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HYDROTHERMAL SYNTHESIS OF MnZn FERRITE POWDERS AND THEIR SINTERING

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Keywords: ceramics, MnZn ferrites, nanocrystalline powders, nanosized powders, powder sintering, hydrothermal synthesis, wet chemical method

Abstract: Hydrothermal synthesis was used to produce nanosized MnZn ferrite powder. The results show that the pH value of the starting suspension has a decisive influence on the composition of the hydrothermally prepared MnZn ferrite powder. The grain size of the powder increases with the temperature and time of hydrothermal treatment and also with the concentration of cations in the mother solution. The nanosized ferrite grains are very prone to oxidation and disintegrate above 250°C in air.

Nanocrystalline ferrite powders are very reactive and can be sintered in inert atmosphere at very low temperatures to nearly theoretical density without sintering additives. In compacts prepared from superstoichiometric powders, the formation of intergranular porosity was observed when the sintering temperature exceeds 1000°C. The formation of porosity is a consequence of oxygen evolution from MnZn ferrites in the reaction incorporating excess α - Fe_2O_3 into the spinel lattice.

Hidrotermalna sinteza MnZn feritnega prahu in njegova sinterabilnost

Ključne besede: keramika, MnZn feriti, prahovi nanokristalinični, prahovi nanometerski, sintranje prahov, sinteza hidrotermalna,metode keramične mokre

Povzetek: S hidrotermalno sintezo smo pripravili nanokristalinični prah MnZn ferita. Rezultati so pokazali, da ima pH vrednost izhodne suspenzije hidroksidov precejšen vpliv na sestavo feritnega prahu pripravljenega s hidrotermalno sintezo. Velikost delcev narašča z višjo temperaturo sinteze in s koncentracijo kationov v izhodni suspenziji. Nanokristalinični prah je zelo reaktiven in se pri temperaturah nad 250°C oksidira. V inertni atmosferi se nanokristalinični prah sintra pri nizkih temperaturah do visoke gostote brez dodatkov za sintranje. V oblikovancih z nadstehiometrično sestavo se pri višjih temperaturah sintranja na mejah med zrni pojavi poroznost in gostota sintranim vzorcem se opazno zniža. Povečanje poroznosti pripišemo sproščanju kisika pri vgrajevanju α - Fe_2O_3 v spinelno rešetko ferita.

Introduction

Fine powder preparation has become an important part of modern ceramics research. There is a strong trend towards the application of chemical methods for powder preparation in electronic ceramics. In spite of their initially higher cost than ceramic powders prepared by conventional solid-state reaction of mechanically mixed and calcined starting materials, the improved performance and reproducibility achievable with chemically - derived powders ultimately saves money and adds value. There are various methods of fine powder preparation such as coprecipitation, spray drying, freeze drying, the sol-gel process and the hydrothermal process /1/. Among these processes the hydrothermal method is very promising. It is a typical build-up method where fine particles are made from much smaller particles, such as clusters, molecules, ions and atoms. With ever increasing energy costs, the hydrothermal method could possibly become very attractive for fine powder preparation because of the low temperatures involved and the good sinterability of the powder prepared. The advantages of this process, such as for example the improved control of powder homogeneity and particle uniformity, could make the use of this process dominant for electronic ceramics in the next few years /2,3/.

When we neutralize a nitrate solution of Fe^{3+}, Mn^{2+} and Zn^{2+} ions with ammonia and treat this suspension under controlled hydrothermal conditions a nanosized MnZn ferrite powder can be obtained. The hydrothermal synthesis of ferrites is associated with the chemical reaction (1) /4/;

$$xMn^{2+} + yZn^{2+} + (3\text{-}x\text{-}y)Fe^{3+} + 8OH^- \rightarrow \rightarrow Mn_xZn_yFe_{3-x-y}O_4 + 4H_2O \quad x+y=1 \qquad (1)$$

The aim of this work was to study the relationship between the yield and the composition of the ferrite powder, its homogeneity, morphology and the processing parameters, i.e. the starting composition, the pH value of the suspension, the temperature and the time of synthesis. Additionally, the thermal stability, grain growth and the sintering of nanosized ferrite powder was investigated.

