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Effects of addition of bismuth oxide and glass on the properties of lithium ferrite for ferrimagnetic pastes

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Lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$, has been prepared by decomposition of organometallic complexes at 800° C, and the optimization of heating schedule for conversion into ferrite has been studied. The effects of addition of glass, essential for adhesion of the ferrite film to alumina substrates, and bismuth oxide, as a sintering aid, on the properties and densification of lithium ferrite have been examined. X-ray diffraction, electron probe micro analysis (EPMA) and scanning electron microscopy (SEM) techniques have been used to study the solubility and distribution of bismuth oxide, grain growth and pore morphology. It has been found that the addition of bismuth oxide (up to 1.5 wt%) improves densification and increases resistivity of the lithium ferrite but the addition of glass causes a reduction of the resistivity. Although bismuth oxide forms a solid solution, it is not uniformly distributed throughout the ferrite phase. It is shown that the addition of bismuth oxide improves the insertion loss in microwave devices fabricated using ferrimagnetic pastes.

1. Introduction

Among ferrimagnetic spinels, lithium ferrite has the highest Curie temperature. It has low microwave dielectric losses, low stress sensitivity and excellent square-loop properties. These properties make lithium ferrite attractive for microwave applications [1, 2]. It has been shown that lithium ferrite can be used for fabrication of ferrite pastes which provide an alternative to ferrimagnetic substrates for fabrication of microwave components. Development of thick-film ferrimagnetic pastes using lithium ferrites and their applications in fabricating non-reciprocal microwave components have been reported [3–5].

All thick-film circuit work is essentially a multistep sequence involving firing of conductor, resistor and dielectric pastes as required. To be useful, ferrimagnetic pastes for thick-film applications must be compatible with other commercially-available thick-film compositions which are generally fired in the temperature range of 750 to 950° C with a cycle time of one hour or less. This imposes the condition that the thick-film ferrimagnetic pastes must also be fired in this temperature range with a cycle time of one hour. Since the common technique of applying pressure for densification cannot be used, one has to rely entirely on the choice of composition and fabrication procedures to obtain low porosity in the ferrite film, an essential requirement for low loss at microwave frequencies.

A shortcoming of lithium ferrite preparation is related to considerable irreversible lithium oxide and oxygen losses above 1000° C [2]. For preparation of homogeneous fine-grain ferrites and to avoid loss of oxygen and other volatile components, various preparation techniques such as co-precipitation, spray drying and roasting, freeze drying and decomposition of formates [6–9] have been developed. A very useful technique using decomposition of solidified solution of organometallic complexes has been adopted by Koppen [10] for the preparation of ferrites. It has been established [11] that nearly complete conversion

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of lithium ferrite can be achieved by heating the organometallic salts at 850° C for a period of 2 h.

In the fabrication of lithium ferrite substrates, improved densification, chemical homogeneity and magnetic properties have been successfully achieved by using bismuth oxide as a flux during liquid-phase sintering [1, 12–14].

As the ferrimagnetic pastes are to be fired in the temperature range 750 to 950° C, one would hope that the addition of bismuth oxide would enhance the sintering of the screen-printed ferrite films and lead to better microwave properties. One should, however, note that for adhesion of the ferrite film to alumina and other substrates, it is necessary to add a required amount of glass in the ferrite pastes.

In this paper the effect of addition of bismuth oxide and glass (lead borosilicate glass, Transene Glass Composition – 120, from Transene Co., USA) on the densification of lithium ferrite has been studied. The grain growth and pore morphology have been studied from the fractured surface of the sintered ferrite using scanning electron microscopy (SEM). The effects of these additives on the electrical and magnetic properties have also been analysed. Electron-probe microanalysis (EPMA) and X-ray diffraction analysis have been used to study the distribution and solubility of bismuth oxide in the sintered ferrite.

2. Experimental procedure

Lithium ferrite has been prepared from the decomposition of organometallic complexes [11]. The starting materials were Analar-grade nitrates and carbonates of metals and maleic acid. Differential thermal analysis (DTA) has been used to study the different physical and chemical changes that may occur in dry mixtures of organometallic complexes during their conversion into ferrite. The broad exothermic peak at 420° C is probably due to the decomposition of metal complexes and indicates the possible formation of ferrite at this temperature. To find the optimum heating schedule for the conversion into ferrite, dried complexes were heated at 420° C and 800° C for different durations. The conversion into ferrite was studied by X-ray powder diffraction analysis. The ferrite prepared was powdered by hand in an agate mortar and its density was measured. The average particle size was measured in a Fischer sub-sieve sizer.

