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Low temperature sintering of MgCuZn ferrite and its electrical and magnetic properties

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Abstract. The low temperature sintering of MgCuZn ferrite was investigated using the usual ceramic method. The effect of Cu substitution on the properties of MgZn ferrites was also investigated and it was found that the densification of MgCuZn ferrite is dependent upon Cu concentration. The sintered ferrite with a density of 4·93 g/cm^3 and electrical resistivity > 10^{11} Ω-cm was obtained for the ferrite with 12 mol% Cu at relatively low sintering temperature (910°C). The magnetic properties of the ferrites also improved by the Cu substitution. The chip inductors made of the ferrite fired at 910 C with 12 mol% Cu exhibited higher d.c. resistance. From these studies it is concluded that the good quality chip inductor can be obtained using the MgCuZn ferrites.

Keywords. Low temperature sintering; MgCuZn ferrite; shrinkage; resistivity; permeability; quality factor.

1. Introduction

Chip inductors are one of the passive surface mount devices (SMD). They are important components for the latest electronic products such as cellular phones, video cameras, notebook computers, hard and floppy drives etc and those that require small dimensions, lightweight, and better functions (Ono *et al* 1991; Nomura and Nakano 1992). The traditional wire-wound chip inductors can only be miniaturized to a certain limit and lack of magnetic shielding leads to the development of new materials for the multilayer chip inductors. In this process only NiCuZn ferrites were developed as the material used in the chip components (Nakano *et al* 1992; Nakamura 1997). But, it was found that these ferrites are comparatively sensitive to stress and magnetic properties easily changed or deteriorated by the stress caused at the internal electrode.

Silver is generally used as the material for the internal conductor of the multilayer chip inductors due to its low resistivity, resulting in the components with high quality factor, Q (Nakano *et al* 1992). In addition to this, Ag paste is commercially available at lower cost than Ag–Pd paste. Since the melting point of silver is 961°C, the sintering temperature of ferrite used for the manufacture of chip inductor should be below 940°C. This is because of the need to prevent Ag diffusion into the ferrite that would increase the resistivity of the internal conductor. Further, the segregation of Cu^{+2} from the ferrite induced by the diffused Ag can be avoided and thus no deterioration of magnetic properties of the material.

In order to overcome these problems, MgCuZn ferrites were found to be suitable (Koh and Yu 1984; Bhosale *et al* 1997; Park *et al* 1997). Normally, MgCuZn ferrites were sintered at temperatures higher than 1000°C (Koh and Yu 1984; Koh and Kim 1986; Bhosale *et al* 1997). In order to use these ferrites in multilayer chip components, the sintering temperature must not be over the melting point of Ag. Therefore, MgCuZn ferrites were selected and a detailed study of the effect of Cu substitution on the densification characteristics has been carried out. Electrical and magnetic properties such as resistivity, quality factor, and inductance, permeability and saturation magnetization of the prepared ferrites were also measured. The properties of the fabricated chip inductors are measured.

2. Experimental

Samples with the composition $Mg_{0·6-x}Cu_xZn_{0·4}Fe_2O_4$ with $x = 1$ to 14 mol% were prepared using the sintering method. High purity chemical reagent powders of Fe_2O_3, MgO, ZnO and CuO were mixed in a ball mill for 6 h. A study of the effect of calcining temperature on the densification of MgCuZn ferrites has been carried out. The resulting powders were calcined between 750 and 900°C for 4 h. The calcined powder was mixed with PVA 6% solution and made into two batches. One batch was pressed in a die under a pressure of 190 MPa for 5 min (without any lubricant) into rods (60 mm in length, 12 mm diameter) and pellets (10 mm diameter, 3 mm thickness), and then sintered at 500, 550, 600, 650, 700, 750, 800, 850, 900, 950 and 1000°C for 12 h to investigate the effect of cupric oxide on densification in the MgCuZn ferrites. The second batch of powder was pressed into pellets (12 mm diameter, 5 mm thickness) and toroids (12 mm outside diameter, 8 mm inside diameter, 4 mm thickness) at a pressure of 190 MPa for 10 min and then sintered at 850, 870, 890, 900, 910, 920, 930 and 950°C for 12 h in air at atmospheric pressure. In order to avoid cracking of the samples, the following sintering schedule was followed. All the samples were slowly heated up to 500°C at the rate of 4°C/h. Then, the temperature was raised to the firing temperature at the rate of 20°C/h. After sintering the samples were cooled at the rate of 20°C/h up to 300°C and at this stage the furnace was switched off. At each stage of sintering, the weight and dimensions of the samples were measured at room temperature to know the bulk densities.

