

Dispersant-assisted hydrothermal synthesis of MnZn ferrites from raw oxides

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MnZn-ferrite powders were prepared using hydrothermal syntheses of a homogenous mixture of the raw oxides, i.e., Fe_2O_3 , ZnO and Mn_3O_4 , at 280°C in air. The hydrothermal synthesis was performed in the presence of various amounts of an anionic dispersant. The final results of the hydrothermal reaction between the raw oxides were fine powders with a heterogeneous phase composition mostly composed of iron oxide and spinel products. The composition of the spinel products depended to a great extent on the amount of dispersant in the hydrothermally treated suspension. Without the dispersant addition, Zn ferrite and Zn manganate spinel products were formed, while in the presence of the dispersant, the ferrimagnetic MnZn-ferrite spinel product was obtained. A larger amount of the dispersant in the reaction mixture increased the conversion rate of the raw oxides into the Mn,Zn ferrite spinel product. Additionally, polyvinyl alcohol (PVA) was used during the hydrothermal synthesis in order to bind the chlorine impurities, introduced into the hydrothermally prepared powder with the raw Fe_2O_3 . With the PVA burnout, the level of chlorine impurities was decreased by approximately 50%. © 2003 Kluwer Academic Publishers

1. Introduction

One of the most important steps during the processing of MnZn-ferrite (MZF) cores is the preparation of the MZF powders. To a large extent it is the powders' characteristics that determine the final electromagnetic properties of the sintered MZF cores. Large-scale production of MZF ceramic materials is based on ceramic technology that involves presintering (calcination) of a homogeneous mixture of appropriate starting oxides at temperatures around 1000°C. During pre-sintering in air, the Mn,Zn Fe_2O_4 spinel phase is formed. However, during cooling from the pre-sintering temperature in air, Mn^{2+} from (Mn,Zn) Fe_2O_4 is oxidized and MnO_2 is formed below 500°C. In practice, a combination of different manganese oxides, iron oxide and different spinel products (Zn Fe_2O_4 , Zn Mn_2O_4 , Mn,Zn Fe_2O_4) is present in the presintered mixture [1]. This mixture is then milled to prepare the ferrite powder, which is then shaped into green compacts. After binder removal at about 500°C in air, these green ferrite, compacts are then sintered at temperatures above 1300°C in a defined N_2/O_2 atmosphere.

Besides this conventional ceramic procedure, various other routes have been developed in the past for

the preparation of fine MZF powders on a laboratory scale, these routes include co-precipitation, spray drying, freeze drying, sol-gel, the hydrothermal method and others. Among these processes the hydrothermal method has been demonstrated to be a potentially superior method for the production of advanced ceramic MZF powders [2].

There are two main hydrothermal routes used for MZF preparation:

- (i) The hydrothermal treatment of a suspension of mixed hydroxides of Fe^{3+} , Zn^{2+} and Mn^{2+} obtained by neutralizing of Fe^{3+} , Mn^{2+} , and Zn^{2+} ions in aqueous ammonia³;
- (ii) The syntheses of MnZn-ferrite powder via the hydrothermal treatment of an intimate mixture of raw oxide Fe_2O_3 , ZnO and Mn_3O_4 [4].

The later method might have the potential for large-scale production of MZF in the near future due to the simplicity of the production process, which is much more energetically efficient than the classic ceramic technology. Furthermore, it is believed that using this hydrothermal method, powders of better homogeneity

and reactivity can be prepared, which will lead to MZF ceramics with improved magnetic properties [5].

