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Influence of PbO and Ta_2O_5 on Some Physical Properties of MgCuZn Ferrites

Two series of MgCuZn ferrites are prepared by addition of Ta^{5+} and Pb^{2+} ions, separately. The variations of the sintered density, initial permeability, saturation magnetization, Curie temperature and electrical resistivity with the dopant concentration have been studied. The sintered density was found to increase when PbO content is 0.6 wt% or larger. Samples doped with PbO exhibit an appreciable higher resistivity compared to Ta-doped and undoped samples as a result of the insulating layers on the grain boundaries. The temperature dependence of the electrical resistivity shows a change in slope in the neighbourhood of Curie temperature for all samples and this has been attributed to the influence of the magnetic ordering on the conduction mechanism. Also PbO addition improves the temperature dependence of the initial permeability. The origin of the beneficial effect of PbO compared to Ta_2O_5 is believed to be attributed to the melting of PbO and formation of liquid phase at grain boundaries.

Keywords: ferrites; additives; densification; magnetic properties; electrical properties

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1. Introduction

MgCuZn ferrite is a pertinent magnetic material for applications owing to its properties at higher frequency (high resistivity, high Curie point, environmental stability, low cost) and lower densification temperature than Ni-Zn ferrite (REZLESCU N. et al., 1998; REZLESCU E. et al., 1998). Indeed, they can be prepared easily by standard ceramic technology.

It is known that the intrinsic parameters of a ceramic material depend on the composition, technological factors and additives or substitutions (MOULSON, HERBERT). By introduction of a relatively small amount of foreign ions, an important modification of both structure and electromagnetic properties can be obtained.

First of all, it is important in many applications to control the electrical resistivity of the ferrites to asure low losses. Secondly, for high frequency application, porosity is the main problem for Mg-based polycrystalline ferrites. Generally, these two problems can be solved by controlling the firing temperature and atmosphere or by selected additives.

Previously we investigated the effect of additives including CaO, Na_2O, ZrO_2, Li_2O, K_2O, and Sb_2O_3 on the properties of LiZn and NiZn ferrites (REZLESCU et al., 1992; REZLESCU, REZLESCU, 1995). It has been shown that certain additives act beneficially on the densification of the ferrites and other additives can make it possible to increase remarkably the electrical resistivity.

The additives chosen for the present work are PbO and Ta_2O_5. Owing to its melting point (880^0C), PbO acts as a flux, which significantly reduces the sintering temperature and facilitates the growth of grains. The influence of PbO on MgCuZn ferrites has not appeared in the literature. Tantalum oxide, Ta_2O_5, is known to be an effective additive to form a fine-grained microstructure (ZDINARSIC, LIMPEL, DROFENIK).

The effect of PbO (doping level: 0 – 1.5 wt%) and Ta_2O_5 (doping level: 0 – 0.6 wt%) on the ceramic parameters of a MgCuZn ferrite (grain size, density), on the crystallographic (lattice constant) and on the electromagnetic properties (magnetization, initial permeability, Curie temperature, electrical resistivity) is investigated. The objective of this study was to enhance the properties of MgCuZn ferrites by sintering at temperatures as low as possible. The beneficial effect of PbO on the densification and resistivity was observed. The results are compared with those of pure MgCuZn ferrite.

2. Experimental procedure

The primary ferrite composition, $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ has been selected for the studies. Two series of MgCuZn ferrites have been prepared by addition of Ta^{5+} and Pb^{2+} non-magnetic ions, separately. The Ta_2O_5 and PbO were added in the range from 0 to 1.5 wt%. The chemical constituents (MgO, CuO, ZnO, Fe_2O_3, Ta_2O_5 and PbO) were mixed in a ball mill for 2 hours and then were pressed with mechanical hand press into toroid and disc shapes, using an uniaxial pressure of $5 \cdot 10^7$ N/m^2 without any lubricant. The pressed discs (17 mm diameter, 5-6 mm thick) and toroids (16 mm outside diameter, 8 mm inside diameter, 5 mm thick) were sintered in a closed alumina crucible to prevent evaporation of volatile oxides. For sintering experiments, the samples were sintered for 2 hours at one of the followings temperatures: 800, 900, 950, 1000, 1050 and 1100^{0}C, for each treatment. The heating and cooling rates were of 2 – 5 grade/min. After each treatment, the weight and dimensions of the pellets were measured at room temperature to determine sintered densities. All samples were investigated by means of X-ray diffraction, using CoKα radiation to confirm spinel structure and the absence of secondary phases. Microstructure investigations were carried out on fractured surfaces of the samples using optical microscopy.