All the samples were characterized using the X-ray diffraction. After the samples had been polished and annealed at 500 C, the microstructure photographs were taken with a scanning electron microscope (Philips SEM 515). The mean intercept D_m is taken both as a measure and a definition of grain size. D_m corresponds to the mean chord along an arbitrary line across a microstructure picture. The mean intercept thus determined is a number average and has the advantage of representing a unique definition of grain size, which does not depend on the actual grain shapes. Grain sizes were determined from pictures taken at various parts of the sample to determine the average mean linear intercept D_m. Typically, 100–150 grains were counted for each ferrite. The d.c. resistivity (r) at room temperature was measured by the bridge method using silver-paste contacts. The initial permeability (m_i), quality factor (Q), and inductance (L) at room temperature were measured using an impedance analyzer (HP 4294 A). The temperature (T) variation of initial permeability was also measured in the range 300–600 K at a frequency of 1 kHz in a field of 5 mOe. The Curie temperature (T_C) of the samples was obtained from the m_i vs T plots. The saturation induction (B_s) and coercive field (H_c) values for the samples were obtained from the recorded hysteresis loops at room temperature using the vibrating sample magnetometer (VSM).

The ferrite powders were mixed with ethylcellulose and organic solvent using a roll mill. The ferrite plates were printed alternately with Ag paste to form the internal winding in a green chip, which was 4·8 turns in 2012 type. The green chips were fired at 890, 900 and 910°C in air. The d.c. resistance, inductance (L) and quality factor (Q) of the prepared inductors were also measured at room temperature. The inductance of the chip inductor was also measured at room temperature in the frequency range 0·1–1 MHz.

3. Results and discussion

In order to sinter MgCuZn ferrites below the melting point of silver, the effect of chemical composition MgCuZn ferrites on the densification characteristics were investigated. The influence of Cu^{+2} ion concentration on the densification of the MgCuZn ferrites for various sintering temperatures from 500 to 1000 C is summarized in figure 1. It is observed from the figure that when CuO content increased from 1 mol% to 12 mol% the densification curve shifted towards low temperature area with increase of CuO content. The densification characteristic clearly increased for the CuO content in the range of 1 mol% to 12 mol%. With increased CuO content, the densification temperature of MgCuZn ferrites decreased. But this effect of CuO content is not enough for sintering ferrites below melting point of Ag. More information is required in this regard. Therefore, the effect of specific surface area on the densification of MgCuZn ferrites was investigated for all the samples. It was found that the densification curve shifted towards low-temperature side with increasing specific surface area from 5·8 m^2/g to 16 m^2/g.

As calcining temperature plays an important role in the preparation processes of the ferrites, this temperature was selected after conducting a study of the effect of calcining temperature on the densification characteristics of MgZnCu ferrites. Figure 2 gives the results of such an investiga-

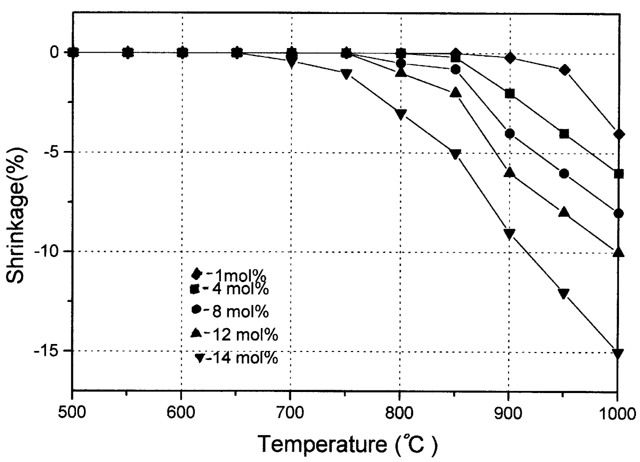

Figure 1. Effect of cupric oxide content on the densification of MgCuZn ferrites.

