

Microstructure and magnetic and electrical properties of low-temperature sintering Ni-Zn, Li-Zn and Mg-Zn-Cu ferrites without and with addition of lead oxide

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The impact of PbO addition on the densification, microstructure and magnetic and electrical properties of NiZn, LiZn and MgCuZn ferrites prepared by ceramic method has been studied. Sintering experiments were carried out with small amounts of PbO, between 0 and 1.5 wt%. Due to low melting point, PbO favors sinterability of ferrites at lower temperatures. A sintered density of about 5 g/cm³ was achieved with 1.2 wt% PbO addition by sintering at 1100°C, that is impossible without PbO. The densification behavior and physical properties of PbO-doped ferrites are closely related to microstructural changes caused by PbO. It was evidenced significant growth of grain size without compromising desirable material properties except for electrical resistivity.

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1. Introduction

Ferrite systems such as Ni-, Li- and Mg-based ferrites are receiving considerable attention for use as electronic materials because of higher Curie temperature, high electrical resistivity and low cost. The preparation of these ferrites by conventional ceramic processing implies high ferritization temperature (1300°C). Two methods can be used to reduce the sintering temperature: (a) the incorporation of dopants into the ferrite lattice [1,2] and (b) the use of sintering aids (low melting additives) able to form a liquid phase (liquid phase sintering) [3,4].

In this work it was investigated the role of the lead oxide addition in the sintering process of three stoichiometric ferrite compositions: Ni_{0.36}Zn_{0.64}Fe₂O₃, Li_{0.3}Zn_{0.4}Fe_{2.3}O₄ and Mg_{0.2}Zn_{0.5}Cu_{0.3}Fe₂O₄ and its effect on the material properties. PbO is a good choice as sintering aid for micro structured modifications since this has a relatively low melting point (880°C) and thus provides an excellent medium for liquid phase sintering. Low levels of PbO are beneficial to the liquid-assisted densification. The material transport assisted by liquid phase accelerates the densification process by facilitation of the lattice diffusion process of the cations and thus the ferritization temperature can be significantly reduced. PbO was less used as additive in the spinel ferrites, probably because of high radius of Pb ions (1.33 Å) [5] compared to host spinel lattice.

2. Experimental

For investigations, three molecular compositions, namely (Ni_{0.36}Zn_{0.64}Fe₂O₃, Li_{0.3}Zn_{0.4}Fe_{2.3}O₄ and

Mg_{0.2}Zn_{0.5}Cu_{0.3}Fe₂O₄) were selected to which x wt% PbO (x = 0.3, 0.6, 0.9, 1.2 and 1.5) was added. The starting reagents (Li₂CO₃, ZnO, Fe₂O₃, NiO, MgO, CuO and PbO) were of high purity (over 99.5%).

The specimens were prepared by usual ceramic technology. The chemical components were mixed in a ball mill for 2 hours and the resulted powder was pressed with a mechanical handpress into toroids and discs using a uniaxial pressure of 5.10⁷ N/m², without any lubricant. The green compacts were heat treated at low temperatures (100, 1000, 1050 and 1100°C in order to prevent Zn or Li volatilization. After each treatment experiment, the weight and dimensions of the discs were measured at room temperature to determine the volume shrinkage and density.

Microstructure and intrinsic parameters were investigated on LiZn and MgCuZn ferrites sintered at 1050°C and on NiZn ferrite sintered at 1100°C, for 4 hours.

The phase analysis was determined by powder X-ray diffraction (XRD, DRON-2) using CoK α radiation. The microstructure was investigated by scanning electron microscope (SEM, Tesla 340) on fracture surfaces.

The d.c. electrical resistivity ρ was measured by Wheatstone bridge on the disc samples silvered by vacuum thermal evaporation. The average grain size D_m was determined by the linear intercept method [6] on the SEM micrographs.

