signal by using Impedance Analyzer. It is observed that the initial permeability decreases with increases in doped Bi2O3 additives, while it falls abruptly close to the Curie point. From these are figure shows that permeability falls sharply when the magnetic state of the ferrite samples changes from ferromagnetic to paramagnetic. When the anisotropy constant reaches to zero just below the Curie temperature (Tc), µi its maximum value and drops off sharply to minimum value at Curie point.

The Tc mainly depends upon the strength of A-B exchange interaction. As the A-B exchange interactions increases with the density and the magnetic moment of the magnetic ions. On other hand, greater amount of thermal energy is required to offset the effects of exchange interaction. It is observed in Table II that Tc decrease continuously with increase of doped Bi2O3 additives in Ni-Cu-Zn ferrites. This decreases the number of bonds or linkages between the magnetic ions that determine the magnitude of the Tc.

<table>
<thead>
<tr>
<th>Bi2O3</th>
<th>Tc=1150°C</th>
<th>µi at constant 100 (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>113</td>
<td>280</td>
</tr>
<tr>
<td>0.4</td>
<td>110</td>
<td>238</td>
</tr>
<tr>
<td>0.6</td>
<td>107</td>
<td>236</td>
</tr>
<tr>
<td>0.8</td>
<td>102</td>
<td>222</td>
</tr>
</tbody>
</table>

Fig. 5 shows the variation real part of complex permeability (µ/) spectra in Ni0.28Cu0.10Zn0.62Fe2O4+ x wt.% Bi2O3 (x = 0.2, 0.4, 0.6 and 0.8) sintered at 1150°C for 6 hours. The permeability of all composition was stable up to 1MHz and the cut off frequencies of samples were above 120MHz, the maximum frequency limit of the instrument. The dispersion was to the much higher permeability of composition 0.2wt.% Bi2O3 compared to other. However, the permeability decreased with higher Bi2O3 (> x = 0.2) substitution. This might be due to the presence of higher amount BiFeO3 phase. From the Fig. 5, the range of operating frequency in the x = 0.2 sintered at 1150°C/6h simply wider which shows the compositional stability and quality of the ferrite samples.

Moreover as the sintering temperature increases dispersion of µ// - f spectra also shifts to the lower frequency range as result of increasing density and grain size, as prepared by Nakamura [14]. Generally application range of frequency is best suited below the frequency from where the µ// starts rising sharply.

For a device application, the frequency ranges up to which the material can be used an inductor is always much less than the frequency at which µ// attains its maximum value. This means that high frequency and high permeability cannot go together or in other words if we want to use the ferrite inductor for high frequency application, then the permeability of the device materials must be sacrificed. Again if a device needs very high µ// then it must be used ferrite materials having lower resonance frequency i.e. the device is suitable for lower frequency range application. It is observed Table II, the initial permeability (µi) and Tc decreases with increases of doped Bi2O3 and magnetic loss tangent (tanδ) which could be explained by a combination of low density small grain size and more lattice defects.
Fig. 6. Frequency dependence complex permeability, $\mu''$ of Ni$_{0.28}$Cu$_{0.10}$Zn$_{0.62}$Fe$_2$O$_4 + x$ wt% Bi$_2$O$_3$ ($x = 0.2, 0.4, 0.6$ and $0.8$) sintered at 1150°C for 6 hrs.

Fig. 7. Frequency quality factor of Ni$_{0.28}$Cu$_{0.10}$Zn$_{0.62}$Fe$_2$O$_4 + x$ wt% Bi$_2$O$_3$ ($x = 0.2, 0.4, 0.6$ and $0.8$) sintered at 1150°C for 6 hrs.

frequency dependence of quality factor of the samples with doped Bi$_2$O$_3$ at sintered 1150°C for 6 hours were measured and Figure shows that the results. Factor signifies the merit of the material from the application point of view. The variation of the quality factor with frequency showed a similar trend all the samples. Quality factor increases with increases of frequency showing peak and then decreases with further increase of frequency. It is seen that quality factor deteriorates beyond $8 - 120$MHz. A very high value of relative quality factor or extra ordering low value of loss tangent is found. The resonance frequency peaks are the results of the absorption of energy due to matching of the oscillation frequency of the magnetic dipoles and the applied frequency.

