Solid solutions in the system jacobcite $MnFe_2O_4$ – franklinite $ZnFe_2O_4$

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Introduction

Spinel is the general name for all oxide minerals with formula AB_2O_4 (Kostov, 1993). Ferrospinels are spinels containing Fe^{3+} as three-valent ion B^{3+} (Letiuk, Zhuravlev, 1983). The ceramic materials based on ferrospinels are known as ferrites (Gerasimov et al., 2003). The mixed manganese-zinc ferrites $Mn_{1-X}Zn_XFe_2O_4$, like the nickel-zinc ferrites $Ni_{1-X}Zn_XFe_2O_4$, are classified as magnetically soft with usual hysteresis curves and have versatile applications: in radio engineering, radio electronics, radiolocation devices and radio relay systems, as memory units, etc.

The magnetic properties and microstructure of the manganese-zinc ferrites containing CaO have been studied by other authors (Znidarsic, Drifenik, 1999). The mixed Mn-Zn ferrites $Mn_{1-X}Zn_XFe_2O_4$ with X = 0.50, 0.65 and 0.85 sintered in nitrogen atmosphere at 1100°C have 80—85% of the theoretical density and their magnetization is about 90% of the theoretical one (Botta et al., 2004). The size of their crystals is about 5 mm.

The magnetic properties of Mn-Zn ferrite were summarized in (Moulin et al., 2000). The properties of these ferrites depend on their grain size with the limit thickness of the non-magnetic layers being 1.5 mm. The magnetic properties of a composite material formed as Mn-Zn ferrite film deposited onto (100) of monocrystalline periclase were studied by Doesey et al. (1995). Mn-Zn ferrite film with 30 μm thickness was prepared as moisture sensor (Arshaka et al., 2002). The influences of the relative humidity, temperature and time (in months) on sensor resistance were also studied.

The present work is a systematic study on the preparation and properties of the mixed Mn-Zn ferrites.

Experimental

The phase and chemical compositions of the solid solutions synthesized in the system jacobcite $MnFe_2O_4$ — franklinite $ZnFe_2O_4$ are presented in table 1. The table shows also the apparent density and crystal sizes of the mixed manganese-zinc ferrites after sintering at 1300°C for 2 h.

The manganese-zinc ferrites were prepared by a two-stage ceramic technology involved the following operations: grinding and homogenization of the initial mixtures; ferritization; grinding and homogenization of the ferritized material; moulding; sintering. The grinding and homogenization was carried out in a steel ball mill for 6 h at ratio (material)/(mill balls)/(water) equal to 1/4/1. After drying the

Table 1. Composition, apparent density (?) and crystal sizes (d) of Mn-Zn ferrites

Sample	Mn-Zn ferrite	Oxides*, wt.%			Total	1300 °C – 2 h			
		MnO	ZnO	Fe_2O_3		ρ	d, μm		
							d min	d max	d mean
1	$Mn_{0.45}Zn_{0.55}Fe_2O_4$	13.48	18.90	67.62	100.00	5.00	3	20	8
2	$Mn_{0.50}Zn_{0.50}Fe_2O_4$	15.04	17.26	67.70	100.00	4.95	3	21	11
3	$Mn_{0.55}Zn_{0.45}Fe_2O_4$	16.58	15.56	67.86	100.00	4.93	3	24	12
4	$Mn_{0.60}Zn_{0.40}Fe_2O_4$	18.12	13.87	68.01	100.00	4.92	3	28	15
5	$Mn_{0.75}Zn_{0.25}Fe_2O_4$	22.81	8.72	68.47	100.00	4.80	25	420	200
6	$Mn_{0.80}Zn_{0.20}Fe_2O_4$	24.38	7.00	68.62	100.00	4.79	30	480	240
7	$Mn_{0.85}Zn_{0.15}Fe_2O_4$	25.97	5.26	68.77	100.00	4.78	44	500	400

*MnO was introduced as $MnCO_3$. The initial materials — $MnCO_3$, ZnO and Fe_2O_3 were with purities ***p*** and ***pa***.

