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The application of effective-medium theory for the nondestructive characterization of ceramic composites

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Abstract

In this paper is presented the application of effective-medium theory (EMT) on ferrite ceramic composites with various volume fractions of spinel phase in an M-hexaferrite matrix in order to determine the phase composition. The permeabilities, which were calculated with effective-medium theory from measured permeabilities of single-phase samples, were matched with measured effective permeability of composite samples. From analysis of composites sintered at two different temperatures it is also shown that by presented method one can detect the formation of new phases. In this way obtained volume fractions of spinel phase were compared with values from the X-ray powder diffraction (XRD) analysis and the nominal composition mass. It is shown that EMT quantitative phase determination of magnetic composites is comparable to XRD quantitative phase analysis and represents a simple and fast complementary alternative.

Keywords: Composites; Ferrites; Magnetic properties; Nondestructive evaluation

1. Introduction

A ceramic composite has properties that depend on the properties of the constituent phases, but the overall properties are different to those of the individual phases, and in many cases the composite's properties can vary a great deal with the composition.[1] The quantitative determination of the phase composition is usually done with methods like X-ray powder diffraction[2] (XRD) or estimating the mass fractions of the final phases based on the known phase equilibria of the nominal composition. Since in real samples equilibrium is not always reached, XRD methods have been considered as the only option for a quantitative phase analysis of crystalline multiphase samples. However, for cases where the phases have distinctly different electromagnetic properties this can be done by measuring of electromagnetic properties and calculating the volume fractions of the phases by applying mixing rules.

Determining the mixture properties as a function of the constituents' properties is a well-established procedure, particularly in the field of electric properties, and there are several expressions for evaluating the effective properties of a composite.[1,3,4] By measuring both the constituents' and the composite's properties one can obtain the volume fractions of the individual constituents. If the constituent phases react during sintering, the phase composition changes, and thus do so the electromagnetic properties of the composite. This complicates any determination of the volume fractions; however, by comparing the electromagnetic properties and calculated volume fractions for different temperatures one can easily determine the temperature of the reaction and estimate the volume fraction of the new phases.

In this paper we present the results of such a characterization procedure on ferrite ceramic composites with various volume fractions of spinel phase in an M-hexaferrite matrix (S–M). We examined S–M composites that were sintered at two different temperatures: below and above the reaction temperature. A self-consistent effective-medium approximation is applied to the problem of ferromagnetic inclusions in the composite medium to determine the volume fractions of phases from the measured effective permeability. We will compare these results with those of the XRD analysis and the nominal composition mass, as well as discussing the necessary assumptions and limitations of the method.

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2. Theory

The characteristic electromagnetic property of ferrites is the frequency-dependent complex permeability, with a large imaginary component in the regions of the domain-wall (DW) relaxation and the ferromagnetic (FM) resonance.[5] In general, the frequencies of DW relaxation and FM resonance cannot be arbitrarily shifted. Since the regions of DW relaxation and FM resonance are different for different materials, by preparing ceramic composites, mixtures of ferrites with different complex permeabilities, the effective permeability of the composite can be a result of different mechanisms. This is definitely the case with the spinel–hexaferrite composites used in our study, where the region of DW relaxation in the hexaferrite overlaps with the region of FM resonance in the spinel ferrite. This requires some assessment of the applicability of mixing rules and the actual development of magnetism in the composite.

There are several expressions for evaluating the effective permeability of a composite,[4,6,7] usually taken as a mixture of matrix and inclusions, most notably the Bruggemann effective-medium theory (EMT) for composites with spherical inclusions (particles):

$$F\frac{\mu_\mathrm{p}-\mu_\mathrm{eff}}{\mu_\mathrm{p}+2\mu_\mathrm{eff}}+(1-F)\frac{\mu_\mathrm{m}-\mu_\mathrm{eff}}{\mu_\mathrm{m}+2\mu_\mathrm{eff}}=0 \qquad (1)$$

where F is the volume fraction of the particles (p) and the indices m and eff denote the matrix and the effective material, respectively. This mixture rule was shown to be relevant for demagnetized composites[7] and was used in the subsequent calculations.

