

The effect of the additives and sintering temperature on the structure and humidity sensitivity of a spinel ferrite

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The humidity-sensitive characteristics of MgZn ferrite as a function of the additive type and sintering temperature are investigated. As dopants are used CaCl_2 , KCl, LiCl and NaCl. The microstructure is dependent upon the sintering temperature and additive kind. All samples exhibit a significant decrease in the specific resistance in the humidity interval 33% RH – 98%RH. The KCl doped ferrite, characterized by higher porosity, shows a shorter response time (3 – 4 minutes) than that of the CaCl_2 doped sample (of about 6 minutes).

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1. Introduction

The polycrystalline magnesium ferrites are of great interest in many applications due to their high resistivity ($> 10^5 \Omega\cdot\text{cm}$). These ferrites have the advantage to have chemical and thermal stability. During the last years, magnesium ferrite has been investigated as sensing material in automatic humidity controlling systems. A great advantage of Mg ferrites is their porosity, which is a requirement for a humidity ceramic sensor. Also, this ferrite is an inexpensive material and does not require special conditions for preparation. Seki et al [1] have reported the ferrites utilization as humidity sensors. In the humidity sensors, the carrier concentration and electronic conductivity change with the amount of adsorbed water [2].

Basically, a ceramic sensor can detect humidity on the basis of the variation of the electrical conductivity by water adsorption. A good sensor element must allow a pronounced variation of the electrical conductivity and a short response time when the environmental humidity changes. For a ceramic sensor, the microstructure and specific resistance of the sensor element are two key parameters on which depends the sensor performance.

The present study was concentrated on magnesium-zinc ferrite doped with CaCl_2 , LiCl, KCl and NaCl. These salts can dissociate into alkali and Cl ions by the reaction with adsorbed water and thus, the carrier concentration increases [2]. Vaingankar et al [3] have investigated the humidity sensitivity of electrical properties of CuZn ferrite and they reported that the humidity dependent properties are considerably enhanced by doping with CaCl_2 and LiCl.

The microstructure, electrical resistivity and humidity sensitivity of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite doped with 1% of salts were investigated in this paper.

2. Experimental Procedure

The ferrites were prepared by classical technology, using reagent grade Fe_2O_3 , MgO, ZnO powders. The

additives (NaCl, KCl, LiCl and CaCl_2) of high purity were added in percent of 1% of the host ferrite. The resulting powders were mixed in a ball mill and compacted by uniaxially pressing in a stainless die under $5 \times 10^6 \text{ N/m}^2$. The pressed pellets (17 mm diameter, 3-4 mm thickness) were sintered in air, at three temperatures: 1050, 1100 and 1200°C. For every sintering temperature, we used green samples. After each sintering, the weight and dimensions of the pellets were measured, at room temperature, to determine sintered density and porosity.

The microstructures of the samples were examined by scanning electron microscopy (SEM). The grain size was determined by linear intercept method [4] from micrographs on the fracture surfaces. The phase analysis was made by X-ray diffraction using DRON-2 diffractometer and $\text{FeK}\alpha$ radiation.

For electrical measurement, the flat surfaces of the pellets were chemically silvered at 600°C. The a.c. electrical resistance was measured with LCR meter. The variation of a.c. resistance as a function of relative humidity was made at 100 Hz by using a test chamber in which the various humidities above some saturated salt solutions were obtained.

3. Results and discussions

X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurements were used to analyse the structure of samples. All samples contain a single phase of the spinel structure. The lattice constant was evaluated to be $8.406 \pm 0.0005 \text{ \AA}$ and X-ray density, d_x , was found to be 4.92 g/cm^3 .