A study of the hydrothermally assisted reaction between the starting raw oxides as a function of processing parameters was published [6]. The hydrothermal treatment of Fe_2O_3 , ZnO and Mn_3O_4 raw oxides resulted in fine powders composed of the residual reactants (Fe_2O_3 , Mn_3O_4) and two types of spinel-structure-based reaction products; ferrite ($(\text{Mn}^{2+}, \text{Zn})\text{Fe}_2\text{O}_4$) and manganate ($(\text{Zn}, \text{Mn}^{2+})\text{Mn}_2^{3+}\text{O}_4$). The composition of the ferrite products as well as the ratio of ferrite products to manganate products was found to be mainly a function of the atmosphere in the autoclave during the reaction. When the hydrothermal reaction was conducted in air, almost pure Zn ferrite was obtained, while manganese was present mainly in the form of manganate-based spinel ($\text{ZnMn}_2^{3+}\text{O}_4$) [6]. The crystallites of the ferrite product had an octahedral shape and were of a size comparable to that of the starting Fe_2O_3 particles ($\sim 0.3 \mu\text{m}$), while the rounded particles of the manganate product were much smaller (their size was below $0.1 \mu\text{m}$, comparable to that of the starting Mn_3O_4 particles). Those small manganese-rich particles showed a strong tendency to agglomerate in the aqueous environment of the hydrothermal synthesis, making the powders difficult to sinter and decreasing the homogeneity of the sintered ceramics [7]. Thus, one of the major problems with this method for ferrite-powder preparation is in the nonhomogeneity of the prepared powders related to the relatively low conversion rate of raw oxides into the MnZn-ferrite product. Another problem when using hydrothermally prepared powders for the production of MZF ceramics is the presence of chlorine impurities, which are intrinsic to the commercially available raw Fe_2O_3 . During the pre-sintering step of the classic ceramic technology, which is currently used for the mass production of MZFs, chlorine is released from the ferrite powder; after hydrothermal synthesis the chlorine is retained in the treated powder mixture and has the added disadvantage of damaging the kilns during the sintering of the ferrite compacts when the chlorine is released.

The purpose of this study was to investigate the influence of a dispersant during the hydrothermal treatment of a water suspension of starting raw oxides and to use polyvinyl alcohol (PVA), a chlorine-philic organic compound, in order to bound the chlorine from the suspension and to decrease its content in the MZF compacts prior to final sintering in the production kilns.

2. Experimental

A water suspension of an oxide mixture (400 g of oxide mixture per 1 L of water) with a nominal composition corresponding to the formula $\text{Mn}_{0.66}\text{Zn}_{0.27}\text{Fe}_{2.07}\text{O}_4$ was prepared by homogenizing the starting raw oxides in an attritor mill. The following raw oxides were used: Fe_2O_3 (purity better than 99.5%, $A_s = 3.92 \text{ m}^2/\text{g}$, chlorine impurity content 0.09 wt%) Voest-Alpine HPG, Linz, Austria, ZnO (purity better than 99.8%, $A_s = 3.86 \text{ m}^2/\text{g}$) Zinkweiss Pharma A, Grillo Zinkoxid GmH, Wien, Austria, and Mn_3O_4 (purity 92.0% MnO , $A_s = 11.6 \text{ m}^2/\text{g}$) MMG Sogemet, South Africa. An anionic

dispersant Dolapix CE64 (Zschimmer & Schwarz, Lahnstein, Germany) was added to the water suspension prior the hydrothermal treatment in concentrations from 0 to 9 wt% with respect to the solids. Dakskobler and Kosmač [9] reported on an analysis of the Dolapix CE64 dispersant and showed that it is an ethanolaminic salt of citric acid with an average molecular mass of 320 g/mol. Dolapix was found to serve as an agent which is able to maintain the reducing conditions during the synthesis. The water suspensions of the homogenized oxide mixtures were hydrothermally treated in an autoclave (Model 4522 M, Parr Instrument Co., Moline, IL) for 20 h at 280°C and an equilibrium water pressure.

In order to decrease the level of harmful chlorine impurities introduced into the hydrothermally prepared ferrite powders with the raw Fe_2O_3 we added 0.4 wt% of polyvinyl alcohol (PVA) with respect to the solids, to the water suspension of the starting oxides prior to the hydrothermal treatment.

The powders were characterized by means of X-ray powder diffractometry (XRPD) and a combination of imaging, selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDXS) in transmission electron microscope (TEM). X-ray diffractograms, recorded on a diffractometer (AXS-Bruker/Siemens D 5005), were used for a quantitative phase analysis. In each sample the concentrations of Fe_2O_3 , ZnO and Mn_3O_4 were determined using the matrix-flushing method [9], while the concentration of spinel phases, formed by the hydrothermal reaction, were calculated by difference from 100 wt%. Al_2O_3 was used as the flushing agent.

For the TEM analysis, the powders were deposited on a copper-grid-supported transparent carbon foil. A TEM (Model JEM 2000 FX, JEOL, Tokyo, Japan) equipped with the EDS system (Model AN 10000, Link Systems, High Wycombe, UK) was operated at 200 kV.

The specific surface areas of the powders were measured using the Brunauer-Emmett-Teller (BET) method (Model 212 D Sorptometer, Perkin-Elmer, Norwalk, CT), while the magnetizations of the powders were measured with a suscepto/magnetometer (DSM-8 Manics 76120, Ernalsheim/B).