Experimental

Stock solutions containing Fe^{3+}, Mn^{2+} and Zn^{2+} ions were prepared using $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2.xH_2O$ and $Zn(NO_3).xH_2O$ (Johnson Matthey) as source materials. The solution of appropriorate ammount of nitrates in deionized water was then hydrolized with diluted aqueous ammonia in a teflon cup. The pH value was varied from 7 to 12 and the residue obtained after filtration was analyzed by atomic absorption spectros-

copy. The pH value was maintained around a value where the concentration of both ions, i.e. Zn^{2+} and Mn^{2+}, found in the residue after filtration was the lowest. When the desired pH value was obtained the teflon cup was mounted in a Parr autoclave (Model 4563M) and heated at a rate of about 3°C/min. The hydrothermal synthesis was carried out under equilibrium water pressure.

After hydrothermal treatment the pressure vessel was cooled and the product was washed free of ammonia salts with hot water and with ethanol to prevent the formation of hard agglomerates, which can cause inhomegeneities in green samples and consequently in the sintered ferrites /5/. The wet powder was granulated with 0,2 % of PEG in ethanol media. The residue obtained after filtration was analyzed by using flame atomic absorption spectroscopy, (Varian - AA5). Individual grains of ferrite were inspected and analized using a TEM (Joel 2000 FX) equipped with a Link EDX system. The particle size determination was performed by employing the XRD line broadening effect /6/. TEM and SEM (Leitz) were used to observe the morphology of the powder and the individual particle size. Thermogravimetric (TGA) and differential thermal analysis (DTA) studies were carried out in an inert atmosphere and air at a heating rate of 5°C/min. The measurements were performed using a Netzsch - STA 409 apparatus. Sintering behavior was checked by dilatometric measurements (BÄHR) and with density measurements.

Results and discussion

Synthesis of powder

In Fig. 1 the pH value of the starting suspension vs. the MnZn ferrite composition after the hydrothermal synthesis is shown. From the diagram we can see that the composition of the MnZn ferrite formed by hydrothermal synthesis strongly depends on the pH value of the starting suspension. $Zn(OH)_2$ is amphoteric and readily dissolved in excess ammonia, while $Mn(OH)_2$ is stable in the more alkali media. The excess of $Fe(OH)_3$ retained when the pH value is not close to 8,6 transforms into α - Fe_2O_3 during hydrothermal treatment. The composition of the powder formed during hydrothermal synthesis from the nominal composition $Mn_{0.5}Zn_{0.5}Fe_2O_4$ can be written as:

$$(0,5\text{-}x)MnO(0,5\text{-}y)ZnO(1\text{-}x\text{-}y)Fe_2O_3 + (x+y)Fe_2O_3.$$

When $x + y > 0$ the excess of α - Fe_2O_3 can be detected in the synthesized ferrite powder. The morphology of the synthesized powder depends on the temperature and time of synthesis as shown on Fig. 2. Fig. 3 shows the TEM image and corresponding diffraction pattern of MnZn ferrite powder prepared at 140°C.

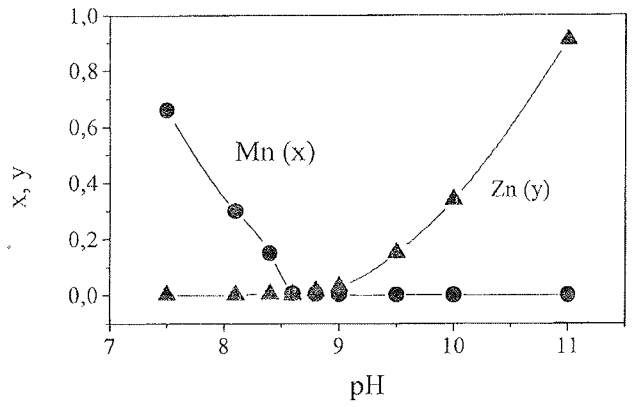

Fig. 1: Composition of the ferrite powder (1/2-x)MnO(1/2-y/)ZnO(1-x-y)Fe_2O_3 +(x+y)Fe_2O_3 formed during hydrothermal synthesis at 140°C vs. the pH value of the initial suspension.