The specific saturation magnetization σ_s was measured on the spherical samples (3 mm diameter) prepared from toroids, at room temperature, by a vibrating sample magnetometer, in a field of 5 kOe. The initial magnetic permeability μ_i was measured at a frequency of 1 kHz by the bridge method in an a.c. field of 5 mOe. The d.c. resistivity ρ was measured on the silvered pellets by the bridge method too.

3. Results and Discussion

The amounts of Ta_2O_5 and PbO added to the $Mg_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ ferrite are the followings: for PbO: 0.3, 0.6, 0.9, 1.2 and 1.5 wt%; for Ta_2O_5: 0.05, 0.1, 0.2, 0.4 and 0.6 wt%. The effect of mentioned additives on the MgCuZn ferrite are discussed through sintering behaviour, microstructure evolution and magnetic properties.

3.1. Densification and structure

The crystal structure was identified by XRD, using CoKα radiation (λ = 1.789 Å). All compounds studied crystallise in cubic symmetry, even in the presence of Jahn-Teller ions. The lattice constant a_0 for some samples sintered at 1050^{0}C are given in Table 1.

The slight increase of a_0 in the range 8.4006 – 8.4196 Å, should be attributed to the presence of a few Ta^{5+} or Pb^{2+} ions on the substitutional or interstitial positions in the host spinel lattice. However, for high doping level, a_0 does not differ so much from that of the undoped sample. This fact reveals a good formed crystalline structure.

Table 1: Lattice constant a_0 for some samples sintered at 1050°C

Additive content (wt%)	a_0 (Å)	Standard deviation
no additive	8.4006	0.0020
0.05 Ta_2O_5	8.4165	0.0048
0.2 Ta_2O_5	8.4131	0.0049
0.6 Ta_2O_5	8.4029	0.0044
0.3 PbO	8.4158	0.0040
0.6 PbO	8.4196	0.0024
1.2 PbO	8.4094	0.0026