SEM micrographs (Fig.1 and 2) on the fracture surfaces of the samples doped with KCl and CaCl_2 evidenced the dependence of the microstructure on the sintering temperature and additive type. Generally, all samples are characterised by a fine granulation. The average grain sizes are within the range 0.5 – 2 μm . The ferrite particles being small, a tendency towards

agglomerations can be observed. Also, one can observe that KCl favours a submicron fine granulation by sintering at 1050°C and a grain growth with sintering temperature more evident than in the case of CaCl₂. In the CaCl₂ doped ferrite (Fig.2) the grain growth seems to be inhibited by segregation of Ca ions on the grain boundaries. Also, one can remark the change of the grain shape from the rounded to faceted crystallites and pore coarsening by increasing sintering temperature from 1050 to 1200°C. Large pores, above 1 µm in diameter, distributed along the grain boundaries and to the junctions between the grains, are necessary for rapid response of sensor, because the adsorption rate of water is controlled by diffusion rate of water vapour. These structures indicate that the investigated ferrites can easily exhibit adsorption and condensation of water vapours. Furthermore, the porous structure is an advantage in discouraging fracture due to thermal shock.

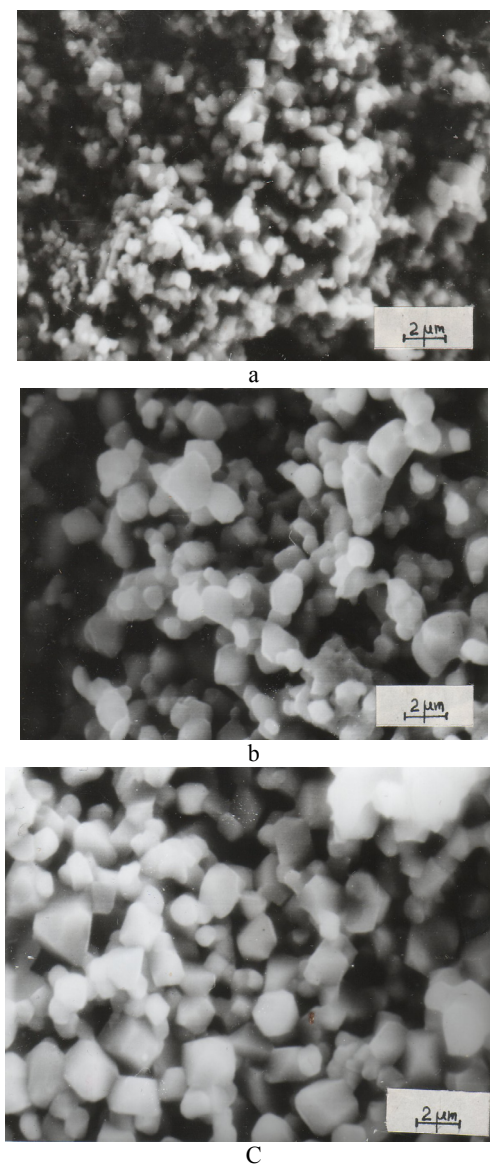


Fig. 1. SEM photographs for KCl doped MgZn ferrites sintered at different sintering temperatures: a – 1050°C; b – 1100°C; c – 1200°C.