The specific saturation magnetization σ_s was measured by a vibrating sample magnetometer, in a field of 5 kOe, on spherical samples, prepared from toroids. The initial magnetic permeability μ_i was measured at a frequency of 1 kHz, by inductance bridge in a field of 5 mOe.

3. Results and discussion

Figs. 1 and 2 show the X-ray diffractograms of LiZn and NiZn ferrites undoped and PbO doped, respectively. XRD patterns confirm the single-phase nature of all compounds and the formation of the cubic spinel structure.

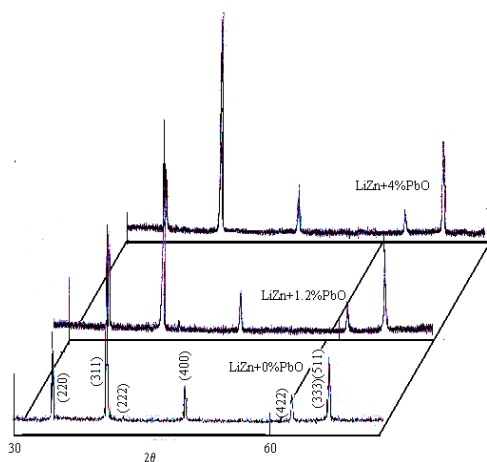


Fig. 1. XRD patterns for three samples of LiZn ferrites sintered at 1050°C

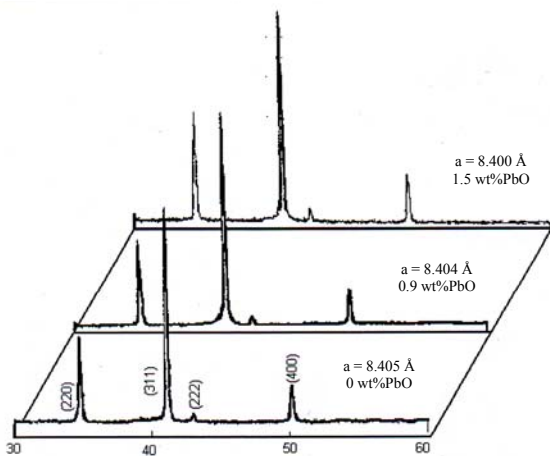


Fig. 2. XRD patterns for three samples of NiZn ferrites sintered at 1100°C.

The effect of PbO on the ferrite microstructure evidently results from the SEM images (Fig. 3). One can remark that the morphology is significantly affected by the PbO content. A spectacular increase in the grain size of the doped ferrites compared to pure ferrites can be seen.

One can also observe a duplex structure in the PbO doped ferrites, consisting of small grain bridges around the large crystallites. These microstructure characteristics of the PbO doped ferrites are specific to the liquid phase sintering mechanism [7-10] the sintering temperature being far above the melting point of PbO (880°C). In this case, the grain growth is a result of interparticle mass transport, where the larger particles grow at the expense of the smaller ones [11]. The mass transport assisted by liquid phase is much faster and a rapid increase of the grains takes place.