In order to study the effect of the addition of bismuth oxide and glass on the electrical and magnetic properties and the density of the lithium ferrite, samples with different percentages of additives were prepared by heating at 950° C for 6 h. Bulk density, initial permeability and direct current (d.c.) resistivity were measured using standard techniques. Variation of initial permeability with addition of bismuth oxide and glass has also been studied in the frequency range of 5 to 90 MHz. The formation of any other phase except that of lithium ferrite due to the addition of bismuth oxide has been analysed by X-ray diffraction technique and the distribution of bismuth in ferrite grains has been studied using the electron-probe micro analyser.

3. Results and discussion

The DTA curve for the dried mixture of organometallic complexes is shown in Fig. 1. The broad exothermic peak around 420° C indicates that decomposition of complexes occurs at this temperature. During decomposition, the oxides of metals formed are in an active state and eventually ferrite formation starts. Samples were heated at 420° C for different durations: 0.5, 1, 2 and 4 h. It has been found from the X-ray diffraction patterns that the relative heights of the peaks of the samples heated for 2 and 4 h are the same. It was found earlier [11] that lithium ferrite may be prepared at a temperature of around 850° C by the decomposition of organometallic complexes. In the present work samples have been heated at 800° C for different durations to ensure complete conversion into ferrite. Fig. 2 shows the X-ray diffraction patterns for samples heated at 800° C for 0.5, 1, 2 and 4 h. In case of samples heated for 2 and 4 h the relative heights of the peaks are the same, indicating complete conversion. A comparison of the relative heights of the peaks of the X-ray diffraction patterns (Fig. 2d and e) shows that complete conversion into ferrite is not possible at 420° C. The ferrite prepared has been found to have a powder density of 4.7 g cm^{-3} (pyrometric) compared to an X-ray density of 4.75 g cm^{-3} [15]. The average particle size was measured to be 3.8 μm (Fischer sub-sieve sizer) which is much smaller than that obtained by the spray roasting technique (ranging from 5 to 10 μm) [16].

Table I shows the variation of density of the samples sintered at 950° C for 6 h with different amounts of bismuth oxide and glass added. It is noted that with increase of the amount of bismuth

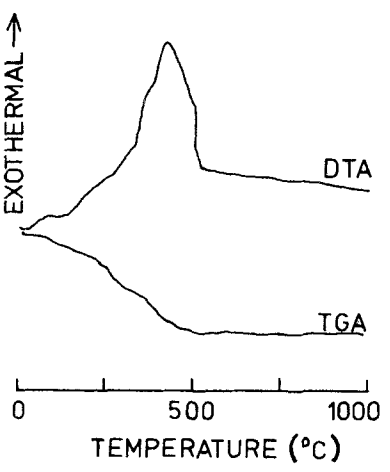

Figure 1 DTA and TGA curves for the mixture of organometallic complex at a heating rate of 10° C min^{-1}.

oxide the density increases, attaining 93.6% of the theoretical density at 1.5 wt% addition, after which the density decreases. At concentration levels lower than 1.5 wt%, the density increases due to better fluxing action with increase of bismuth oxide concentration. Peshev and Pecheva [14] assumed from DTA studies that eutectic melting of lithium ferrite–bismuth oxide was responsible for densification, since there was an endothermic peak at 720° C. In the present investigation, X-ray diffraction patterns for lithium ferrite (85 wt%)–bismuth oxide (15 wt%), sintered at 950° C for 6 h, do not show any other phase except that of lithium ferrite. This indicates that bismuth oxide forms a solid solution with ferrite during the present sintering condition.

It is evident from SEM fractographs that the addition of bismuth oxide enhances grain growth and pores are trapped inside the grains (see Fig. 3). It has not been possible to attain more than 93.6% of the theoretical density with the heating schedule used in this investigation; this may be due to pore trapping. The effect on densification of bismuth oxide, when added as a starting ingredient,

TABLE I Resistivity and percentage theoretical density of lithium ferrite sintered at 950° C for 6 h with different amounts of bismuth oxide and glass additives.