In both cases the derivation is based on magnetostatic calculations for a ferromagnetic particle in an external magnetic field, i.e., on solving the Laplace equation for the magnetic potential.[6,7] In the case of fully demagnetized samples the susceptibility (permeability) tensor is intrinsically diagonal because of the averaging over the domains inside the particle, and for many cases it can be viewed as scalar. In such cases the effective susceptibility of a composite with demagnetized particles can be calculated by the usual scalar effective-medium equation, provided that the intrinsic susceptibility of the particles is used. For all other cases the mixing rules for tensor permeability should be applied.

For a demagnetized sample as used in our case both DW and FM permeability have a scalar form and are equivalent from the standpoint of mixing rules. Therefore, one can regard the effective permeability as a sum of all types of permeability, as long as the individual types do not change in the composite due to the different microstructure.

3. Experimental procedures

Ferrite powders based on spinel/M-hexaferrite (S–M) composites were prepared with solid-state reaction from Ba carbonate and Fe and Ni oxides at two temperatures, 1228 and 1296 °C. We prepared five types of samples with different weight ratios of spinel and M-hexaferrite, as shown in Table 1. The density of the samples was obtained by measuring the dimensions and the mass of all the samples.

Table 1
Weight ratios of hexaferrite and spinel in ceramic composite samples

	Hexaferrite (wt.%)	Spinel (wt.%)
Sample 1	90	10
Sample 2	80	20
Sample 3	70	30
Sample S	0	100
Sample M	100	0

All the samples were characterized with X-ray diffraction (XRD) analysis using a D4 Endeavor (Bruker AXS) diffractometer and Cu Kα radiation. The mass ratios of the constituent phases were determined with a Rietveld refinement[8] or from the integral intensities of the XRD peaks from diffractograms refined using the Pawley method[9] and the crystallographic program Topas2R 2000 from Bruker AXS, Karlsruhe, Germany. The diffractograms were refined using the space groups $Fd3m$ (2 2 7) for the spinel, and $P6_3/mmc$ (1 9 4) for the M-hexaferrite. In this paper the second method will be, for the sake of simplicity, referred as the Pawley method, and the intensity will refer to the integral intensity.

The permeability and permittivity of the materials were obtained by measuring the S-parameters with an Anritsu 37369C Vector Network Analyzer (measurements were made from 100 MHz to 10 GHz).[10] A short-circuited APC-7 coaxial line was used as the sample holder and the samples were machined to fit into the coaxial line. With such a measurement set-up there are no demagnetization factors and the obtained permeability is the intrinsic permeability of the material. Therefore, we can use this permeability for the calculations with the effective-medium equation. For determining the best match of the calculated effective permeability with the measured permeability, and subsequently the relevant volume fractions of spinel and hexaferrite phases, we compared the difference of the integrals of both permeabilities over the frequency range 0.1–3.0 GHz.

4. Results

The densities of all the samples were measured to be about 4.8 ± 0.1 g/cm^3. Since the theoretical densities of spinel and hexaferrite are roughly the same,[5] we can presume that the porosities of the sintered specimens are equal, around 10%. Because of the similar theoretical density and porosity of spinel and hexaferrite we can take that the volume fraction of the individual phase in the composite is roughly equal to the mass fraction.

Since the permittivity is approximately the same for ferrite phases and our objective was to differentiate various contributions in the composite, we focused our analysis on the permeability, where the differences between the various phases can be significantly larger. In order to analyze the volume fractions of hexaferrite and spinel phases in the composites we also had to measure the permeabilities of the pure phases (samples M and S). The results of the measurements of the permeability for samples sintered at 1228 °C are shown in Fig. 1. The spinel