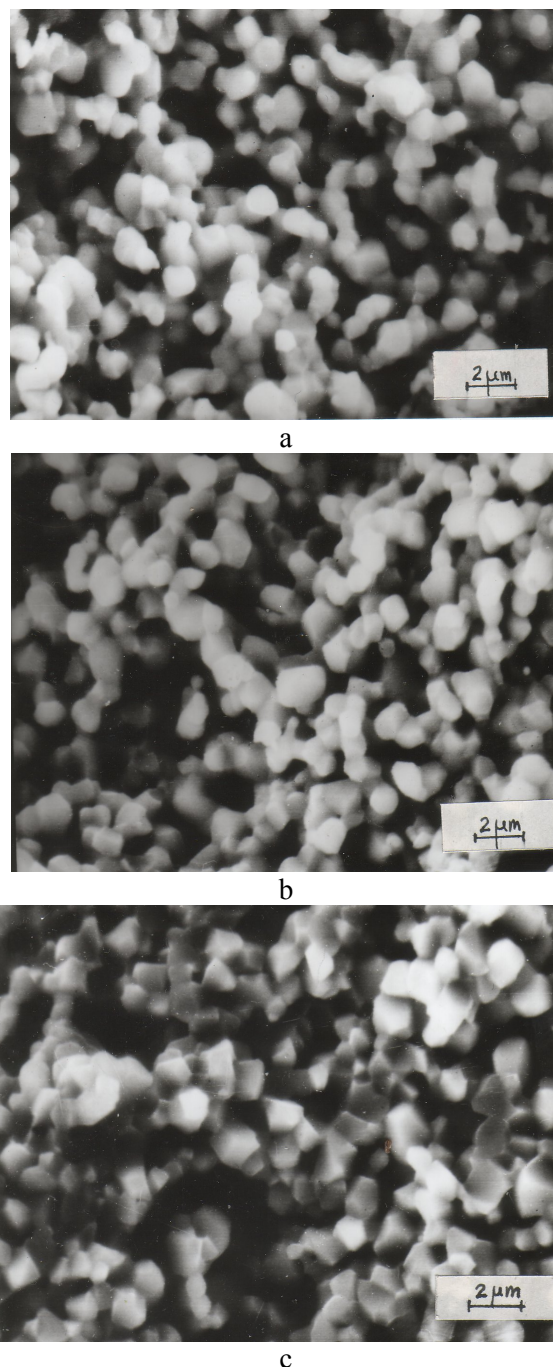


Fig. 2. SEM photographs for CaCl₂ doped MgZn ferrites sintered at different sintering temperatures: a – 1050°C; b – 1100°C; c – 1200°C.

Experimental results (Fig.3) reveal that the porosity is in close relation with the structural changes caused by the dopants and sintering temperature. Thus, MgZn ferrites doped with Ca or Li chlorides achieved a lower porosity by sintering at 1200°C compared to KCl and NaCl doped ferrites sintered at the same temperature. This result can be explained by a better package of the faceted crystallites by doping with CaCl₂, as can be seen in Fig.2c. However, the porous structure is favourable for the adsorption and condensation of water vapours.

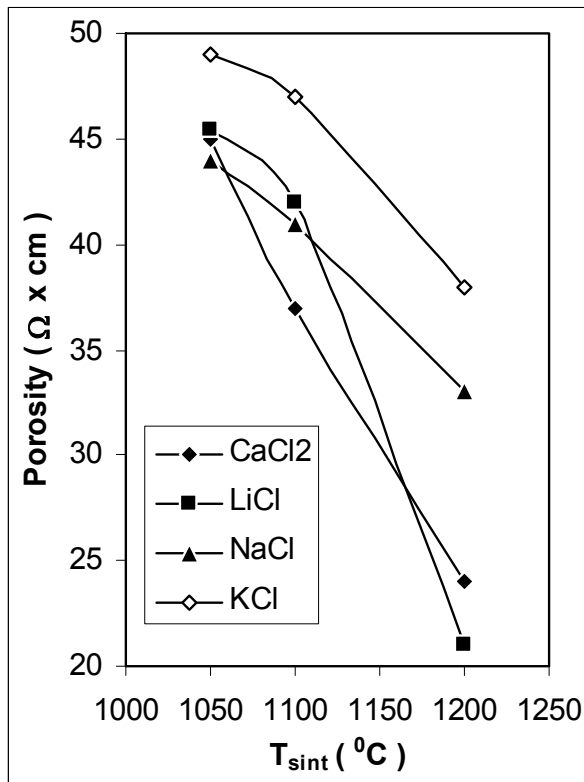


Fig. 3. Porosity for MgZn ferrite doped with CaCl₂, LiCl, NaCl and KCl as a function of sintering temperature.