The concentration of chlorine in the powders was measured with an automatic analyzer (ORION 960, EMPA, Dübendorf, Switzerland) using a chlorine ion-selective electrode.

3. Results and discussion

The XRPD analysis showed a multiphase material for the hydrothermally prepared powders (Fig. 1). Generally, all the samples were composed of remaining reactants Fe_2O_3 and Mn_3O_4 and products with a spinel structure. However, it can be clearly seen that the relative intensity of the diffraction peaks corresponding to the spinel-structure products (marked with S in Fig. 1) increases with the addition of the dispersant, indicating an increase in the conversion rate of the raw oxides into the spinel products. The mass balance of the hydrothermal reactions, made on the basis of the results that were obtained via quantification of the X-ray diffractograms

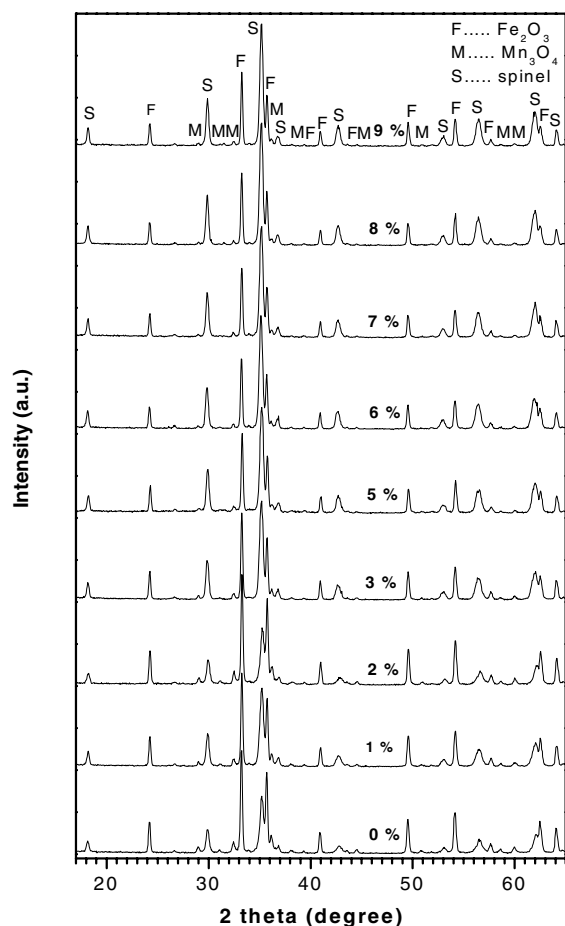


Figure 1 X-ray diffractograms of hydrothermally synthesized powders containing various additions of the dispersant.

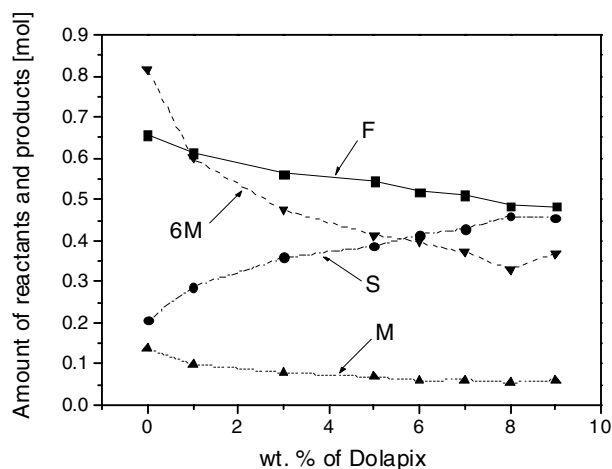


Figure 2 The relative amount of reactants (Fe_2O_3 and tetragonal Mn_3O_4) and spinel products in the powder after hydrothermal treatment as a function of the dispersant addition.

proved that the amount of spinel phase increases in parallel with the addition of dispersant. In Fig. 2 the relative amounts of the reactants and the spinel products are given in moles of individual species present in the powders as a function of the addition of dispersant. The decrease of Fe_2O_3 and Mn_3O_4 during the hydrothermal synthesis in air is a consequence of spinel-product formation. The diagram in Fig. 2 does not contain the ZnO concentration, which reacts forming spinel at the very beginning of the synthesis [6]. Its concentration in the