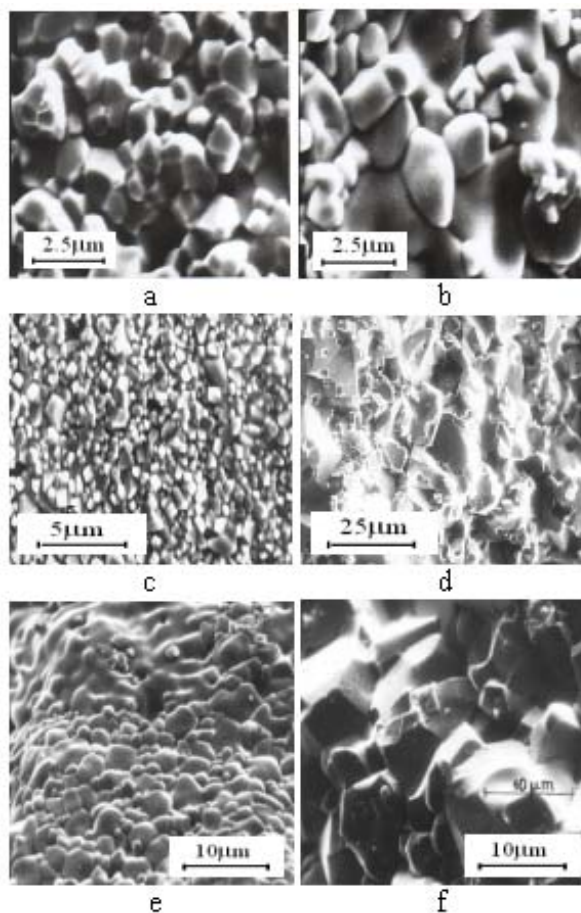


Fig. 3. SEM micrographs of: a) NiZn ferrite with 0%PbO; b) NiZn ferrite with 1.5%PbO; c) LiZn ferrite with 0%PbO; d) LiZn ferrite with 0.9%PbO; e) MgCuZn ferrite with 0%PbO; f) MgCuZn ferrite with 1.2%PbO.

The morphology changes achieved by PbO doping can favor the densification process of the ferrites as can see in Fig. 4 for NiZn ferrites. An important increase in density was obtained by adding 1.2 wt% PbO and for sintering temperature of 1100 °C.

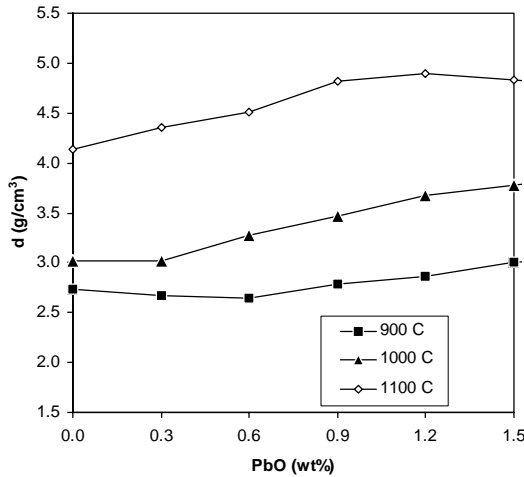


Fig. 4. Sintered density of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrites as a function of PbO additive content, sintered at different temperatures

During the sintering, the densification process of the compacts is accompanied by important volume shrinkage. The relative volume shrinkage ($\Delta V/V_0$, where V_0 is the initial volume of the disc sample) can attain 50% for ferrites having the best densification (Fig.5).

Table 1. Resistivity ρ ($\Omega.cm$), initial permeability μ_i , specific magnetization σ_s (emu/g), density d (g/cm^3) and average grain size D_m (μm) of undoped and 1.2 wt% PbO doped ferrites.

Property	NiZn ferrite sintered at 1100°C		LiZn ferrite sintered at 1050°C		MgCuZn ferrite sintered at 1050°C	
	Undoped	Doped	Undoped	Doped	Undoped	Doped
ρ	10^7	10^6	$2 \cdot 10^6$	$4.3 \cdot 10^2$	$2.2 \cdot 10^5$	$1.2 \cdot 10^3$
μ_i	370	390	126	170	1180	1220
σ_s	51.5	56	72	74.7	57.5	60.2
d	4.1	5	3.9	4.7	4.2	4.8
D_m	0.8	2.0	1.0	20.0	3.0	12.0

