Effect of Bi$_2$O$_3$ and Sintering Temperature on the Ultrasonic Properties of Mn-Zn Ferrite

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Abstract: The pure and mixed Mn-Zn ferrites with Bi$_2$O$_3$ were prepared by using the conventional ceramic technique at various sintering temperatures ($t$) of 800 – 1200 °C. The additions of Bi$_2$O$_3$ were used to promote grain growth and to increase magnetic permeability during sintering of Mn-Zn ferrites. The Ultrasonic velocity ($v_l$), attenuation coefficient ($\alpha$) and density ($\rho$) studies in pure Mn$_{0.58}$Zn$_{0.37}$Fe$_{2.05}$O$_4$ and mixed ferrite with Bi$_2$O$_3$ at 2 MHz frequencies using Pulse Echo Selection (PES) technique was reported. The results were discussed and analyzed in the light of micro-structural and ultrasonic properties.

Keywords: Ceramic technique, Sintering, Ultrasonic velocity, Ultrasonic attenuation, Micro-structure.

1. Introduction

The micro-structural, ultrasonic and magnetic properties play an important role in the field of ferrites applications in the software industry. Mn–Zn ferrites are superior over the other ferrites at low frequencies, because of high initial permeability, low losses, high saturation magnetization, and relatively high Curie temperature. Ferrite properties are very sensitive to the preparative conditions like sintering temperature ($t$), atmosphere in the furnace, rate of heating and cooling. The magnetic properties of ferrites strongly depend on the microstructure. It is reported that the increasing grain size [1-4] and the rectangularity of B-H loops increases when there are numerous defects that hinder the magnetic domain wall motion in the grains [5-7].

It is reported [8] that the magnetic properties of Mn–Zn ferrites are improved by the addition of a small amount of MoO$_3$. There are a number of reports [9-12] concerning the effects of sintering agents (additives) on the microstructure and ultrasonic properties of ferrites. It was reported that, effects [13, 14] of Bi$_2$O$_3$ and V$_2$O$_5$ on the memory core characteristics of substituted lithium ferrites. It was reported [15-17] that the memory core characteristics of the substituted lithium ferrites improved significantly when Nb$_2$O$_5$ was added and degraded if Bi$_2$O$_3$ was added.

Recently [18] the additions of V$_2$O$_5$ were used to promote grain growth and to increase magnetic permeability and formation of a microstructure composed of giant grains with trapped pores embedded in a normal microstructure during sintering of Mn-Zn ferrites.

The present study is directed towards determining the micro-structural and ultrasonic properties of Mn–Zn ferrites with additive percentages of Bi$_2$O$_3$ to investigate the sintering mechanisms for these ferrites by the subsequent ultrasonic attenuation and the longitudinal ultrasonic velocity ($v_l$) and density ($\rho$) values as it promote the grain growth and increase the magnetic permeability.

2. Experimental Details

The powder samples of pure Mn-Zn and adding with 0.003%, 0.006% and 0.015% of Bi$_2$O$_3$ mixed in a ball mill with agate balls for 12 h. All of the mixtures were dried and calcined at 975°C for 2 h. Bi$_2$O$_3$ and calcined products were wet milled together for 12 h. The fine powder then pressed into disks with a diameter of 10 mm and a thickness of 8-12 mm. The disks were sintered at 800 – 1200°C for 12 h in air. The sintered samples were classified in to four:

a). Mn$_{0.58}$Zn$_{0.37}$Fe$_{2.05}$O$_4$ with 0%Bi$_2$O$_3$

b). Mn$_{0.58}$Zn$_{0.37}$Fe$_{2.05}$O$_4$ with 0.003%Bi$_2$O$_3$

c). Mn$_{0.58}$Zn$_{0.37}$Fe$_{2.05}$O$_4$ with 0.006%Bi$_2$O$_3$

d). Mn$_{0.58}$Zn$_{0.37}$Fe$_{2.05}$O$_4$ with 0.015%Bi$_2$O$_3$

Figure 1: Block diagram of Ultrasonic Pulse Echo Selection (PES) Technique.
The measurement of ultrasonic velocity \( v_l \) and echo-amplitudes \( a_n \) were carried out by Electronic Pulse Echo Selection (PES) method at a frequency of 2 MHz, supplied by innovative Instruments, Hyderabad, INDIA, and at different sintering temperatures. The PES technique is more accurate for measuring ultrasonic velocity and echo-amplitudes of low absorptive solids and liquids. The accuracy of the technique is 2 parts in 10^4.