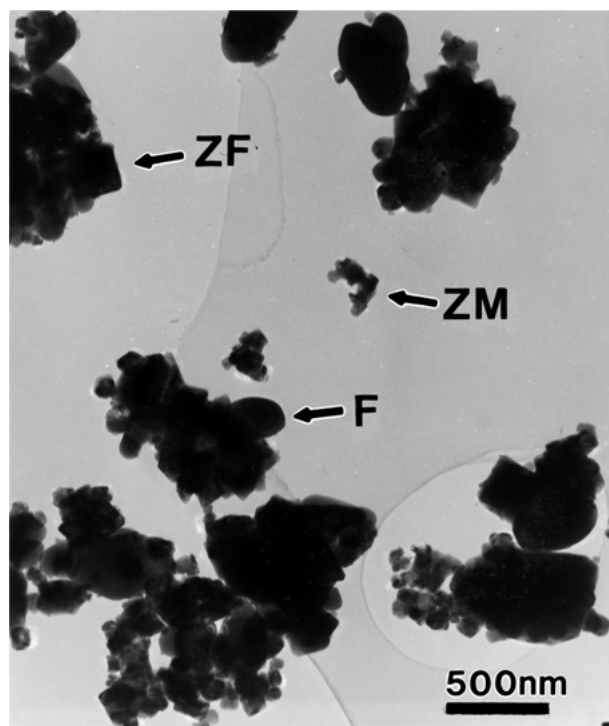


Figure 3 TEM image of the powder, hydrothermally prepared without the addition of the dispersant ($\text{F-Fe}_2\text{O}_3$, $\text{ZF-ZnFe}_2\text{O}_4$, $\text{ZM-ZnMn}_2\text{O}_4$).

powder without the addition of any dispersant was already below the detection level of the equipment.

A detailed analysis of the powders using a combination of SAED and EDX in the TEM confirmed that the powders were composed of well-crystalline particles, that had different morphologies and different chemical compositions. The oblong particles of Fe_2O_3 were around $0.5 \mu\text{m}$ in size, while rounded particles of Mn_3O_4 were much smaller, approximately $0.1 \mu\text{m}$ in size. The composition of the spinel product depended on the addition of the dispersant to the water suspension of the raw oxides before the hydrothermal treatment. Fig. 3 shows the powder prepared with the hydrothermal treatment of the water suspension of oxides without the addition of any dispersant. In this powder the spinel-structured particles had two different morphologies and compositions. The EDXS analysis showed that the larger (approximately $0.25 \mu\text{m}$ in size), octahedrally-shaped spinel-structure particles (marked in Fig. 3 with ZF) were composed mainly of iron, zinc and oxygen, while the concentration of manganese in this particles was very low. The smaller (approximately $0.1 \mu\text{m}$ in size), rounded spinel-structure particles (marked in Fig. 3 with ZM) were composed of zinc, manganese and oxygen. It is known that during the hydrothermal treatment of the oxide mixture in air, zinc-ferrite-based spinel and zinc-manganate-based spinel are formed [6]. Fig. 4 shows the powder prepared with hydrothermal treatment of the water suspension of oxides with the addition of 7 wt% of dispersant. When the dispersant was added to the water suspension of oxides before the hydrothermal treatment the spinel products were almost only present in the form of octahedrally shaped crystallites (marked in Fig. 4 with MZF). The EDXS analysis showed that these crystallites were

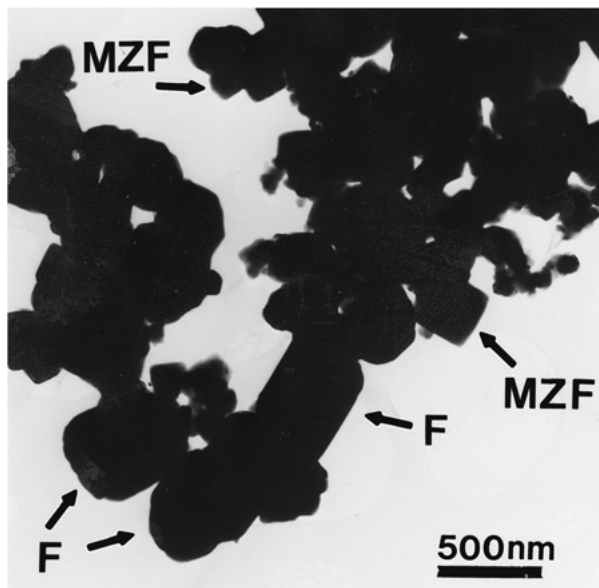
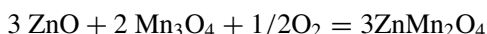
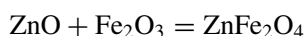


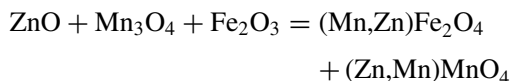
Figure 4 TEM image of the powder, hydrothermally prepared with the addition of 8 wt% of the dispersant (F-Fe₂O₃, MZF-Zn,MnFe₂O₄).

composed of iron, zinc, manganese and oxygen, proving that MnZn ferrite was formed.