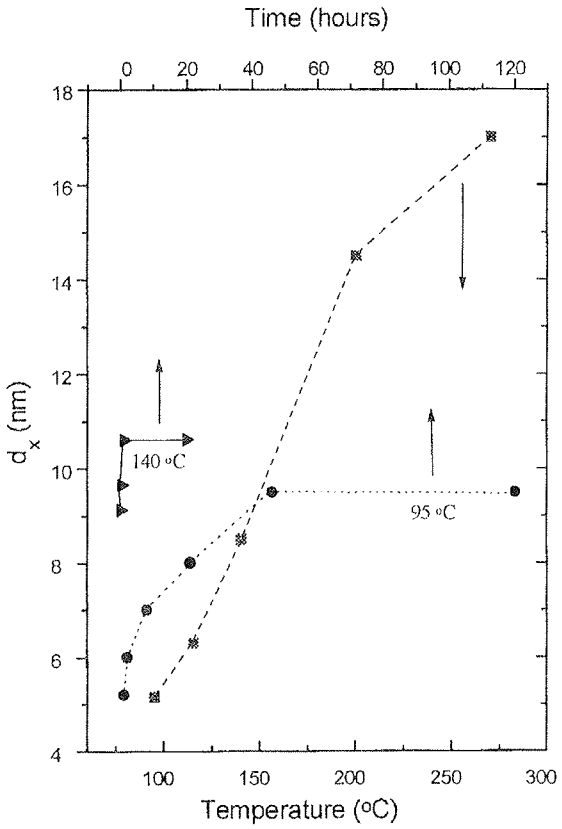

Fig. 2: Average grain size of MnZn ferrite hydrothermally treated for 2 hours at different temperatures and at 95°C and 140°C for various times.

Nanosized hydrothermally prepared powder is superparamagnetic /7/ and above 200°C disintegrates in an oxidizing atmosphere according to the reaction:

$$Mn_xZn_{1-x}Fe_2O_4 + \frac{x}{4}O_2 \rightarrow (1-x)ZnFe_2O_4 + \tag{2}$$

$$+\frac{x}{2}Mn_2O_3 + xFe_2O_3$$

Nanosized MnZn ferrite powder is reactive and can be sintered to high densities at low temperatures.

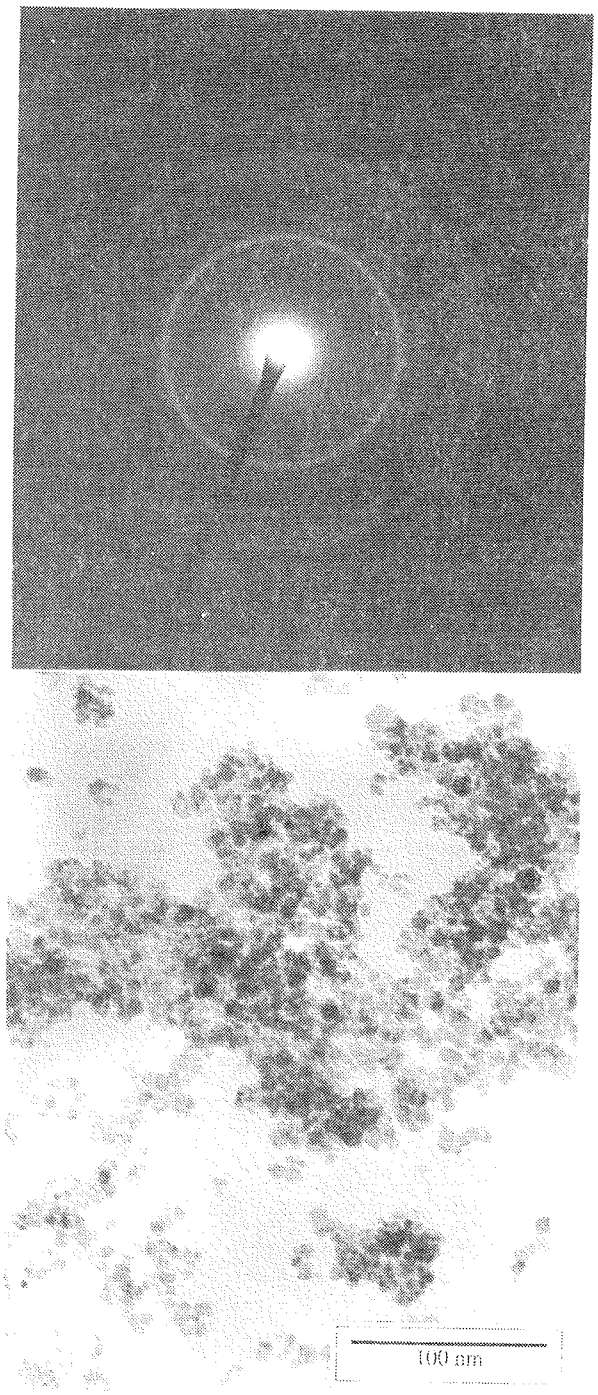

Fig. 3: *TEM image with corresponding diffraction patterns of hydrothermally synthesized* $Mn_{0.49}Zn_{0.48}Fe_{2.03}O_4$.