The electronic circuitry required for PES technique consists of a high voltage pulse generator to excite the transducer, a continuous wave oscillator with high resolution a delayed strobe pulse generator to aid intensification of the trace and timer counter built into a single compact instrument as shown in Figure 1. In this method, a transducer of Lead Zirconate Titanate (PZT) X-cut for a longitudinal wave having fundamental frequency 2 MHz is attached to one end of the sample holder.

The ultrasonic pulsed energy is transmitted by the transducer through the sample under test and gets reflected from the other end of the sample column and is being received by the sample transducer. Here the transducer acts both as transmitter and as a receiver. The echo pattern received by the transducer is fed to Cathode Ray Oscilloscope (CRO) after suitable amplification Figure 2. The delay between first two echoes are generally preferred as they are of higher amplitude and better resolved. Now removing Z-BNC from channel - B and connecting the same to Z-axis (for intensity modulation) to rear side of CRO. Now we see selected echoes on the screen Figure 3. Now to make measurements, one can approximate the travel time between two echoes selected for overlapping from the oscilloscope time scale. The travel time and amplitudes of different echoes are displayed on the timer and attenuation display. The X-BNC is connected to trigger mode of the CRO and the selection is achieved by the delays, as shown in Figure 4.

The longitudinal ultrasonic velocity, \( v_l = \frac{2l}{T} \)

where \( l \) – length of liquid column
\( T \) – travel time of ultrasonic wave

The Ultrasonic attenuation, \( \alpha = \frac{\ln(a_0/a_n)}{z/m} \)

Where \( a_0 \) = the amplitude of transmitted pulse
\( a_n \) = amplitude of \( n^{th} \) echo
\( n \) = the number of echo

3. Results and Discussion

The ultrasonic properties of Mn-Zn ferrites with the addition of Bi\(_2\)O\(_3\) and the sintering behaviour have been investigated by examination of density, ultrasonic velocity and attenuation measurements. The densities of Mn-Zn ferrites with various additive percentages of Bi\(_2\)O\(_3\) as a function of sintering temperature are shown in Figure 1. It can be seen that the additive Bi\(_2\)O\(_3\) enhances the sintered density. The density values for all the samples of Mn-Zn with Bi\(_2\)O\(_3\) additive percentages of 0%, 0.003%, 0.006% and 0.015% were increasing trend.

It is clear that for pure Mn-Zn (with 0% Bi\(_2\)O\(_3\)), the sample density is increasing sharply from 900°C to 1075°C sintering temperature above which it becomes constant till 1200°C as shown in Figure 5. The ultrasonic velocity is also increasing in a similar manner as the density which is shown in Figure 6. But it is found to be slow for 0.006% and 0.015% of Bi\(_2\)O\(_3\) in Mn-Zn ferrite as shown in Figure 7 and 8. Figure 7 show a kink at about 925°C at which the additive 0.003% Bi\(_2\)O\(_3\) takes a transition state from solid to liquid phase. But the Figure 8 of 0.015% Bi\(_2\)O\(_3\) shows a sharpened kink at the same temperature.

The increased velocity and the sharpening of the kink at 975°C the lower temperature side is due to the fact that as the sintering temperature increases the interatomic distances decreases and the atoms become closer. Hence, the density...
increases with this effect. This increased effect of density causes the ultrasonic velocity to increase in these samples of all compositions and pure Mn-Zn ferrite.