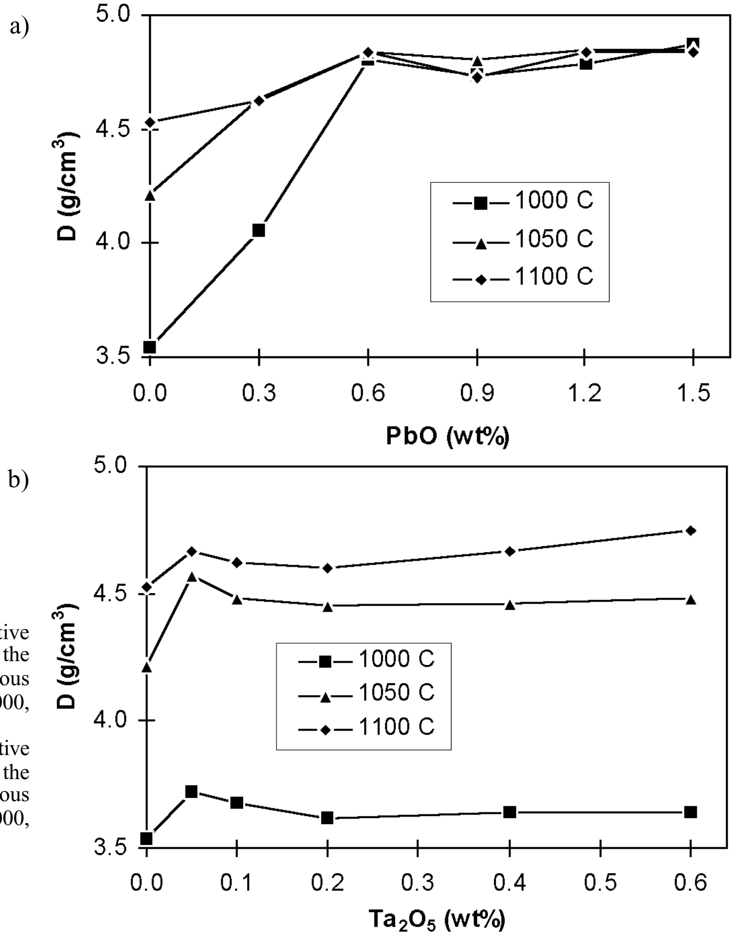

Fig. 1: a) - Effect of PbO additive content on the bulk density of the MgCuZn ferrite at various sintering temperatures (1000, 1050 and 1100°C)
b) - Effect of Ta_2O_5 additive content on the bulk density of the MgCuZn ferrite at various sintering temperatures (1000, 1050 and 1100°C)

Figs. 1a and 1b shows the effect of PbO and Ta_2O_5 content on the bulk density of the MgCuZn ferrite sintered at 1000, 1050,and 1100°C. There is an essential difference between the two dopants. The PbO leads to an important increase in the bulk density for the PbO content of 0.6 wt% after that remained constant with a further increase of PbO independent on the sintering temperature.

Contrary to PbO, Ta_2O_5 has a minor influence on the bulk density, independent on the amount. As revealed in Fig. 2, the density of the Pb-doped ferrites was significantly increased as sintering temperature was raised to 1000^0C. Beyond 1000^0C, the bulk density remains practically constant or has a slight tendency to decrease.

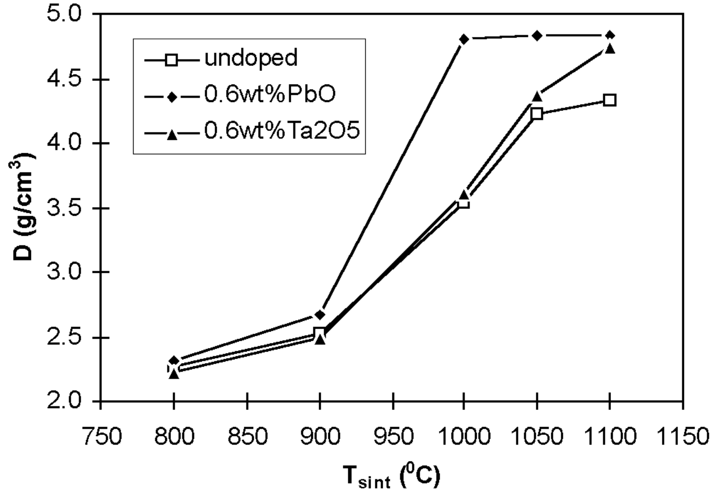

Fig. 2: Densification curves for the Mg Cu Zn Fe_2O_4 ferrite undoped and doped with 0.6 wt% PbO and 0.6 wt% Ta_2O_5, respectively

The bulk density of Ta-doped ferrites shows a continuous increase, which means that a higher temperature is necessary to reach a higher density. The results clearly indicate that an addition of PbO of minimum 0.6 wt% can improve the sintering temperature. During sintering experiments, a strong compaction of specimens was observed.

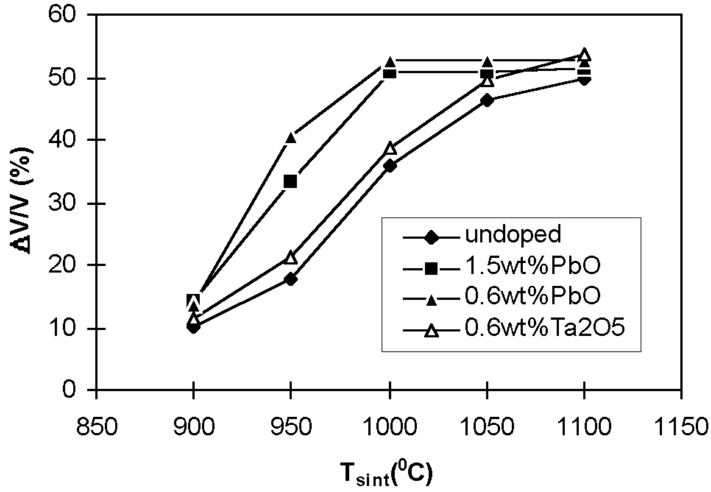

Fig. 3: Relative shrinkage vs sintering temperature for samples undoped and doped with PbO and Ta_2O_5