The structural characteristics of the specimens doped with CaCl₂ and KCl are summarized in Table 1. The surface area A_{sp} was calculated with formula [5]

$$A_{sp} = \frac{S}{Vd} = \frac{6}{dD_m},$$

where S and V are the surface and volume of the ferrite particle, D_m is the average particle size and d is the bulk density. (It was assumed that all the crystallites have the same size and the same shape). One can see that the sintering temperature strongly influences the structural parameters. The specific surface area and porosity of the specimens decrease with increasing sintering temperature, whereas the average grain size and sintered bulk density increase with increase sintering temperature. The largest surface area was found for KCl doped ferrite sintered at 1050 °C and can be attributed to very fine crystallites (see Fig.1a). By increasing the sintering temperature from 1050 °C to 1200 °C the surface area of the KCl doped ferrite decreased by a factor of five due to the growth of crystallites (Fig.1 b and c).

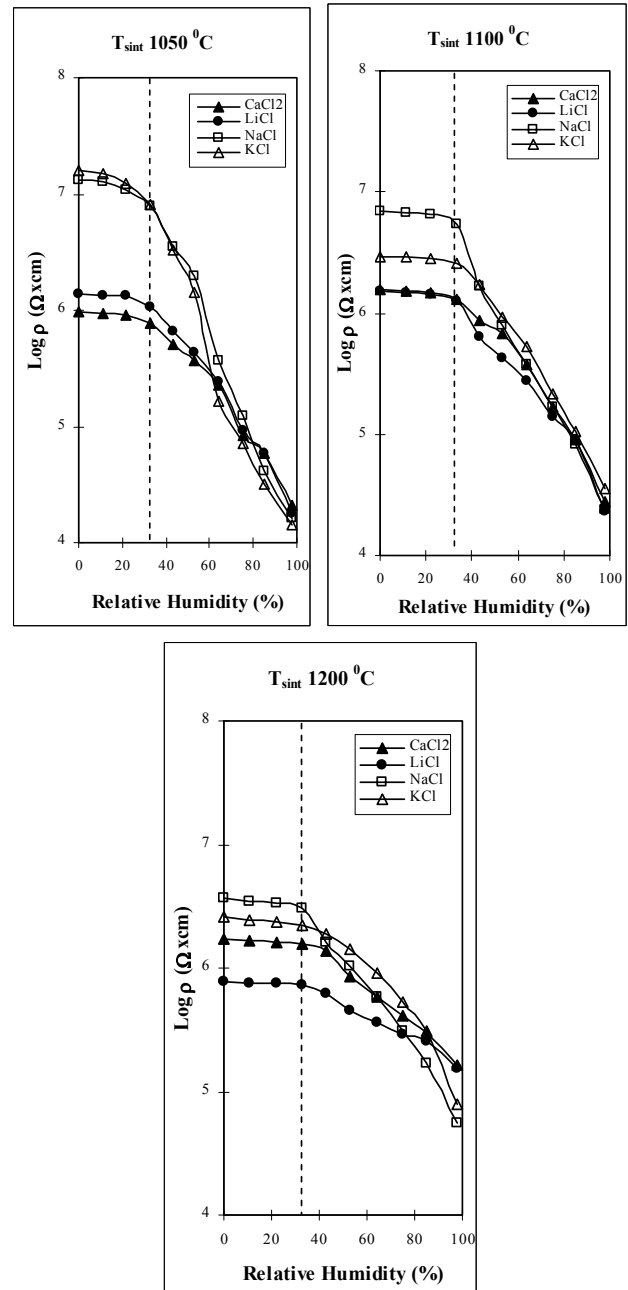


Fig. 4. Log ρ as a function of relative humidity for MgZn ferrites doped with salts and sintered at three sintering temperatures: 1050°C, 1100°C and 1200°C.