**Table 1**: Ultrasonic velocity, Density and Attenuation coefficient with different sintering temperatures and different additive % of Bi₂O₃ with Mn-Zn ferrite

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Attenuation coefficient (α)</th>
<th>Velocity (V, m/s)</th>
<th>Density (ρ, kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>975</td>
<td>3.84</td>
<td>5564.31</td>
<td>0.9825</td>
</tr>
<tr>
<td>1000</td>
<td>4.18</td>
<td>5925.27</td>
<td>0.9913</td>
</tr>
<tr>
<td>1025</td>
<td>4.41</td>
<td>6224.2</td>
<td>1.1025</td>
</tr>
<tr>
<td>1050</td>
<td>4.56</td>
<td>6531.55</td>
<td>1.3212</td>
</tr>
<tr>
<td>1075</td>
<td>4.64</td>
<td>6725.94</td>
<td>1.4728</td>
</tr>
<tr>
<td>1100</td>
<td>4.69</td>
<td>6754.6</td>
<td>1.5025</td>
</tr>
<tr>
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<td>6764.7</td>
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</tr>
<tr>
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<td>6774.75</td>
<td>1.505</td>
</tr>
<tr>
<td>1175</td>
<td>4.71</td>
<td>6774.75</td>
<td>1.505</td>
</tr>
<tr>
<td>1200</td>
<td>4.71</td>
<td>6774.75</td>
<td>1.505</td>
</tr>
</tbody>
</table>

**Figure 5**: Variation of Ultrasonic velocity and density with sintering temperatures for additive percentage of 0% Bi₂O₃ in Mn-Zn ferrite.

**Figure 6**: Variation of Ultrasonic velocity and density with sintering temperature for additive percentage of 0.003% Bi₂O₃ in Mn-Zn ferrite.

**Figure 7**: Variation of Ultrasonic velocity and density with sintering temperature for additive percentage of 0.006% Bi₂O₃ in Mn-Zn ferrite.
Figure 8: Variation of Ultrasonic velocity and density with sintering temperature for additive percentage of 0.015% Bi$_2$O$_3$ in Mn-Zn ferrite.

Figure 9: Variation of attenuation coefficient and density with sintering temperature for additive percentage of 0.003% Bi$_2$O$_3$ in Mn-Zn ferrite.

Figure 10: Variation of attenuation coefficient and density with sintering temperature for additive percentage of 0.003% Bi$_2$O$_3$ in Mn-Zn ferrite.

Figure 11: Variation of attenuation coefficient and density with sintering temperature for additive percentage of 0.006% of Bi$_2$O$_3$ in Mn-Zn ferrite.

Figure 12: Variation of attenuation coefficient and density with sintering temperature for additive percentage of 0.015% Bi$_2$O$_3$ in Mn-Zn ferrite.

All Figures 9 to 12 of attenuation coefficient [$\alpha$] and Density [$\rho$] versus sintering temperature [$t$] show that both values are increasing exponentially with sintering temperature. All the figures indicate that $\alpha$ is increased exponentially due the enhanced density which is due to the liquid phase transition at around 1075°C for pure Mn-Zn ferrite, 950°C in case of 0.015%, around 975°C for 0.006% of Bi$_2$O$_3$ and 1075°C for pure Mn-Zn ferrite.

It was reported [19] that the Bi$_2$O$_3$ particles exist as a liquid during the sintering, however, tend to segregate at grain boundaries leaving few micro voids in the grain when the $T$s is low (below 1000°C) and the grain boundary mobility is small. Optimum addition [20] of Bi$_2$O$_3$ increases the permeability and saturation magnetic induction, at the same time it ensures good frequency stability of permeability.

The results indicate that Bi$_2$O$_3$ mainly segregates and concentrates in the grain boundary regions, promotes solid state reaction and grain growth, reduces porosity and enhances density.

4.Conclusions

The increasing trend of velocity and attenuation of ultrasound indicate that the additive Bi$_2$O$_3$ enhances the
sintering of Manganese Zinc by liquid phase transition which confirms the recent findings. The ultrasonic and magnetic properties can be improved by the optimum addition of Bi₂O₃ with Manganese Zinc Ferrite. Thus the Bi₂O₃ is a better additive to Mn-Zn ferrite used in the software and its ultrasonic application industry.

5. Acknowledgement

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References


Figure Captions

- Figure 5: Variation of ultrasonic velocity and density of 0% Bi₂O₃ in Mn-Zn ferrite at different sintering temperatures.
- Figure 6: Variation of Ultrasonic velocity and density of 0.003% Bi₂O₃ in Mn-Zn ferrite at different sintering temperatures.
- Figure 7: Variation of Ultrasonic velocity and density of 0.006% Bi₂O₃ in Mn-Zn ferrite at different sintering temperatures.
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