In Fig.3 the relative volumic shrinkage $\Delta V/V_0$ is plotted versus sintering temperature for some specimens. One can remark an important change in the sintering behaviour of Pb-doped ferrite compared to Ta-doped ferrite. The shrinkage starts at lower temperatures for the Pb-containing samples as their densification. The volume shrinkage was associated with an interdiffusion mechanism favoured by liquid phase, but not with a loss of weight from the material during the sintering. As can see in Fig.4, the samples doped with Ta_2O_5 and those undoped have a little weight loss ($\Delta m/m_0$), below 0.4 %. The highest weight loss, of 1.6 wt%, was measured for only 1.5 wt% PbO at 1100^{0}C and it decreased below 1% with decreasing PbO content.

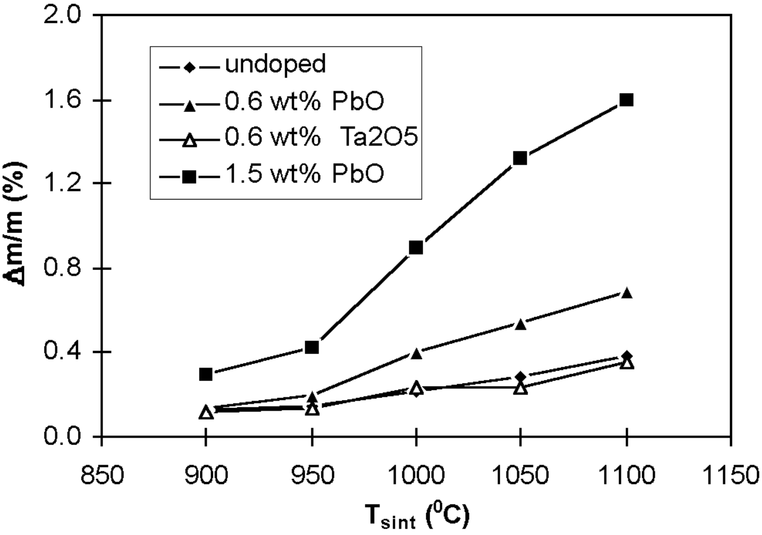

Fig. 4: Weight loss vs sintering temperature for samples undoped and doped with PbO and Ta_2O_5

Table 2: Additive content, average grain size and observations upon microstructure

Additive (wt%)	D (µm)	Observations
No additive	8-10	uniform distribution of small crystallites; a few agglomerated crystallites
0.3 PbO	10-30	spherical granulation; large granule size distribution
0.6 PbO	10-50	spherical granulation; a few large faceted crystallites
0.9 PbO	10-50	spherical granulation; a few large faceted crystallites
1.2 PbO	10-100	spherical granulation; not uniform grain size
1.5 PbO	10-100	spherical granulation; not uniform grain size
0.05 Ta_2O_5	< 1	small crystallites and a few agglomerations of very small crystallites
0.1 Ta_2O_5	5-8	small crystallites; a few large crystallites
0.2 Ta_2O_5	4-6	small crystallites; a few large crystallites
0.4 Ta_2O_5	< 4	homogeneous fine-grained microstructure
0.6 Ta_2O_5	< 4	homogeneous fine-grained microstructure