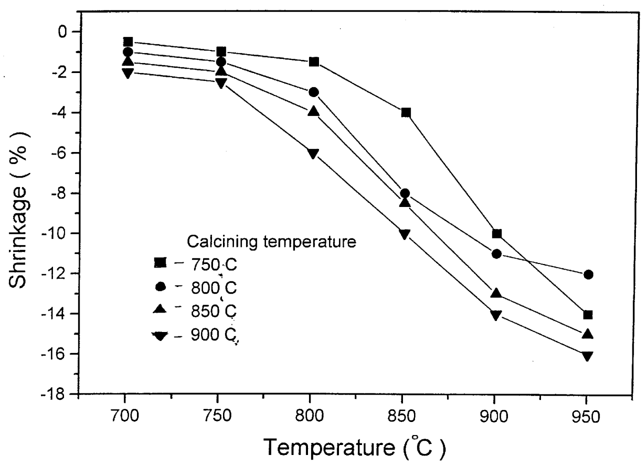

Figure 2. Effect of calcining temperature on the densification of MgCuZn ferrites.

tion. It can be seen from the figure, that when the calcining temperature was 750°C, the ferrite started to shrink at higher temperature. This result is due to the remaining hematite component in ferrite powder and suggests that the firing at a temperature below 700°C is difficult. The densification curve shifted towards low temperature side with increasing calcining temperature. However, the curve shifted towards high temperature side again for the calcining temperature higher than 900°C. Thus, the uniform spinel phase can be obtained in the ferrites by sintering at low temperature.

From the above investigation, it is concluded that for the low temperature sintering of MgCuZn ferrites, we require a calcining temperature in between 750 to 850 C, specific surface area > 5·8 m^2/g and CuO content > 4 mol%.

Table 1 gives the room temperature data such as density (d_X), grain size (D_m), d.c. resistivity (r), initial permeability (m_i), saturation induction (B_s), and quality factor (Q) for the ferrites. It can be seen from the table that by incorporating copper into MgZn ferrite a high density can be obtained at relatively low temperatures. A significant increase of the bulk density was obtained after sintering at 850°C. At higher sintering temperatures a little change in density was observed. Previously, it was observed that over the same sintering temperature range the ferrite without copper showed a little, or no change in density. This means that the materials densification depends on the copper content. The highest densities were obtained for the copper concentration of 12 mol%. For larger copper content, the density decreased. In general, a decrease in density was also observed at higher sintering temperature. The decrease has been attributed to increased intragranular porosity resulting from discontinuous grain growth as observed by Burke *et al* (1958). The detailed atomic mechanism through which CuO improves densification of MgZn ferrites at low temperature is not very clear till today. However, a possible explanation may be the formation of a solid solution. It was supposed that all

Table 1. Room temperature data for MgCuZn ferrites.

Cu content (mol%)	Sintering temperature (°C)	d_X (g/cm^3)	D_m (mm)	m_i (1 MHz)	B_s (Tesla)	r (Ω cm)	Quality factor (Q) at 1 MHz	T_C (K)
1	800	3·351	6·5	350	0·12	$3·5 \times 10^5$	68	470
	850	3·645	6·8	352	0·14	$4·2 \times 10^5$	68	
	870	3·846	7·1	371	0·15	$4·8 \times 10^5$	69	
	890	3·912	7·3	380	0·21	$5·5 \times 10^5$	75	
	910	3·985	7·5	410	0·25	$5·8 \times 10^5$	78	
	920	3·865	7·8	380	0·18	$4·2 \times 10^5$	65	
	950	3·843	7·8	350	0·14	$3·8 \times 10^5$	62	
4	800	3·425	6·8	425	0·14	$5·4 \times 10^7$	85	475
	850	3·721	6·9	435	0·16	$5·8 \times 10^7$	88	
	870	3·855	7·2	440	0·20	$6·0 \times 10^7$	88	
	890	3·946	7·5	465	0·25	$7·4 \times 10^7$	92	
	910	3·995	7·8	468	0·28	$8·6 \times 10^7$	92	
	920	3·910	8·0	424	0·21	$6·8 \times 10^7$	86	
	950	3·855	8·0	403	0·18	$6·2 \times 10^7$	84	
8	800	3·782	6·9	450	0·15	$5·8 \times 10^8$	95	490
	850	3·856	7·2	458	0·18	$6·3 \times 10^8$	95	
	870	3·935	7·5	480	0·20	$7·5 \times 10^8$	98	
	890	3·985	7·9	495	0·28	$8·8 \times 10^8$	98	
	910	4·025	8·2	510	0·30	$9·5 \times 10^8$	99	
	920	3·921	8·5	450	0·26	$8·1 \times 10^8$	93	
	950	3·865	8·5	435	0·25	$7·2 \times 10^8$	91	
12	800	4·686	7·2	480	0·22	$8·2 \times 10^{11}$	103	500
	850	4·745	7·5	495	0·31	$10·5 \times 10^{11}$	103	
	870	4·845	7·8	510	0·32	$12·4 \times 10^{11}$	104	
	890	4·885	8·3	515	0·35	$13·5 \times 10^{11}$	104	
	910	4·928	8·5	538	0·42	$14·8 \times 10^{11}$	108	
	920	4·765	8·8	468	0·32	$11·5 \times 10^{11}$	104	
	950	4·652	9·0	447	0·25	$10·2 \times 10^{11}$	102	
14	800	3·854	8·1	490	0·12	$4·6 \times 10^6$	55	510
	850	3·945	8·6	495	0·13	$5·5 \times 10^6$	58	
	870	4·125	8·9	515	0·15	$5·9 \times 10^6$	58	
	890	4·442	9·4	524	0·16	$6·8 \times 10^6$	62	
	910	4·655	9·6	546	0·18	$7·8 \times 10^6$	62	
	920	4·125	9·8	485	0·16	$5·5 \times 10^6$	58	
	950	4·054	9·8	450	0·14	$4·5 \times 10^6$	54	