The humidity variation of the electrical resistivity was investigated. The log ρ vs. relative humidity RH characteristics are shown in Fig.4, for samples sintered at 1050, 1100 and 1200°C. The graphs clearly show that the electrical resistivity scientifically decreases with increasing relative humidity from 33% to 98% RH. At relative humidities lower than 33% the electrical resistivity practically remains constant because the small quantity of adsorbed water vapour causes an undetectable change in the high value of the resistivity at low humidity. In the humidity range 33% RH – 98% RH, the largest decrease of resistivity was measured for NaCl and KCl doped

ferrites and the smallest variation was measured for CaCl_2 and LiCl doped ones. By sintering at 1050°C the resistivity drops by over three orders in magnitude for NaCl and KCl additions, whereas for CaCl_2 and LiCl additives, the decrease in resistivity is of two orders in magnitude. This behaviour of resistivity shows that, the larger the specific surface area and porosity of the specimens, the more water vapours can be physically

adsorbed, resulting in a larger decrease of resistivity. Indeed, the change of the resistivity by humidity modification is less and less with increasing sintering temperature. For samples sintered at 1200°C the resistivity decreases about one order in magnitude, only, in the interval 33% RH – 98% RH.

Table 1. Structural characteristics of porous sintered MgZn ferrites doped with CaCl_2 and KCl

Sintering temperature ($^\circ\text{C}$)	Additive type	Sintered density d (g/cm^3)	Average grain size D_m (μm)	Specific surface area A_{sp} (m^2/g)	Porosity (%)
1050	KCl	2.53	0.5	4.7	49
	CaCl_2	2.75	1.2	2.2	45
1100	KCl	2.54	1.0	2.4	47
	CaCl_2	3.09	1.0	1.9	37
1200	KCl	3.21	2.0	0.94	35

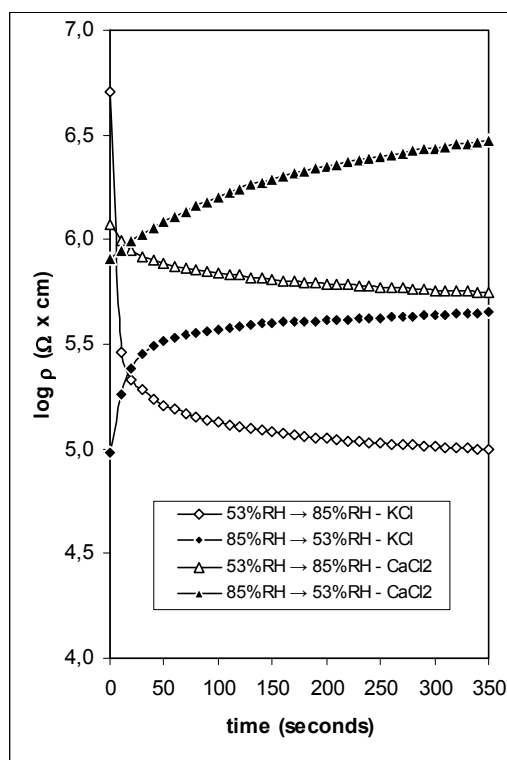


Fig. 5. Response time for $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 0.1\text{wt}\%$ KCl and $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + 0.1\text{wt}\%$ CaCl_2 , sintered at 1100°C .

The response time of the electrical resistivity when the relative humidity increases from 53 to 85% RH and then decreases from 85 to 53% RH is shown in Fig. 5 for MgZn ferrite doped with KCl and CaCl_2 and sintered at 1100°C . The KCl doped ferrite characterized by higher porosity, shows a shorter response time (3 – 4 minutes) than that of CaCl_2 doped sample (of about 6 minutes).

4. Conclusions

The chlorides doped MgZn ferrites sintered at 1050 and 1100°C exhibit a good sensitivity to humidity. In the humidity range of 33% to 98% RH, their resistivity drops exponentially by over two orders of magnitude with increasing the humidity. We think that these materials are promising for use in humidity controlling devices taking in account the low cost and high durability.

References

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