The microstructure observations (Table 2) on the fracture surfaces, of the specimens sintered at 1050^{0}C, revealed important differences between Pb- and Ta-doped ferrites. On the one hand, the Pb-doped samples exhibit a granular structure with spherical shape, while Ta-doped ones contain the grains with faceted shapes. On the other hand, the two types of additives had the opposite influence on the grain size. The Ta-doping reduces the average grain size under 4 μm but PbO increases it very much, from 8-10 μm to about 50-100 μm. Also, one observed the same granular structures for the samples with large amount of dopant and this fact can explain the approximately same densities obtained beyond 0.6 wt% PbO (Fig.2). Although the precise value of solubility of Pb in MgCuZn ferrite is not known yet, however, it is plausible to suppose that the liquid phase sintering should be a possible mechanism in the PbO-doped ferrites. Material transport assisted by the liquid phase enhances grain growth and can accelerate densification process by the facilitation of the lattice diffusion of the cations (Coble, Gupta, 1967; Gupta, Coble, 1968). On the mechanism of the grain growth in liquid matrices was discussed in (Park, Whang, Yoon).

3.2. Magnetic characteristics

The magnetic parameters are summarised in Table 3. As shown in Table 3 and in Fig.5, PbO addition in MgCuZn ferrite led to minor change in original initial permeability. Only a few samples have slightly higher μ_i values than that of the undoped samples. This means that the magnetic state of ferrite is slightly influenced by the presence of Pb^{2+} ions.

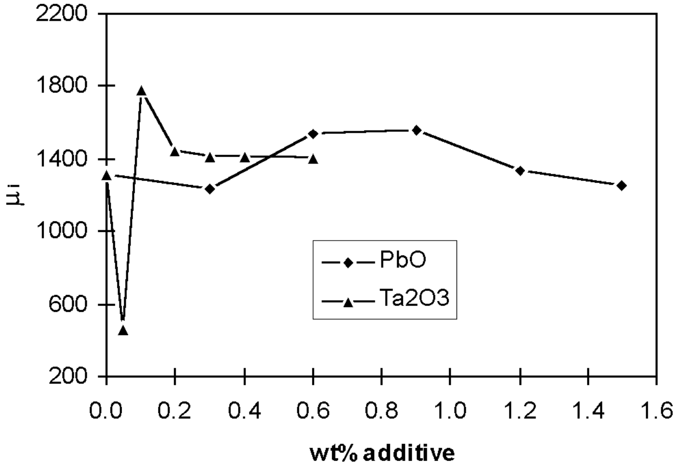

Fig. 5: Effect of PbO and Ta_2O_5 amount on the initial permeability of the samples sintered at 1050°C

Table 3: Initial permeability, saturation magnetization and Curie temperature for Pb- and Ta-doped MgCuZn ferrites

Pb-doped ferrite				Ta-doped ferrite			
PbO (wt%)	μ_i	σ_s (emu/g)	T_c (^{0}C)	Ta_2O_5 (wt%)	μ_i	σ_s (emu/g)	T_c (^{0}C)
0	1180	57.5	128	0	1180	57.5	128
0.3	1120	59.0	138	0.05	480	58.4	132
0.6	1380	59.7	137	0.1	1700	59.5	128
0.9	1370	58.9	137	0.2	1580	58.1	132
1.2	1220	60.2	147	0.4	1430	60.0	127
1.5	1170	62.0	137	0.6	1280	59.2	127

When the doping level is less of 0.6 wt%, the amount of PbO appears to be too low to give homogeneous liquid sintering. At 0.6 wt% doping, the presence of a few large faceted crystallites gives a higher value of μ_i. At higher doping level, the increased liquid phase allows a grain structure with important intragranular porosity and μ_i decreases.