copper ions dissolve in the spinel lattice during heating. This assumption of the solid solution formation was confirmed with lattice parameter measurements. The value of the lattice parameter is found to increase with increasing Cu^{+2} ion content from 8·4064 Å for 1 mol% to 8·4132 Å for 12 mol%. This increase may be attributed to a change of the Mg^{+2} ion distribution on A-sites, taking into account the fact that copper ions prefer the B-sites (Naik *et al* 1988). The increase of the lattice volume usually increases the diffusion path and which in turn increases the rate of cation interdiffusion in the solid solution (Coble and Gupta 1967). But during sintering grain boundary diffusion may play an important role in the grain growth because the activation energy for lattice diffusion is higher for grain-boundary diffusion (Burke 1957). Thus, the sintering of MgCuZn ferrite may be dominated by the two diffusion mechanisms and which of these mechanisms is important may depend on the microstructure analysis.

It can be seen from the table that the grain size of the samples increases with an increase of Cu content and sintering temperature. The value of r for the samples increases with an addition of copper from 1 mol% to 12 mol% to MgCuZn ferrites. This result indicates that the conduction resulting from the substitution of CuO for MgO is less than its decrease occurring as a result of over oxidation. The electrical resistivity $> 10^{11}$ Ω-cm was obtained for the ferrite with 12 mol% Cu at relatively low sintering temperature. For higher Cu concentration, a decrease in resistivity was observed. The increase of conductivity with increasing content of Cu^{+2} ions may be understood from the fact that in the case of MgCuZn ferrite, the B-sites are occupied by both stable Mg^{+2} ions and Fe^{+2} and Cu^{+2} ions which can change between the +2/+3 and the +1/+2 states, respectively, thus providing a greater amount of hopping on the B-sites.

It can be observed from the table that the value of quality factor (Q) increases with an increase of Cu substitution. Among all the specimens the one sintered at 910 C with 12 mol% Cu exhibited the highest quality factor. It is believed to be due to the high resistivity of the material.

It is evident from the table that the saturation induction (B_s) increases with increasing copper content. Out of all MgCuZn ferrites, the highest value of B_s was observed for sample sintered at 910 C with 12 mol% Cu. The Mg-ferrite is a spinel with an inversion degree of about 0·8 (Smit and Wijn 1959) with cation distribution: $Fe_{0\cdot82}$ $Mg_{0\cdot18}\{Mg_{0\cdot82}\,Fe_{1\cdot18}\}O_4$, where brackets denote B-sites. In the case of MgZn ferrites, the stable Zn^{+2} ions occupy the A-sites only. By the addition of Mg^{+2} ions with Cu^{+2} on the octahedral sites (B-sites), an increase of magnetization of B sublattice takes place, leading to increase of the B_s and T_C.

One can observe from the table that m_i increases with increasing copper content in MgCuZn ferrite. The increase of m_i in the ferrites can be correlated with an increase of grain size by the substitution of copper. It is known that the permeability is related to two different magnetizing mechanisms: spin rotational magnetization and domain wall motion. Globus *et al* (1968) suggested that the domain wall motion was affected by the grain size and enhanced with the increase of the grain size. Figure 3 gives the plots of permeability vs temperature for the few selected samples. It is evident from the figure that m_i remains constant over a wide temperature range for all the samples. Among all the ferrites a good thermal stability was observed for the sample with 12 mol% of Cu. For higher copper (14 mol%) content, m_i increases continuously with temperature and shows a broad peak in the vicinity of Curie temperature. The Curie temperature (T_C) was measured from these plots and presented in table 1. The T_C for the present samples increases from 470 ± 1 K to 510 ± 1 K with an increase of Cu content from 1 to 14 mol%. For the polycrystalline samples the shape of m_i–T curve depends strongly on the preparation conditions.