Sintering of powder

Fig. 4 shows the porous microstructure of nanocrystalline MnZn ferrite sintered in air atmosphere. During heating to the sintering temperature, nanocrystalline MnZn ferrites oxidize in according with reaction (2). In this case reaction sintering takes place resulting in a porous microstructure /8/. To prevent ferrite disintegration nanocrystalline MnZn ferrites must be sintered under equilibrium atmospheric conditions. This means

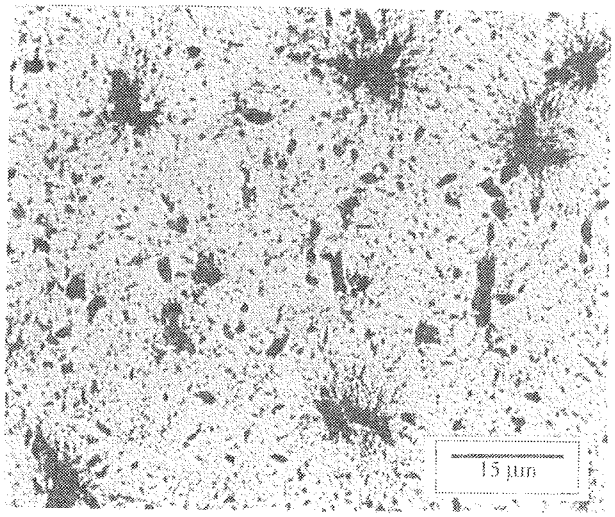

Fig. 4: *Microstructure of MnZn ferrite sintered in air at 1100°C.*

that under 900°C sintering should be performed in an atmosphere of pure nitrogen. In this case very reactive nanosized MnZn ferrites can be sintered to nearly theoretical density at temperatures around 700°C, Fig. 5. However this property can lead in superstoichiometric MnZn ferrites, i.e. a mol ratio of MnO + ZnO/Fe_2O_3< 1, to intergranular porosity when sintering temperature above 900°C is applied. Superstoichiometric MnZn ferrite powders contains excess α - Fe_2O_3 which at temperatures higher than 800°C dissolves in the spinel ferrite lattice, yielding an equivalent amount of Fe^{2+}. This is a desirable for optimization of the magnetic properties of MnZn ferrites. Dissolution of excess α - Fe_2O_3, reaction (3), is associated with oxygen release, as shown in Fig. 6.

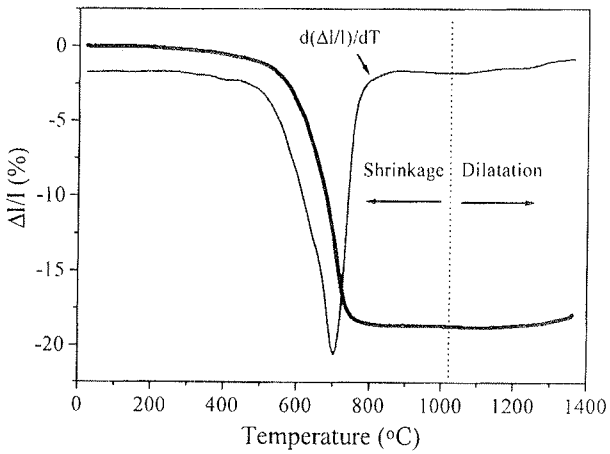

Fig. 5: *Dilatometric curve and its derivation for hydrothermally prepared* $Mn_{0.49}Zn_{0.48}Fe_{2.03}O_4$ *in nitrogen.*