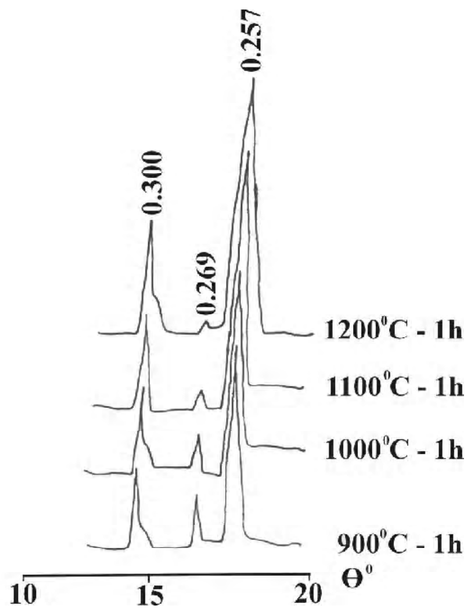

Fig. 1. X-ray diffraction patterns of Mn-Zn ferrite ($Mn_{0.55}Zn_{0.45}Fe_2O_4$) after isothermal retention at 900-1200°C

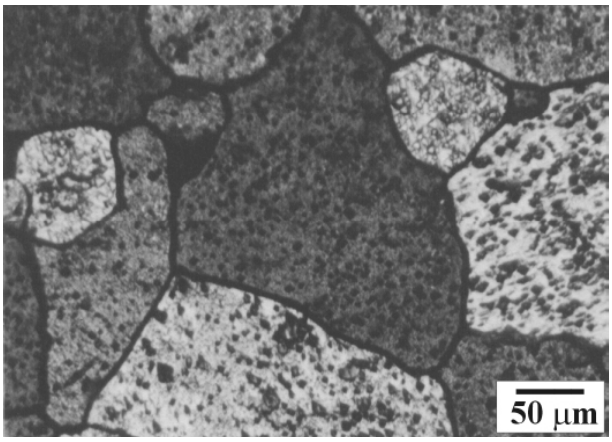

Fig. 2. Manganese-zinc ferrite $Mn_{0.75}Zn_{0.25}Fe_2O_4$ containing 0.05 wt.% MgO. Sintering temperature 1300°C — 2 h. Reflected light. Coarse grained heterogranoblastic structure.

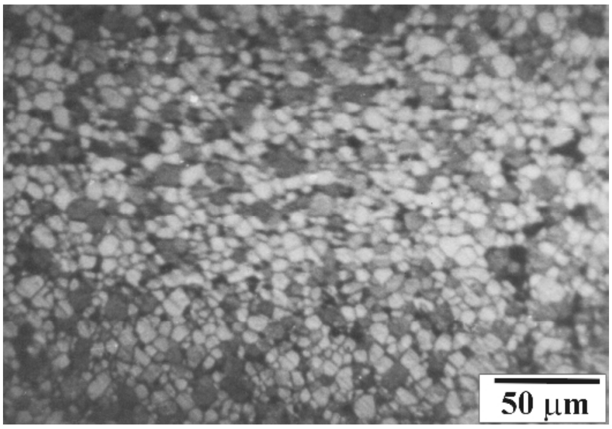

Fig. 3. Manganese-zinc ferrite $Mn_{0.55}Zn_{0.45}Fe_2O_4$ containing 0.05 w% MgO. Sintering temperature 1300°C — 2 h. Reflected light. Non-uniform grain size (homeogranoblastic structure).

product was subjected to ferritization at 1100°C for 1 h to synthesize Mn-Zn ferrospinels. The ferritized mixtures were ground at 6% humidity and granulized through 0.5 mm sieve. Then, test samples were prepared by semi-dry pressing at 50 MPa and sintering at nitrogen atmosphere at 1300°C for 2 h. The sintered samples were rapidly cooled to 100—600°C.

Figure 1 shows the powder diffraction patterns of Mn-Zn ferrites obtained at different temperatures and figures 2 and 3 — the microstructures of the sintered ferrites. The magnetic properties of the Mn-Zn ferrites sintered at 1300°C for 2 h are presented in table 2.

The temperature coefficient of linear expansion of the manganese-zinc ferrites with composition $Mn_{0.55}Zn_{0.45}Fe_2O_4$ was 94,5 . 10^{-7}, deg^{-1}, and the temperature of Curie — 378 K.

Discussion

The formation of spinels in ferrite masses, usually referred to as ferritization, begins at 800°C and ends at 1200°C. The optimal temperature of ferritization - 1100°C (1 h) was determined using the diffraction maxima intensities at 0.269 nm of hematite and 0.255 nm of spinel in the temperature range from 900 to 1200°C (fig. 1). During the process of ferritization, firstly franklinite $ZnFe_2O_4$ is formed and then, at higher temperature (from 900 to 1200°C), Mn^{2+} penetrates the $ZnFe_2O_4$ structure to form mixed manganese-zinc ferrite: $Mn_{1-X}Zn_XFe_2O_4$.