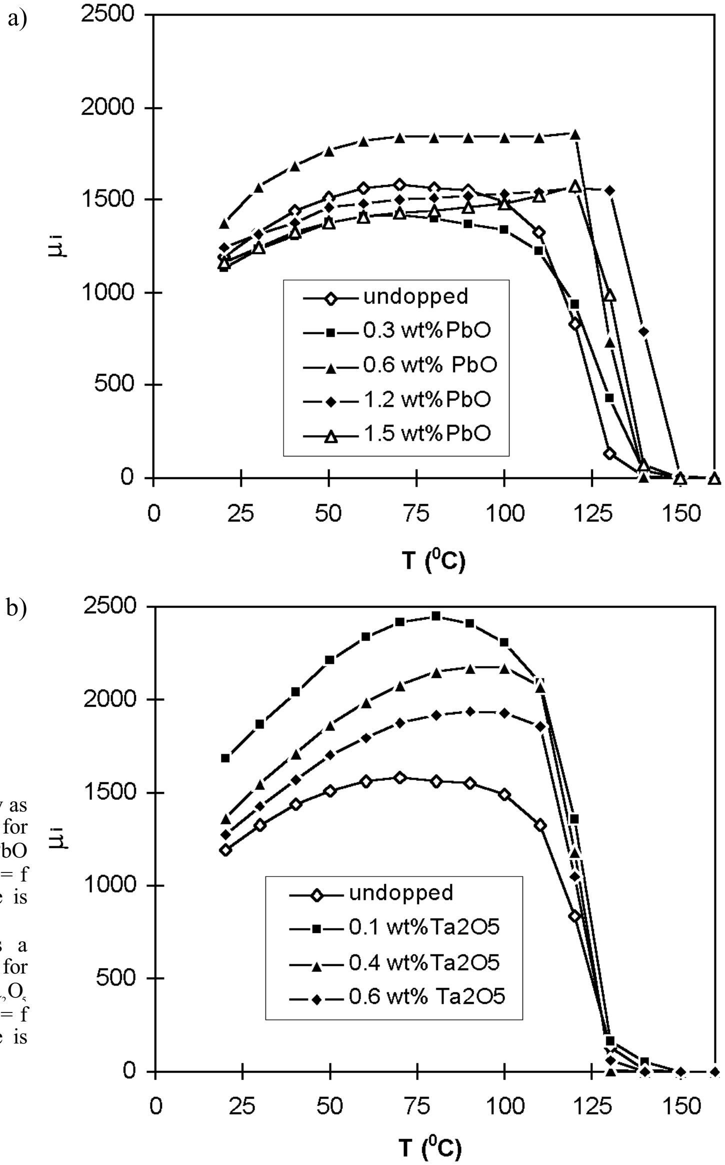

Fig. 6: a) - Initial permeability as a function of temperature for MgCuZn ferrite with PbO additive, sintered at 1050°C; $\mu_i = f(T)$ curve for undoped ferrite is given for comparison
b) - Initial permeability as a function of temperature for MgCuZn ferrite with Ta_2O_5 additive, sintered at 1050°C; $\mu_i = f(T)$ curve for undoped ferrite is given for comparison

For Ta^{5+}-doped samples, the μ_i value decreases sharply for small Ta_2O_5 addition (0.05 wt%), then increases back to the highest value at 0.1 wt% doping level. Beyond this, μ_i decreases again. The low permeability of the samples doped with 0.05 wt% Ta_2O_5 was attributed to the presence of a few agglomerations containing very small crystallites, smaller than a micron. In this case, one can suppose that the permeability is almost determined by the spin rotation magnetizing mechanism (SMIT, WIJN). At 0.1 wt% Ta_2O_5 doping level, the presence of the large crystallites embedded in a fine grain matrix give a higher value of the initial permeability μ_i.

For applications it is very important the temperature dependence of the initial permeability μ_i. Figs. 6a and 6b shows the temperature characteristics of the μ_i for all specimens. One can remark that the PbO addition induces the flattening of the μ_i = f (T) curves over a large temperature range, 50 – 125^{0}C, and a decrease of initial permeability, μ_i, when the doping level is higher than 0.6 wt%. The good temperature dependence of the initial permeability in the Pb-doped specimens can be related to the microstructural changes induced by lead ions. Further investigations will be necessary in order to clarify the factors affecting the temperature dependence of μ_i.

From the Table 3 one can observe that both dopants influence in a small measure the magnetization and the Curie temperature also. The increase of the average particle size should be the cause of the larger values of the magnetization of the Pb-doped ferrites compared to the Ta-doped ones, taking into account that the micronic grain ferrites have a magnetization primarily controlled by domain wall motion (LE FLOC'H, KONN).