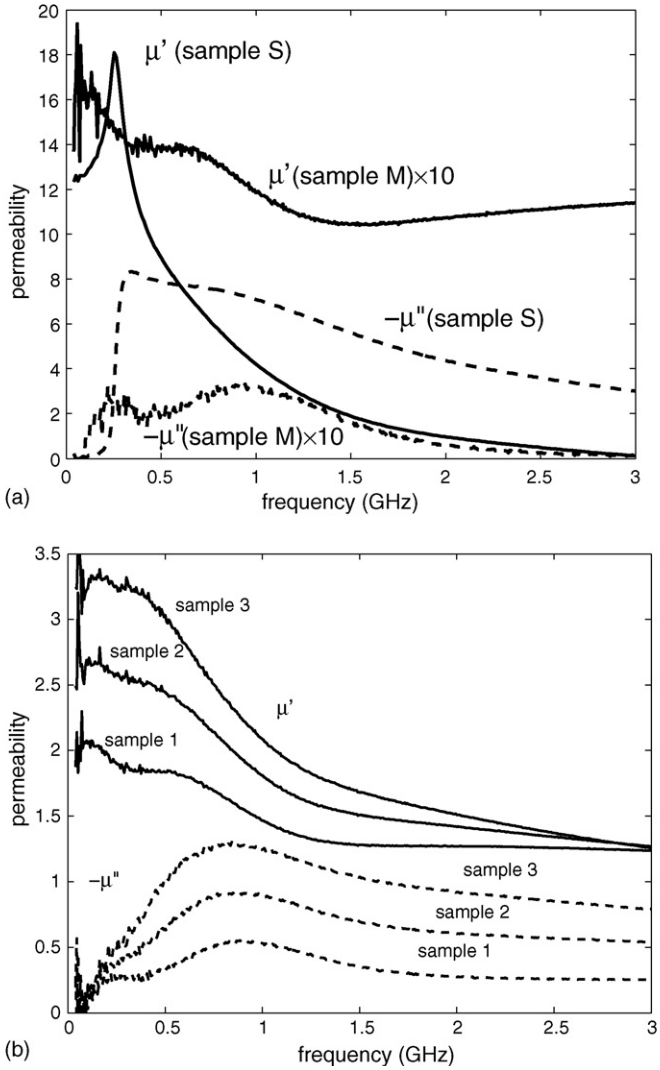

Fig. 1. Measured curves of real permeability μ' (solid lines) and imaginary permeability $-\mu''$ (dotted lines) for samples S, M and 1–3, sintered at 1228 °C. For an easier comparison the permeability of sample M is multiplied by 10.

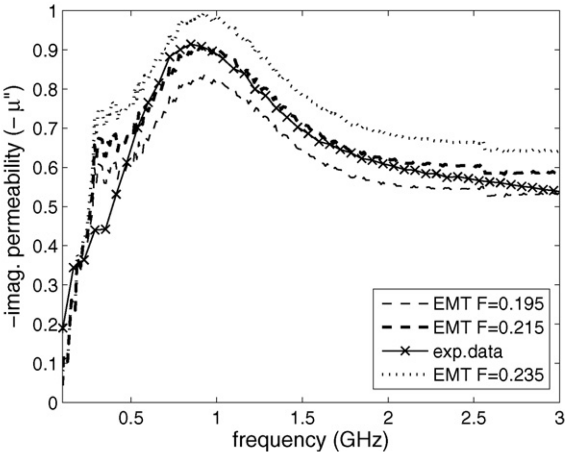

Fig. 2. Experimental data (solid lines) and calculated permeability with EMT (dashed lines) for sample 2, with different volume fractions of spinel for the comparison (best match and variation of ±0.02).

phase exhibits a significant initial permeability and magnetic losses from 300 MHz up, which can be attributed to the mix of the FM resonance and the DW relaxation. In contrast, the M-hexaferrite has the ferromagnetic resonance at a significantly higher frequency[5] and, consequently, the magnetic losses and FM contribution to the initial permeability are low. The observed magnetic losses and the higher intrinsic permeability can be attributed to the DW relaxation; however, the total effective permeability in the observed frequency range is significantly lower than that of the spinel phase. As can be expected, the effective permeability of the composite increases with the mass proportion of spinel phase.