The observed variation in Ms can be explained on the basis of cation distribution and the exchange interactions between A and B-sites respectively. At sintered temperature 1150°C, the initial decrease in Ms with increased additive Bi$_2$O$_3$ is due to the increase of resultant sublattice magnetic moment which can be explained on the basis of Neel’s two sub lattice model. The magnetization of each composition depends on the distribution of Fe$^{3+}$ ions between the two sub lattices A and B, where Zn$^{2+}$, Cu$^{2+}$ and Bi$^{2+}$ ions are nonmagnetic. In perfect ferrites, the A-A, B-B and A-B nearest neighbor exchange coupling are normally antiferromagnetic and the A-B exchange coupling is usually heavily predominant. The slow decrease of Ms from the two sub lattice magnetization unlike ferromagnetic.

**TABLE III: SATURATION MAGNETIZATION OF Ni$_{0.28}$Cu$_{0.10}$Zn$_{0.62}$Fe$_2$O$_4 + x$ wt% Bi$_2$O$_3$ SINTERED AT 1150°C & 1200°C FOR 6 HRS.**

<table>
<thead>
<tr>
<th>X Content Bi$_2$O$_3$</th>
<th>T$_s$=1150°C M(emu/g)</th>
<th>T$_s$=1200°C M(emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>44.86</td>
<td>39.86</td>
</tr>
<tr>
<td>0.4</td>
<td>43.77</td>
<td>38.77</td>
</tr>
<tr>
<td>0.6</td>
<td>43.13</td>
<td>37.13</td>
</tr>
<tr>
<td>0.8</td>
<td>46.28</td>
<td>41.28</td>
</tr>
</tbody>
</table>

Fig. 8 shows the variation of Ms of the Ni$_{0.28}$Cu$_{0.10}$Zn$_{0.62}$Fe$_2$O$_4 + x$ wt% Bi$_2$O$_3$ ($x = 0.2, 0.4, 0.6$ and $0.8$) ferrites as a function of applied magnetic field up to 10kOe.
Dielectric behavior of ferrites may be explained on the basis of the mechanism of the dielectric polarization process and is similar to that of the conduction process. The electronic exchange Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ gives the local displacement of the electrons in the direction of applied electronic field, which induces the polarization in ferrites [15]. All the samples have high value of $\varepsilon'$ in the order of $2 \times 10^5$ at V205 and $4 \times 10^5$ at Bi2O3 as well as same $x = 0.4$wt. % content at low frequencies after all samples is decreased.

All the figures shows the samples $x = 0.4$ and 0.6 showed the maximum dispersion while that the other samples are shown in dopes in Bi2O3. The presence of Fe$^{2+}$ ions in excess amount favors the polarization effects. Thus, the more dispersion observed in the samples are with $x = 0.4$ and $x = 0.6$ can be attributed to the presence of Fe$^{2+}$ ions in excess amount which could be formed at elevated sintering temperature. Similarly the weak dependence of dielectric constant on frequency can be due to the lack of Fe$^{2+}$/Fe$^{3+}$ ions concentration. All the samples have high values of $10^5$ – 10$^6$ at low frequencies.

IV CONCLUSION

The present work has been focused on the synthesis study of structural electrical transport and electromagnetic properties of Ni0.28Cu0.10Zn0.62Fe2O4 + x wt.% Bi2O3 ($x = 0$, $0.2$, 0.4, 0.6 and 0.8) sintered at 1150°C for 6 hrs. All the figures show the samples $x = 0.4$ and 0.6 showed the maximum dispersion while that the other samples are shown in dopes in Bi2O3. The presence of Fe$^{2+}$ ions in excess amount favors the polarization effects. Thus, the more dispersion observed in the samples are with $x = 0.4$ and $x = 0.6$ can be attributed to the presence of Fe$^{2+}$ ions in excess amount which could be formed at elevated sintering temperature. Similarly the weak dependence of dielectric constant on frequency can be due to the lack of Fe$^{2+}$/Fe$^{3+}$ ions concentration. All the samples have high values of $10^5$ – 10$^6$ at low frequencies.