3.3. Electrical properties

Electrical resistivity measurements show the semiconducting behaviour of the compounds and conduction is due to the hopping of charge carriers between Fe^{2+} and Fe^{3+} ions on the octahedral sites. There is an essential difference between Ta_2O_5 and PbO regarding the electrical resistivity values. Samples doped with PbO exhibit an appreciably higher resistivity compared to Ta-doped and undoped samples, as can be seen in Fig. 7.

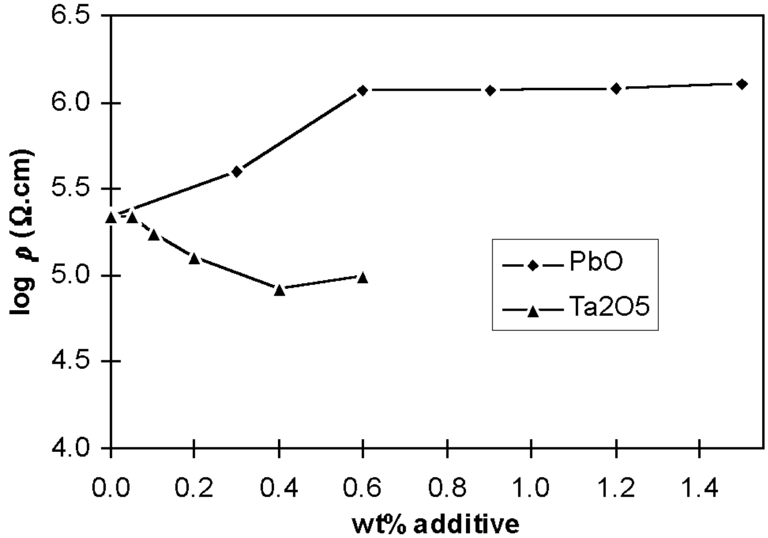

Fig. 7: Effect of PbO and Ta_2O_5 content on the electrical resistivity of the MgCuZn ferrite sintered at 1050^{0}C

The addition of Ta_2O_5 caused decrease in resistivity without grain growth. Although the fine microstructure induced by addition of Ta_2O_5 must lead to increase resistivity due to the increasing the grain boundary surface, however, the Ta-doped ferrites exhibit a decrease in the resistivity. According to the mechanism proposed by Yamamoto (YAMAMOTO, MAKINO, NIKAIDOU), the decrease of the ρ in the Ta-doped ferrites should be closely related to the creation of the cation vacancies to maintain the electroneutrality. These vacancies lead to the increase of electrons as a result of dissociation of oxygen in the vicinity of cation vacancies. On the other hand, the increase of the resistivity of Pb-doped samples by around one order of magnitude was attributed to the insulated liquid films on the grain boundaries.