During hydrothermal treatment in air the manganese in the Mn₃O₄ (MnMn₂O₄) has a tendency to oxidize to the tri-valent state (Mn³⁺), while the formation of ferrimagnetic spinel (Mn,Zn)Fe₂O₄ demands that the manganese be preferentially in the divalent oxidation state. Consequently, the ferrite-based spinel product after treatment in air is ZnFe₂O₄. The majority of manganese forms a manganate-based spinel where the manganese is incorporated preferentially in a trivalent oxidation state [6]. Simplified chemical reactions can be written as follows:



In the case when the oxide mixture was treated in the presence of the Dolapix dispersant that is able to maintain the reducing conditions during the synthesis, the manganese that is present in the raw oxide (Mn₃O₄) in the divalent state retained its starting valence. Consequently, a higher concentration of manganese entered the ferrite-based spinel product during the hydrothermal treatment forming (Mn,Zn)Fe₂O₄:



A larger amount of spinel, which is identified in the X-ray diffractograms of the powders prepared with the addition of the dispersant, can therefore be ascribed to the formation of the ferrimagnetic spinel (Mn,Zn)Fe₂O₄. The formation of the ferrimagnetic (Mn,Zn)Fe₂O₄ product has been confirmed by measurements of the powders' magnetization.

The magnetization of the synthesized powders gradually increases with the addition of dispersant up to

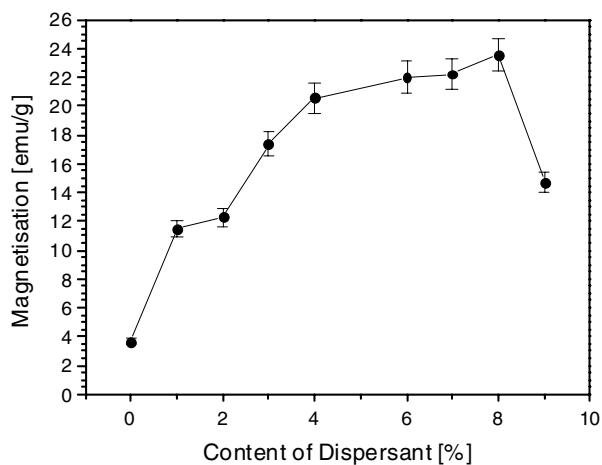


Figure 5 Magnetization of the powders, hydrothermally synthesized in the presence of various amounts of dispersant.

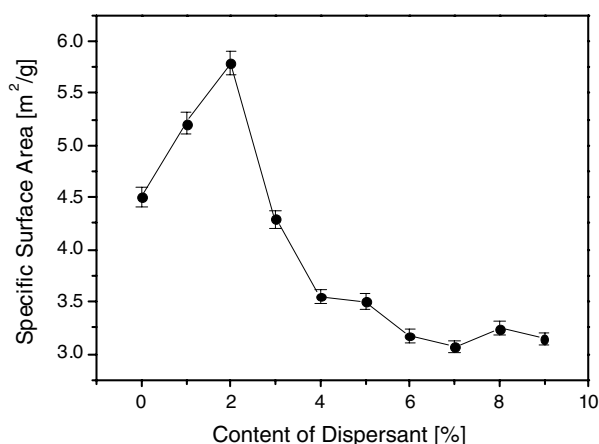


Figure 6 Specific surface areas of the hydrothermally synthesized powders as a function of the dispersant addition.

8 wt%, while at 9 wt% of dispersant the magnetization decreased (Fig. 5). Most probably, all the Mn²⁺ introduced into the reaction batch via the Mn₃O₄ was incorporated into the ferrite spinel product up to dispersant a concentration of 8 wt%.