Additives (wt%)		D.c. resistivity (ohm cm)	Percentage of theoretical density
Bismuth oxide	Glass		
0.5	–	5.63×10^4	88.19
0.8	–	7.80×10^3	90.00
1.0	–	5.00×10^5	90.30
1.2	–	1.12×10^6	91.20
1.5	–	2.10×10^{10}	93.60
2.0	–	1.04×10^{10}	84.04
5.0	–	1.20×10^{10}	79.26
10.0	–	8.30×10^{10}	72.60
15.0	–	3.13×10^{11}	73.85
–	1.0	1.56×10^7	83.22
–	2.0	5.79×10^4	86.48
–	5.0	2.13×10^3	85.56
–	10.0	7.74×10^3	80.95
–	15.0	9.49×10^4	81.45
0.8	1.0	4.05×10^8	84.40
1.0	1.0	3.30×10^7	86.85
1.2	1.0	1.80×10^7	86.00
1.5	1.0	7.40×10^3	86.30
2.0	1.0	1.05×10^3	87.31
4.0	1.0	4.60×10^3	90.12
7.0	1.0	3.70×10^4	90.10

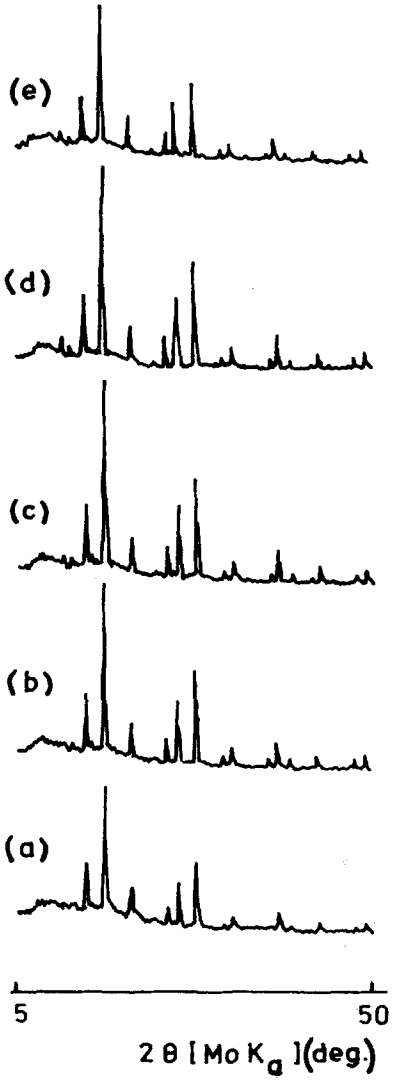

Figure 2 X-ray diffraction pattern of the mixture of organometallic complex heated at: (a) 800° C for 0.5 h, (b) 800° C for 1 h, (c) 800° C for 2 h, (d) 800° C for 4 h and (e) 420° C for 4 h.

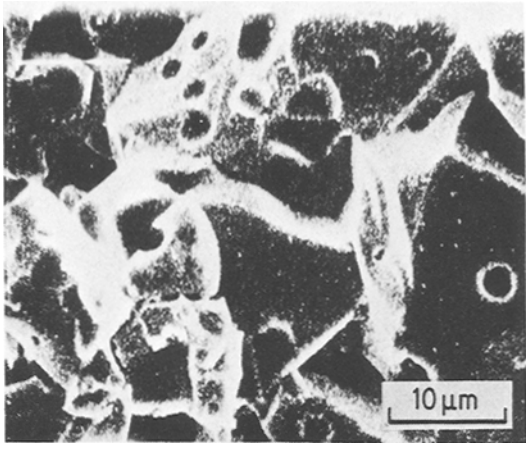

Figure 3 SEM fractograph of 98 wt% $Li_{0.5}Fe_{2.5}O_4$ – 2 wt% Bi_2O_3, heated at 950° C for 6 h.