The linear decrease of lattice constant with additives Bi2O3 doped with Ni-Cu-Zn ferrite indicate that the present systems obeys Vegard’s law. The bulk density is lower than the X-ray density, which is inevitable during ceramic processing and formed developing during the both samples are preparation or the sintering process. Grain growths by increasing the additives Bi2O3 content inter diffusion as results of its segregation to the grain boundaries. During the growth the more different in size of the crystal grains, the more beneficial for longer crystal grains to swallow smaller up to 0.4wt.% Bi2O3. After $x > 0.4$wt.% Bi2O3 additives contents abnormal grain growth occurs, if driving force is inhomogeneous. Tc decreases continuously with the increase of Bi2O3 additives in Ni-Cu-Zn ferrites. This happened due to decreasing linkages between the magnetic ions and exchange coupling that determines the magnitude of the Tc and similar nature both sintering temperature as well as reduce value to effect are greater amount of thermal energy is required to offset of exchange interaction.

The $\mu$ decreases with higher content doped Bi2O3 in Ni-Cu-Zn ferrites but the highest value of quality factor is found for the samples doped 0.4wt.% Bi2O3, which quality factor within the range 20 kHz to 2 MHz frequencies. Thus the frequency range for application area is chosen.

Magnetization increases sharply at very low field (H < 1 kOe) which corresponds to magnetic domain reorientation due to domain wall displacement and there after increase.

It can be seen from all the figures that the dielectric constant is found to decrease continuously with increasing frequency for all the specimens exhibiting a normal dielectric behavior of ferrites. The dielectric dispersion is rapid at lower frequency region and it remains almost independent at high frequency region. The incorporation of Bi2O3 into Ni-Cu-Zn ferrites has no pronounced effect on the dielectric constant in high frequency, but significantly decreases the dielectric constant in the low frequency range.

Fig. 9 shows the temperature dependence of DC resistivity for different composition. DC resistivity is an important parameter and depends upon several factors such as sintering temperatures, time and atmosphere including the grain structure. It is well known that resistivity of ferrites depend on their chemical composition [15] and heat treatment. Ferrite is a semiconductor, which means that its electrical resistivity decreases with temperature.

Its electrical resistivity is at least a million times that of a metal. These are very large resistivity means in turn that an applied alternating magnetic field will not induce eddy currents in a ferrite. This property makes ferrite the best magnetic materials for high frequency application where power losses from eddy currents must be minimized.

Fig. 10 is the variation of dielectric constant, $\varepsilon'$ with frequency for different composition of Ni0.28Cu0.10Zn0.62Fe2O4 + x wt.% Bi2O3 ferrites sintered at 1150°C/6hrs from 100Hz to 120MHz at room temperature respectively.

It can be seen from all the figures that the dielectric constant is found to decrease continuously with increasing frequency for all the specimens exhibiting a normal dielectric behavior of ferrites. The dielectric dispersion is
slowly up to saturation due to spin rotation for both additive Bi2O3 doped in Ni-Cu-Zn ferrites. The magnetization process is connected with soft magnetic behavior of magnetic material. Saturation magnetization (Ms) increases up to x = 0.6 than it increases for Bi2O3 doped at sintering temperature 1150°C/6hrs. The slow decrease or increase of Ms from two sublattices unlike ferromagnetic. The DC electrical resistivity is found to decrease with temperature for all the samples which means these ferrites are semiconductor.

Dielectric constant decreases with increasing frequency exhibiting normally dielectric behavior of ferrites like all the samples. All the figures shows the sample x = 0.4 and x = 0.6 showed the maximum dispersion while that the other samples are shown in dopes Bi2O3 with Ni-Cu-Zn ferrites. The increases in frequency enhance the hopping frequency of charge carriers, resulting in an increase in the conduction process, thereby decreasing the dielectric constant. Dielectric structure to be composed of the fairly well conducting ferrite grain.

Finally, analysis of the experimental results of Ni0.28Cu0.10Zn0.62Fe2O4 + x wt.% Bi2O3 series is appeared that the sample with x = 0.4 shows the properties sintered at both temperatures having constant permeability, low magnetic loss and maximum dielectric dispersion with visible grain size.

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