As the MgCuZn ferrites with 12 mol% Cu and sintered at 910°C possess high resistivity and quality factor, the ferrites were used to fabricate multilayer chip inductors. From the above studies, it was concluded that the MgCuZn ferrites with 12 mol% Cu content could be densified below 910 C, these ferrites were used to fabricate multilayer chip inductors by green sheet lamination and screen-printing. The chips were sintered at 890°C, 900°C, and 910°C for 12 h. The size of the fabricated multilayer chip inductors is 30 × 15 × 0·5 mm. The chips were then coated with Ag terminal electrodes. Table 2 gives the room temperature values of d.c. resistance, inductance (L), and initial permeability (m_i). For the sake of comparison the values of d.c. resistance, L, and m_i for the NiZnCu ferrite chip inductors (Nam *et al* 1995) are also included in the table.

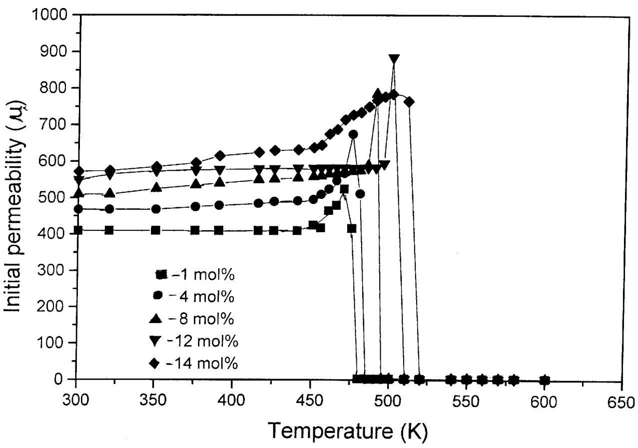

Figure 3. Effect of cupric oxide on thermal variation of initial permeability for MgCuZn ferrites.

Table 2. D.c. resistance of the fabricated multilayer chip inductors.

Composition	Sintering temperature (°C/h)	Initial permeability (m_i)	Resistance (ohms)	Inductance (L) (mH)
MgCuZn	890/12	450	0·104	4·98
NiCuZn	890/6	450	0·1	3·95
MgCuZn	900/12	590	0·115	5·78
NiCuZn	900/6	580	0·104	4·50
MgCuZn	910/12	650	0·215	6·61
NiCuZn	910/6	620	0·127	4·92

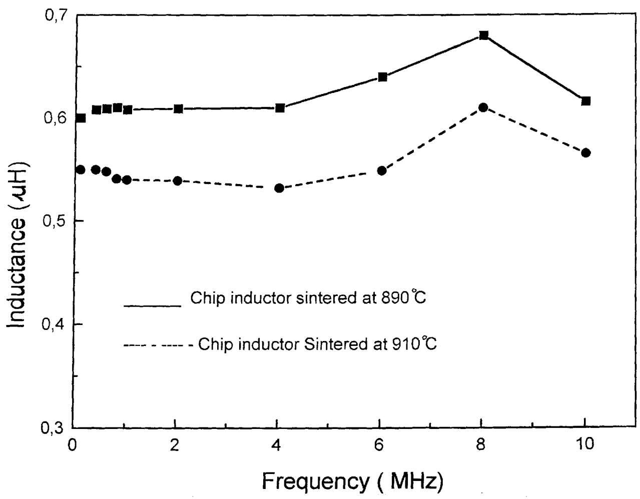

Figure 4. A plot of inductance (L) vs frequency for ferrite chip.

It can be seen from the table that the initial permeability, resistance and inductance of the chip inductors increased with increasing sintering temperature and the inductors sintered at 910°C/12 h exhibited the highest values. It is evident from the table that the initial permeability of MgCuZn ferrite is higher than NiCuZn ferrite, when the ferrites are sintered at 900°C and above. Although both the ferrite chip inductors have almost same permeability, the MgCuZn chip inductors possess higher resistance and inductance.

Figure 4 gives the plot of frequency variation of inductance (L) for the MgCuZn ferrite chip inductors. It can be seen from the table that the inductance for all the chip inductors remains constant in the frequency range 0·1 to 10 MHz. The Q value remains small and decreases with an increase of frequency. From these studies it is expected that good quality chip inductors can be obtained using the MgCuZn ferrites.

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