has also been studied at different temperatures with a heating period of 6 h. However, it has not been possible to achieve more than 96% of the theoretical density. The variation of density with sintering temperature for concentrations of added bismuth oxide of 1, 2, 4 and 7 wt% has been shown in Fig. 4. It is interesting to note that for 1 and 2 wt% additions of bismuth oxide there is no signigicant change in densification for sintering temperatures above 900° C. For samples containing 4 and 7 wt% bismuth oxide the density decreases slightly with increase of temperature from 950 to 1050° C. This is due to the discontinuous grain growth which has a deleterious effect on densification. The addition of 2 wt% bismuth oxide along with the starting ingredients is seen to improve the densification to 96% of theoretical density compared to 93.6% obtained when 1.5 wt% bismuth oxide is added after the ferrite has been formed. Baba *et al.* and Peshev and Pecheva [1, 14] achieved more than 99% of theoretical

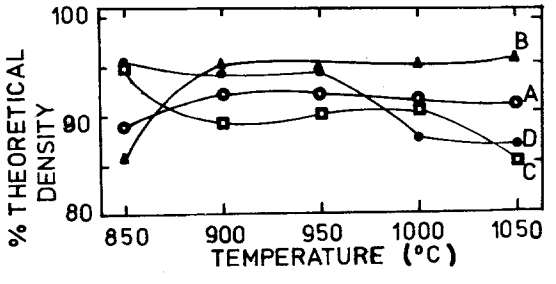

Figure 4 Percentage of theoretical density plotted as a function of sintering temperature for a sintering time of 6 h for lithium ferrite containing: (a) 1 wt% Bi_2O_3, (b) 2 wt% Bi_2O_3, (c) 4 wt% Bi_2O_3 and (d) 7 wt% Bi_2O_3.

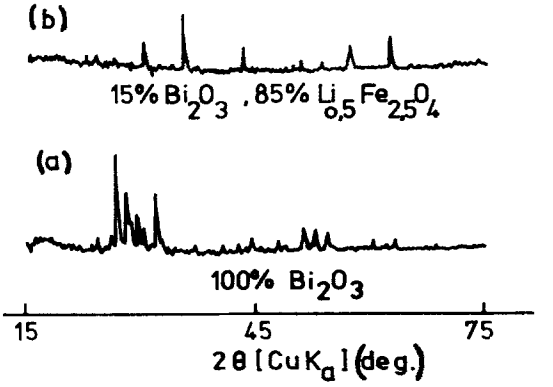

Figure 5 X-ray diffraction pattern of (a) Bi_2O_3 and (b) 85 wt% $Li_{0.5}Fe_{2.5}O_4$ – 15 wt% Bi_2O_3 heated at 950° C for 6 h.

density below 1000° C using bismuth oxide as a starting material. As the densification process becomes sluggish when pores are trapped in grains, such a bulk density may have been achieved by heating for a long period of time.

With the addition of glass (TGC-120, from Transene Co., USA) the density remains within the range of 83 ± 3% of theoretical density; addition of bismuth oxide along with glass does not improve densification significantly, as may be seen from Table I. The change of d.c. resistivity with increase of bismuth oxide concentration has also been shown in Table I. It has been found that with the increase of bismuth oxide d.c. resistivity increases.

Solid solubility of bismuth oxide was evident from the X-ray diffraction pattern up to as much as 15 wt% bismuth oxide in lithium ferrite (sintered at 950° C for 6 h); Fig. 5 indicates the presence of the ferrite phase only. A representative curve of

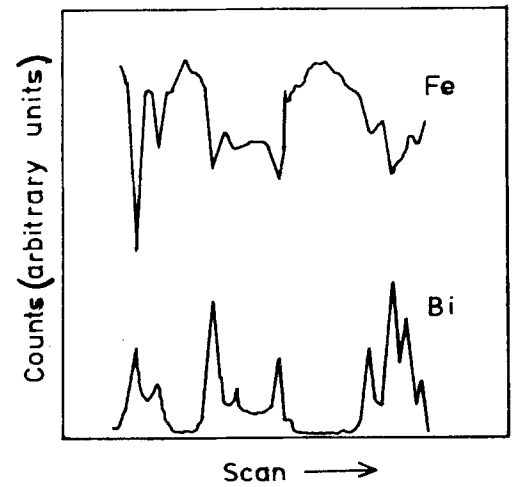

Figure 6 EPMA distribution of iron and bismuth in 85 wt% $Li_{0.5}Fe_{2.5}O_4$ – 15 wt% Bi_2O_3 heated at 950° C for 6 h.

the electron-probe micro analyser study of this sample (Fig. 6) shows the distribution of bismuth and iron in the sintered ferrite. It is seen that bismuth is not uniformly distributed throughout the grains; in fact, under the heating schedule followed, bismuth does not appear to reach the centre of the grain where the concentration of bismuth is almost zero. The presence of a high percentage of bismuth at the grain boundary of lithium ferrite may be responsible for increasing the resistivity of lithium ferrite.