The use of the dispersant during the hydrothermal syntheses significantly changes the specific surface area of the synthesized powders. Fig. 6 shows the specific surface areas of the powders that were hydrothermally treated in the presence of various amounts of dispersant. The specific surface area increased with the addition of up to 2 wt% of dispersant, however, with a further increase in the dispersant concentration the specific surface area of the synthesized powder started to decrease gradually. The change in the specific surface versus the amount of added dispersant can be explained as follows. In the beginning the decrease in the agglomeration of the raw oxide powders in the suspension during the hydrothermal synthesis is a result of the dispersant additions. In particular, the manganese-rich particles (Mn₃O₄ starting oxide and manganate-based spinel product), which have a high specific surface area, show a strong tendency to agglomerate in the water media of the hydrothermal synthesis [7]. When a small amount of dispersant was applied the agglomeration

was hindered and the specific surface area increased. When a larger addition of dispersant was used, more of the fine Mn_3O_4 was consumed for the formation of larger amount of the coarser ferrite-based-product particles and lower amount of the Mn_3O_4 was used for the fine manganate-based-product particles, thus decreasing the average specific surface area of the mixture. Additionally, the increase in the amount of ferrimagnetic Mn,Zn-ferrite particles in parallel with the dispersant addition promotes the agglomeration due to the attraction between the magnetic particles, which might additionally decrease the specific surface areas of the synthesized powders.

The iron oxide that is generally used during the production of MZF can contain up to 0.1 wt% of chlorine impurities. When using classic ceramic technology for the preparation of ferrite powders, including calcination at temperatures around 1000°C, most of the chlorine is released. On the other hand, when the powder is prepared via hydrothermal synthesis, which proceeds at lower temperatures in a closed vessel, the chlorine is retained in the powder. In order to make the hydrothermally prepared powders more acceptable for large-scale production, a decrease in the overall content of chlorine impurities is desirable, because the chlorine impurities in the ferrite powder get released during the sintering of the ferrite compacts and can, after a while, seriously damage the production kilns.

In order to decrease the level of chlorine in the hydrothermally prepared powders, polyvinyl alcohol (PVA) was used. PVA, which also serves as a binder during the pressing of the MZF powder, forms a chemical bond with the chlorine.

PVA was added to the suspension prior to the hydrothermal treatment in order to extract the chlorine from the powder prior to the sintering of the pressed compacts. When the PVA, also acting as a binder, was removed from the green compacts by heating to 500°C the chlorine impurities, which were bound to the PVA, were released as well. In this way a part of the chlorine was removed from the ferrite compacts during binder burnout and less chlorine was released in the production kilns during sintering.

The chemical analyses of the chlorine in the green compacts after heating them to 500°C are given in Table I. The compacts were pressed from powders prepared with or without the addition of PVA in the water suspension of oxides prior to the hydrothermal treatment. The results confirm that about 50% of chlorine can be removed from the green compacts during binder burnout when the PVA is introduced into the suspension before the hydrothermal synthesis. The procedure was

TABLE I Chlorine concentration in the samples synthesized with and without the addition of polyvinyl alcohol and heat treated at 500°C

Sample description	Concentration of Cl^- [% (m/m)]
Ferrite samples synthesized without PVA	0.120
Ferrite sample synthesized with 0.5 wt% of PVA	0.057

not optimised, however can be substantially improved with increasing the amount of PVA.

A large part of the total amount of chlorine present in the hydrothermally synthesized powder can be removed by using a suitable organic compound. We believe that by optimizing this procedure more than 50% of the chlorine can be removed from the ferrite powder that is prepared by hydrothermal syntheses.

There is no reason why this dispersant-assisted hydrothermally synthesized powder is not suitable for a large-scale ferrite production, particularly, when a large amount of the chlorine can be removed prior to the sintering of the ferrite.

By simultaneously applying two organic compounds, i.e., a dispersant and PVA, the properties of the synthesized ferrite powder can be modified so that they are similar to the properties of classically prepared powders.

4. Conclusions

Sub-micrometer-sized ferrite powders were prepared using the hydrothermal treatment of an intimate mixture of raw oxides, Fe_2O_3 , ZnO , and Mn_3O_4 , at 280°C. The raw oxides were partially transformed into spinel products. The percentage of MnZn-ferrite product increased with the percentage of the anionic dispersant (ethanolaminic salt of citric acid) added to the reaction mixture. At a concentration of 8 wt% of the dispersant (with respect to solids) all of Mn^{2+} present in the reaction mixture reacted to form MnZn ferrite. The addition of polyvinyl alcohol (PVA) to the water suspension of the starting oxides prior to the hydrothermal treatment was used to bond the chlorine impurities originating from the raw Fe_2O_3 . The level of chlorine impurities in the ferrite compacts after PVA burnout was decreased by about 50%.

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