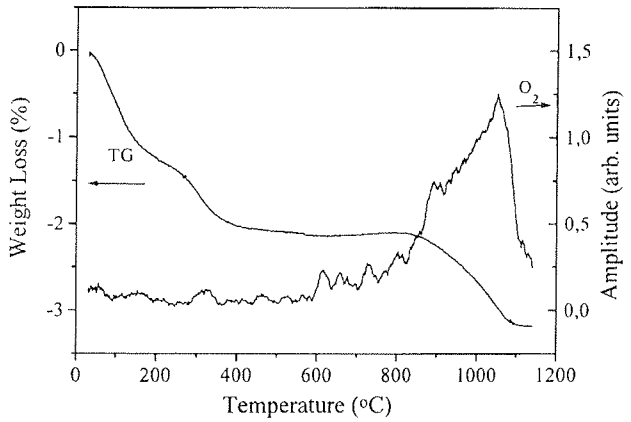

Fig. 6: TGA analysis and evolution of oxygen from superstoichiometric MnZn ferrite powder.

$$Fe^{3+} + \frac{3}{8}V_c + \frac{1}{2}O^{2-} \Leftrightarrow Fe^{2+} + \frac{1}{4}O_{2(g)} \,. \qquad (3)$$

Since the nanosized MnZn ferrites densify to almost theoretical density below the temperature where oxygen release occurs, porosity will be induced in the low permeable dense microstructure. This leads to lower densities of samples sintered at higher temperatures, Fig. 7. To ensure the optimal magnetic properties the grain size of MnZn ferrites should exceed the monodomain size, i.e. 2 μm. A two step sintering profile was applied in order to fulfill this demand. Samples were preheated at 850°C and then sintered at 1150°C. At 850°C a moderate dissolution of α - Fe_2O_3 into the spinel lattice associated with oxygen release can be expected. During further sintering at 1150°C additional grain growth takes place associated with dissolution of the residual α - Fe_2O_3. However in the case of stepwise sintering the accompanying oxygen release and porosity formation will not be so harmful for the microstructure