It may be noted from Table I that, with the addition of glass, the resistivity of the lithium ferrite decreases. It has been shown by Trap and Stevals [17] that the electrical conductivity in glass-like materials is changed by the introduction of oxides of elements of variable valency. In the case of iron oxide, the conductivity is related to the ratio of Fe^{2+} and Fe^{3+} ions, the concentration of iron oxide and the nature of the host glass. Under the experimental conditions of the present work some lithium ferrite gets dissolved in the glass at the grain boundary. The increase of conductivity of the glass at the grain boundary is considered to be responsible for the reduction of resistivity with increase of glass.

The variation of initial permeability of lithium ferrite with addition of different amounts of bismuth oxide (1 to 7 wt%) and 1 wt% glass was measured over the frequency range of 5 to 90 MHz. The results presented in Fig. 7 show that the addition of bismuth oxide increases the initial permeability at low frequencies.

Thick-film ferrimagnetic pastes have been prepared by adding glass powders (as binder to alumina substrates), ethyl cellulose (as resin) and terpineol (as organic vehicle) to lithium ferrite. In

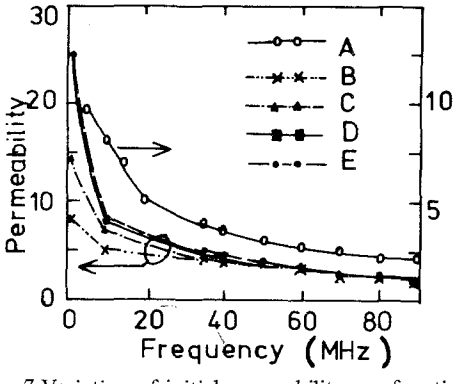

Figure 7 Variation of initial permeability as a function of frequency for (A) 0 wt% Bi_2O_3, (B) 1 wt% Bi_2O_3, (C) 2 wt% Bi_2O_3, (D) 4 wt% Bi_2O_3 and (E) 7 wt% Bi_2O_3.

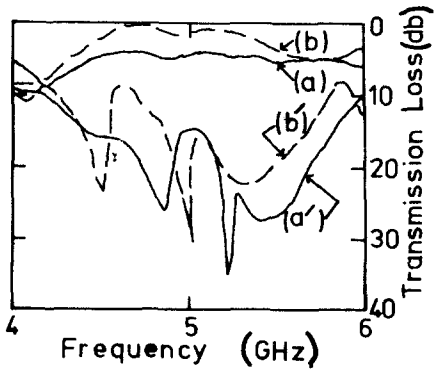

Figure 8 Performance of an edge-guided mode isolator at an applied field of 0.1250 T: (a) and (b) total insertion loss, (a') and (b') isolation.

the present investigation 1 wt% of bismuth oxide has been added to the ferrite paste as the sintering aid and the screen-printed ferrite films were fired at 950° C with a soaking time of 15 min and total cycle time of 1 h.

Edge-guided mode isolators have been fabricated on ferrimagnetic films from lithium ferrites using a thick-film technique. Fig. 8 shows the performance of such an isolator over the frequency range of 4 to 6 GHz for an applied magnetic field of 0.1250 T. In Fig. 8, Curves a and b represent the total insertion loss of the isolator made on the ferrimagnetic film without bismuth oxide and with 1 wt% bismuth oxide addition, respectively. It may be seen that the total insertion loss is reduced by about 2 dB with the addition of 1 wt% bismuth oxide. This is due to the enhanced sintering of the ferrite film at 950° C.

4. Conclusions

It is concluded that fully-reacted lithium ferrite can be prepared at a temperature as low as 800° C by using the technique of decomposition of solidified solution of organometallic complexes and it is shown that bismuth oxide has a beneficial influence on the ferrite properties. An addition of bismuth oxide up to 2 wt% results in a substantial increase in the resisitivity and improvement in densification while the addition of glass causes a reduction of the resistivity. Microwave loss properties of the devices made using the thick-film technique are also seen to improve on addition of about 2 wt% of bismuth oxide to lithium ferrite pastes.

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