Fig. 2 shows the results of an effective-permeability calculation from the data for single-phase materials in comparison with the measured data from sample 2. The match is poorer in the low-frequency region, and we will discuss the possible reasons for this later. Figure also shows the effect of varying the volume fraction of the calculated effective permeability, where thin lines represent a variation of ±0.02 in the volume fraction of the spinel phase around the best match. The difference is most evident for the imaginary part of the permeability.

A much better fit, and also better sensitivity, can be obtained by using measurements from two other composites instead of single-phase materials, as shown in Fig. 3. Of course here we will get the composition of our unknown composite (sample 2) in terms (volume fractions) of the other two composites, samples 1 and 3. If we assume that 0.1 and 0.3 are the volume fractions of spinel phase in samples 1 and 3, respectively, we can calculate that the obtained volume fraction of sample 1 ($F^* = 0.425$) in sample 2 corresponds to 0.21 volume fraction of spinel phase in sample 2. The shown variations of the composites' volume fractions (±0.1) correspond to ±0.02 variation of the spinel phase's volume fraction in sample 2.

Fig. 4 shows the calculated and measured imaginary parts of the permeability for samples 1 and 3, and the measured perme-

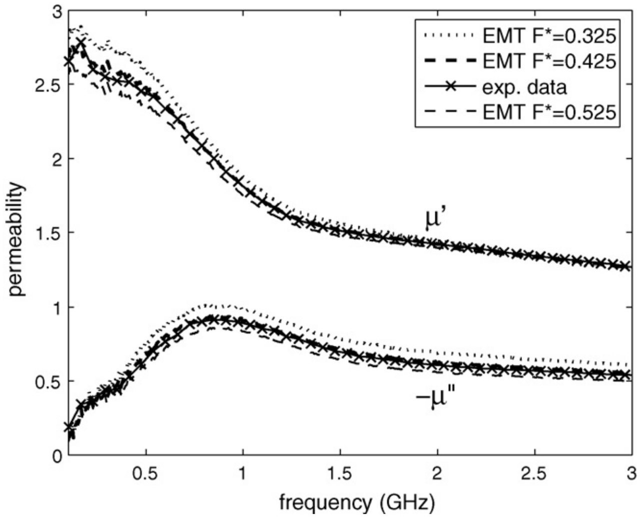

Fig. 3. Experimental data (solid line) and EMT calculations (dashed lines) for sample 2, where samples 1 and 3 were taken as the input parameters. Volume fraction F^* is defined as proportion of sample 1. The thicker dashed line is for the case of best match ($F^* = 0.425$), the thinner dashed lines for cases with varied volume fractions.

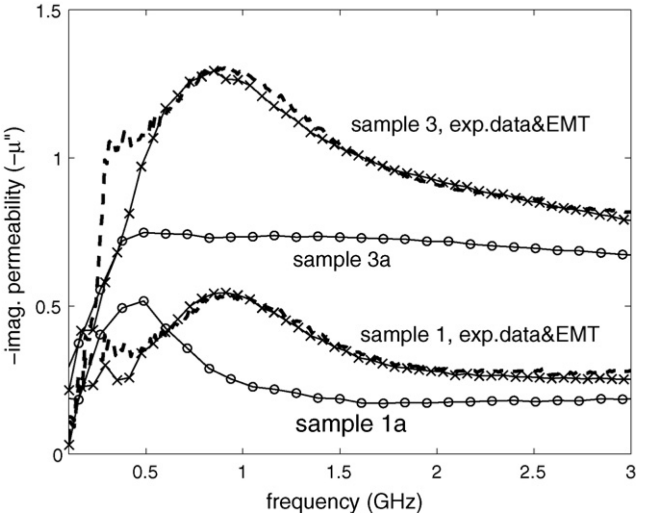

Fig. 4. Experimental data (solid line) and EMT calculations (dashed line) of imaginary permeability $-\mu''$ for samples 1 and 3. The calculated volume fractions of spinel phase are 0.1 and 0.305, respectively. Experimental data for samples 1a and 3a, which were sintered at higher temperature (1296 °C), are added.

abilities for samples 1a and 3a sintered at a higher temperature. There is a substantial reduction of permeability for the latter two samples. Indeed, the calculation shown in Fig. 5 show a substantially lower volume fraction of spinel phase and thus indicate the reaction of spinel with M-hexaferrite. This was confirmed with the XRD analysis.