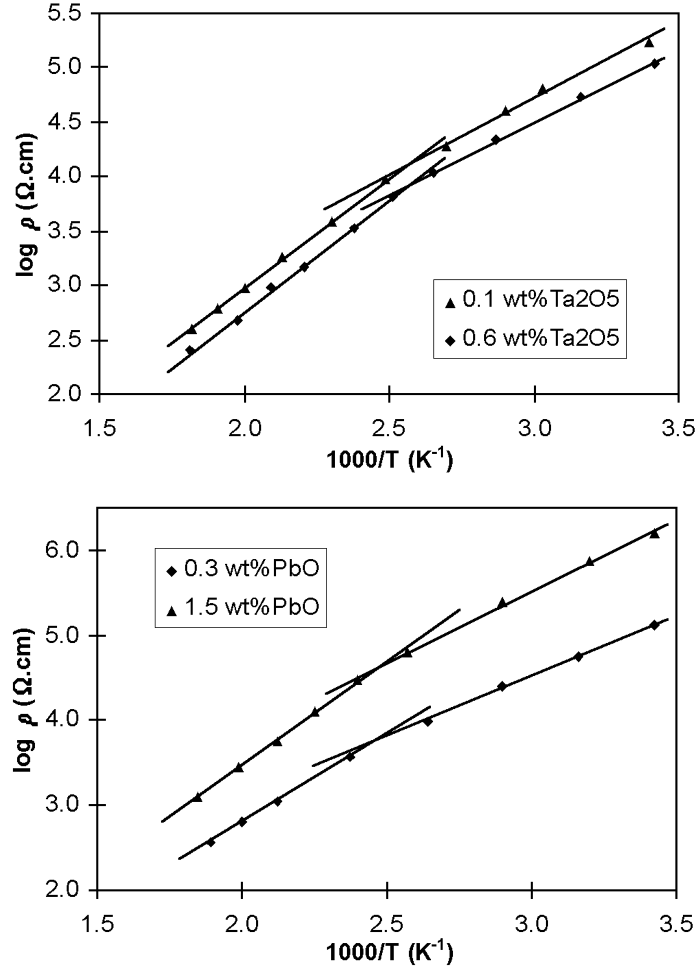

Fig. 8: a) - Logarithm of electrical resistivity as a function of reciprocal temperature for Ta-doped MgCuZn ferrite, sintered at 1050°C
b) - Logarithm of electrical resistivity as a function of reciprocal temperature for Pb-doped MgCuZn ferrite, sintered at 1050°C

The temperature dependence of ρ was measured between room temperature and 250°C. The variation of the log ρ as a function of reciprocal temperature for the samples doped with Ta_2O_5 and PbO is plotted in Figs. 8a and 8b. One can observe the followings: (1) In the investigated temperature range, the resistivity decreased by about three orders of magnitude.

This strong increase in the conductivity with temperature must be regarded mainly as due to the thermally activated mobility of the charge carriers, but not to a thermally activated creation of these carriers; (2) All curves show a change of the slope in the neighbourhood of the Curie point. This is a proof of the influence of the ferrimagnetic ordering on the conductivity process; (3) An increase in the activation energy on passing from the ferrimagnetic to paramagnetic region was obtained.

Table 4: Resistivity and activation energy for undoped and doped MgCuZn ferrites

Sample	ρ (Ω cm)	Activation energy (eV)	
		Below T_c	Above T_c
undoped	$2.20 \bullet 10^5$	0.291	0.411
0.1 wt% Ta_2O_5	$1.73 \bullet 10^5$	0.289	0.402
0.2 wt% Ta_2O_5	$1.30 \bullet 10^5$	0.284	0.404
0.4 wt% Ta_2O_5	$8.44 \bullet 10^4$	0.240	0.357
0.6 wt% Ta_2O_5	$1.01 \bullet 10^5$	0.247	0.370
0.3 wt% PbO	$1.16 \bullet 10^5$	0.290	0.400
0.6 wt% PbO	$1.17 \bullet 10^6$	0.300	0.440
0.9 wt% PbO	$1.18 \bullet 10^6$	0.294	0.475
1.2 wt% PbO	$1.20 \bullet 10^6$	0.356	0.488
1.5 wt% PbO	$1.26 \bullet 10^6$	0.366	0.498

The activation energy calculated from the slopes of plots log ρ vs. $10^3/T$ (both above and below the Curie point) is related to the change of the d.c. resistivity: it decreases for the Ta_2O_5 additive and increased for PbO (Table 4) and this result suggests the existence of a conduction sensitive to structure. The small values for the activation energies confirm the electronic character of the conduction process that consists in the hopping of electrons between Fe^{2+} and Fe^{3+} ions, statistical situated on octahedral spinel sites ("hopping process") (SMIT, WIJN).

4. Conclusions

The above results reveals that from the viewpoint of effectiveness, the PbO was found to be better than Ta_2O_5 for improvements in the magnetic and electrical properties of the MgCuZn ferrite used in high frequency.

The added PbO, because of its low melting temperature, can favour both densification of the ferrite at lower temperature (1000^{0}C) and the grain growth when the doping level is more than 0.6 wt%. PbO increased the electrical resistivity of the original ferrite with about one order of magnitude. Also, PbO improves the temperature dependence of initial permeability over a large temperature range (50 – 125^{0}C).

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