For the selection of optimal sintering temperature (1300°C for 2 h), the ferrite samples were subjected to isothermal treatment in nitrogen medium in the range 1250—1350°C with step of 50°C for 0.5, 1.0, 2.0 and 3.0 h. The changes in the apparent density, microstructure and other properties of the Mn-Zn ferrites were used to determine the optimal temperature and time for sintering. The rapid cooling of the ferrites obtained in the temperature interval 100-600°C was carried out to avoid the oxidation of Mn^{2+} to Mn^{3+} and the resulting ferrite decomposition.

As can be seen from table 1, the increase of $ZnFe_2O_4$ content in the mixed Mn-Zn ferrites leads to increase of the apparent density and decreased the average size of the crystals. The manganese-zinc ferrites with low content of $ZnFe_2O_4$ have coarse grained heterogranoblastic (non-uniform sized) structure, while those with higher $ZnFe_2O_4$ content — fine grained homeogranoblastic (uniform grain

Table 2. Initial magnetic permeability ($м_н$), induction at saturation (B_m), residual induction (B_r) and coercive force (H_c) of Mn-Zn ferrites after sintering at 1300°C for 2 h.

Sample	Mn-Zn ferrites	$μ_н . 10^6$, H / m	B_m, T	B_r, T	H_c, A / m
2	$Mn_{0.50}Zn_{0.50}Fe_2O_4$	2500	0.220	0.060	7.32
3	$Mn_{0.55}Zn_{0.45}Fe_2O_4$	3866	0.290	0.120	9.40
4	$Mn_{0.60}Zn_{0.40}Fe_2O_4$	3022	0.294	0.125	9.55
5	$Mn_{0.75}Zn_{0.25}Fe_2O_4$	700	0.298	0.180	23.20

size) structure. The mixed manganese-zinc ferrites with homeogranoblastic structure have high initial magnetic permeability and low values of residual induction and coercive force (table 2). The highest initial magnetic permeability has the ferrite with composition $Mn_{0.55}Zn_{0.45}Fe_2O_4$. The same ferrite alloyed with 0.05 mass% MgO has initial magnetic permeability of $4044x10^{-6}$ H/m, induction at saturation 0.320 T, residual induction 0.150 T and coercive force 7.20 A/m. Its structure was homeogranoblastic with small grain size dispersion: d_{mean}=10 µm, d_{min}=7 µm and d_{max}=12 µm.

The scheme used to control ferrites properties involved selection of an optimal composition ($Mn_{0.45}Zn_{0.55}Fe_2O_4$) containing 0.05 wt.% of MgO and technology (ferritization at 1100°C — 1 h and sintering at 1300°C — 2 h in nitrogen medium followed by rapid cooling from 1000 to 600°C) to obtain mixed manganese-zinc ferrite with high density, desired microstructure and properties.

Conclusion

The mixed manganese-zinc ferrites with composition $Mn_{0.55}Zn_{0.45}Fe_2O_4$ have high apparent density and homeogranoblastic structure and provide high initial magnetic permeability and low coercive force. The same ferrite alloyed with 0.05 mass% MgO have initial magnetic permeability of $4044x10^{-6}$ H/m and coercive force of 7.20 A/m.

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Твърди разтвори в системата якобсит $MnFe_2O_4$ – франклинит $ZnFe_2O_4$

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Резюме. Изследван е фазовият и химичен състав на синтезирани твърди разтвори в системата якобсит $MnFe_2O_4$ — франклинит $ZnFe_2O_4$. Определени са привидната плътност и размерите на кристалите на смесените манган-цинкови ферити от типа $Mn_{1-X}Zn_XFe_2O_4$ след изпичане при 1300°C — 2 часа. Като суровини са използвани оксиди на съответните метали с чистота *p* и *pa*. MnO е внесен като $MnCO_3$. Манган-цинковите ферити са изготвени по двукратна керамична технология, включваща следните операции: смилане и хомогенизация на изходните шихти; феритизация; смилане и хомогенизация на феритизирания материал; формуване; изпичане. Изпечените образци се охлаждат бързо в температурния интервал от 1000 до 600°C. Измерени са: начална магнитна проницаемост ($м_н$), индукция на насищане (B_m), остатъчна индукция (B_r) и коерцитивна сила (H_c).