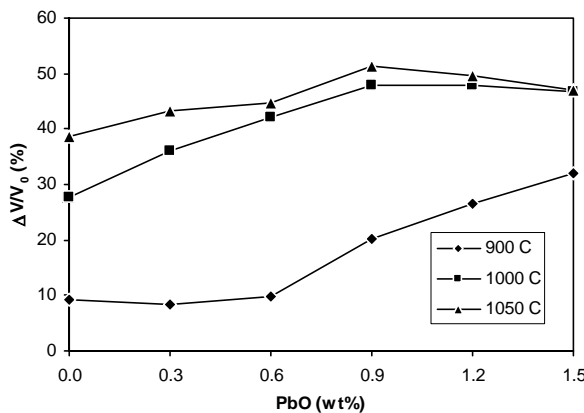


Fig.5 Relative shrinkage versus PbO content for LiZn samples sintered at 900, 1000 and 1050°C

The effect of the micro structural modifications generated by PbO additive on some material parameters was investigated in this work also. In Table 1 are given the density d , average grain size D_m , resistivity ρ , initial permeability μ_i and specific magnetization σ_s of undoped and 1.2 wt% PbO doped ferrites. One can see that PbO did not given a consistent improving of the magnetic parameters (μ_i , σ_s) in the spite of the spectacular increase of the density and grain size. The presence of the intragranular pores or non-homogeneities inside large grains can justify the obtained results. The lack of PbO is that the PbO doped ferrites exhibit a decrease in the resistivity that can be associated to a decrease of the grain boundary surface. However, the main advantage of PbO doped ferrites is their ability to sinter at reasonable low temperatures (1000 – 1100°C) without large energy consumption, that is nearly impossible without PbO addition.

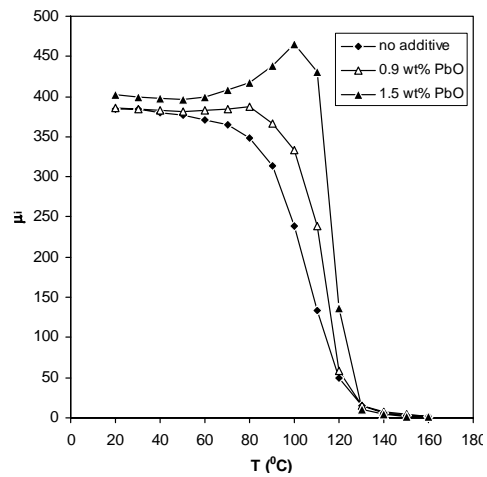


Fig. 6. Temperature dependence of the initial permeability for some NiZn ferrites samples sintered at 1100°C for 3 hours

For applications, it is very important the temperature variation of resistivity and initial permeability. In Fig.6 one can observe that the PbO incorporation in NiZn ferrite induces a good thermal stability of μ_i over 20 – 70°C temperature range.

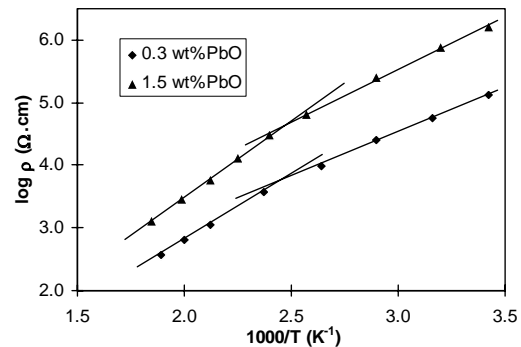


Fig. 7. Logarithm of electrical resistivity as a function of reciprocal temperature for PbO-doped MgCuZn ferrite, sintered at 1050°C

In Fig. 7 is plotted the temperature variation of ρ between room temperature and 250°C for MgCuZn ferrite doped with PbO. 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 neighborhood of the Curie point. This is a proof of the influence of the ferrimagnetic ordering on the conductivity process.

4. Conclusions

The low temperature sinterability of LiZn, NiZn and MgCuZn ferrites has been improved by doping with PbO.

By sintering experiments it was appreciated that an addition of 1.2 wt% PbO to ferrite composition is recommended to obtain high density at relatively low sintering temperature. Higher concentrations of PbO can favor an exaggerated grain growth and the occurrence of intragranular pores deteriorating the material parameters.

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