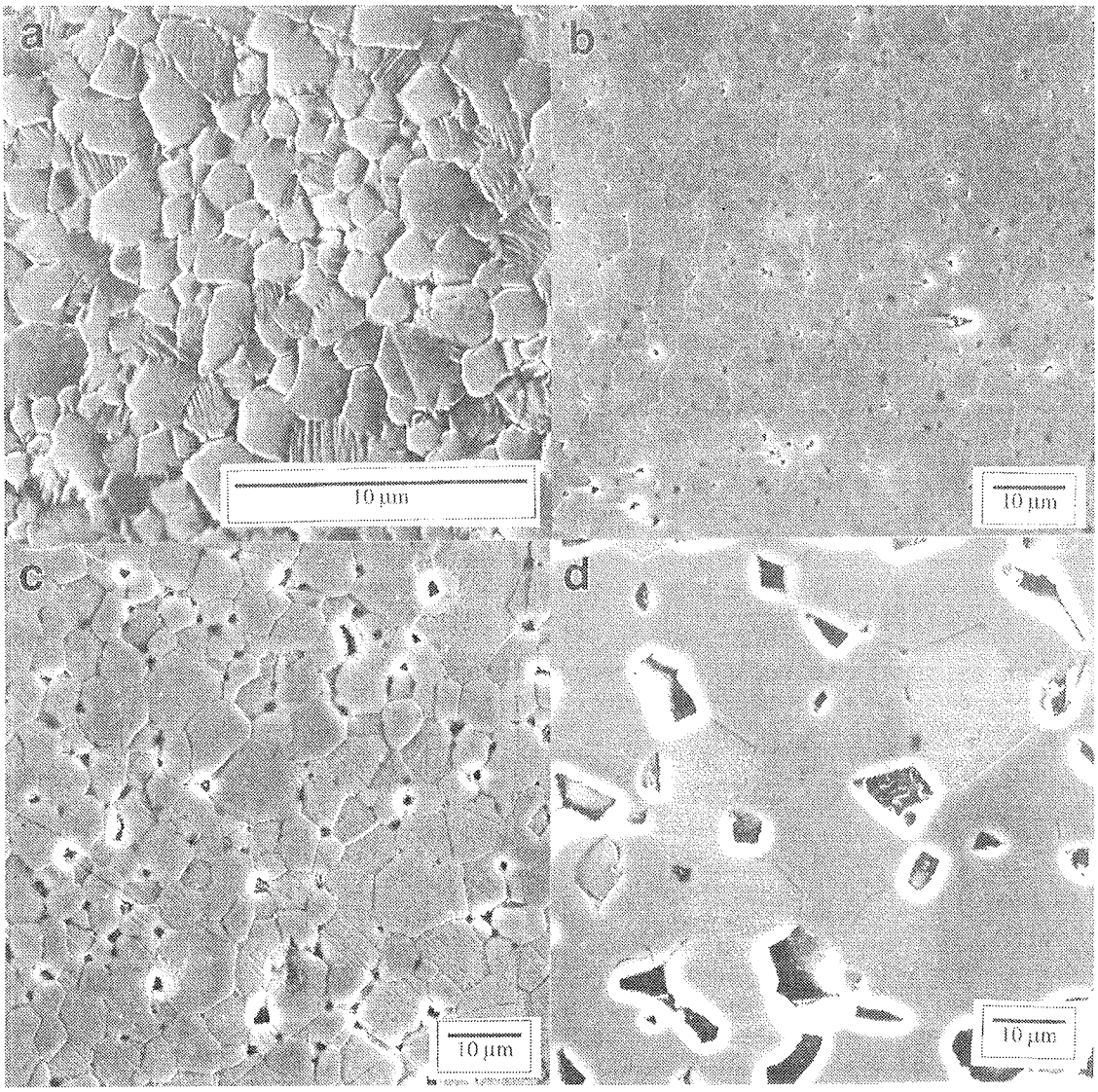

Fig. 7: Microstructures of nanocrystalline $Mn_{0.49}Zn_{0.48}Fe_{2.03}O_4$ sintered under equilibrium atmosphere at: a.) 1000°C , b.)1100°C , c.)1200°C , d.) 1300°C.

evolution. The result of the stepwise sintering is a microstructure with the grain size beyond the monodomain size and with high relative density, i.e. $\overline{D}$ = 4 μm, ρ = 98 % t.d., Fig. 8.

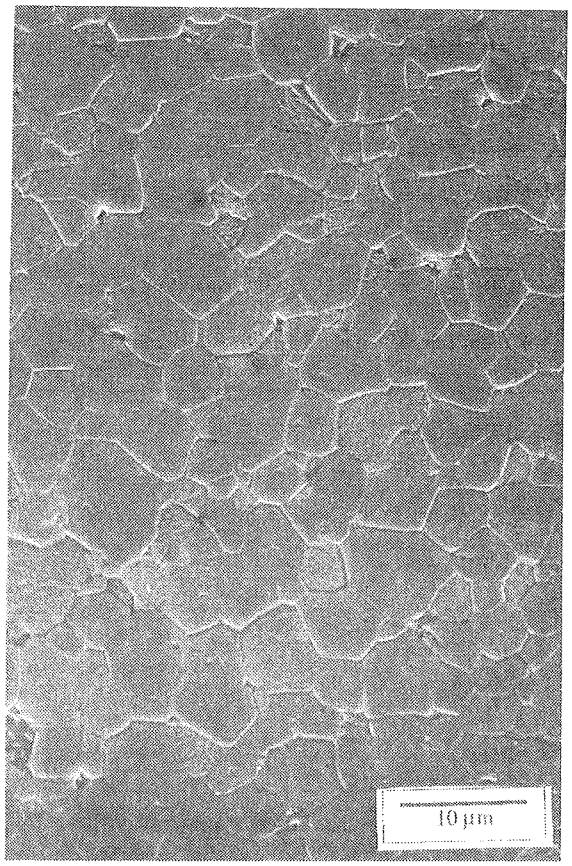

Fig. 8: Microstructure of $Mn_{0.49}Zn_{0.48}Fe_{2.03}O_4$ sintered at 850°C and 1150°C.

Conclusions

Hydrothermal synthesis of MnZn ferrite powder from nitrates neutralized with ammonia yields a nanosized crystalline powder. Control of the stoichiometry of the powder is strongly dependent on the pH value of starting suspension. The ideal pH value for synthesis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ is 8.6.

Nanocrystalline MnZn ferrites are extremely sensitive to oxidation and completely disintegrate at 600°C in air.

Sintering in air leads to a very porous microstructure due to reaction sintering of disintegration products.

To achieve nearly theoretically dense ferrites, sintering must be performed at low temperatures, between 700°C and 900°C. At higher temperatures (especially above 1200°C) the density of ferrite compacts was significantly lower due to evolution of oxygen.

Stepwise sintering at 850°C and 1150°C enables the preparation of MnZn ferrite samples with a high relative density and grain dimension above the monodomain size.

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