Fig. 6 shows X-ray diffractograms of the samples 1–3 sintered at 1228 and 1296 °C. For the sake of clarity, only Müller indexes of the peaks relevant for the following discussion are marked. The diffraction peaks of the samples sintered at 1228 °C correspond to the spinel and M-hexaferrite structures only, while additional diffraction peaks corresponding to W-hexaferrite can be observed in the diffractograms of the samples sintered at 1296 °C. This indicates that the two constituent phases reacted during the sintering at 1296 °C. W-hexaferrite was formed as a result of this reaction. This is in agreement with the reported phase-diagram data, according to which the formation of W-hexaferrite from spinel and M-hexaferrite starts at 1250 °C.[11] Furthermore, this explains the observed differences in the permeability of the differently sintered samples shown in Fig. 4 and the lower volume fractions of both constituent phases calculated for the high-temperature samples (Fig. 5).

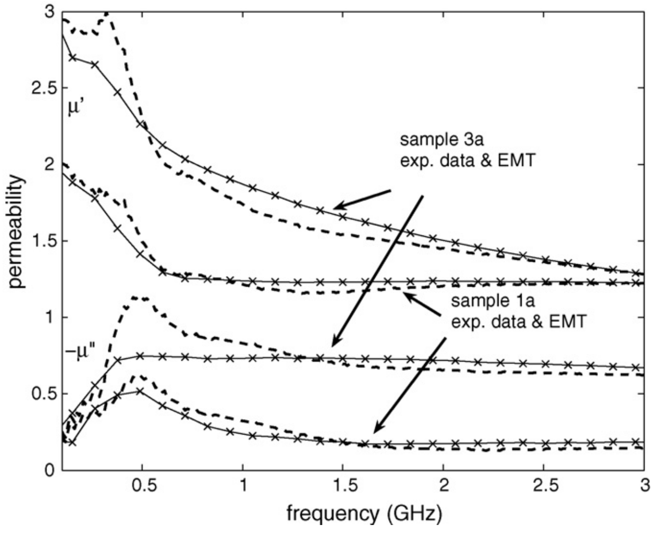

Fig. 5. Measured (solid line) and calculated (dashed line) permeabilities of samples 1a and 3a. Volume fractions of spinel phase for the fit were 0.06 and 0.23, respectively, compared to the nominal weight composition of 0.1 and 0.3.

5. Discussion

In the presented cases we had only two different phases; however, the described method for determining the volume fractions of phases can be readily extended to systems with more phases. A more serious limitation is that when there are phases with similar permeabilities in the composite the presented method cannot easily distinguish between them. Fortunately, this problem can be identified early on with a comparison of the measured permeabilities of single-phase samples, thus preventing incorrect results.

Further, with the above-described calculations we used some assumptions that have to be analyzed. The first assumption was that the porosity of the samples and the microstructure inside the individual phase does not vary significantly between single-phase samples and ceramic composites. This was confirmed with density measurements of all the samples.

The second assumption was that the permeability of a given phase, obtained with a single-phase sample, remains the same in the ceramic composite. If the permeability is an intrinsic property that is due to ferromagnetic resonance there should not be much difference if the phase is bulk or isolated in individual grains or islets. However, when the permeability is due to domain-wall motion, the size of the inclusions would considerably affect the value of the DW permeability of the inclusions.[5] In contrast, the DW permeability of the matrix would be relatively unaffected for lower volume fractions of inclusions.

In our case we had spinel inclusions in a hexaferrite matrix. By comparing the measured permeabilities of samples 1–3 with that of sample M (pure hexaferrite) we can observe a similar double-peaked character of permeability for both sample M and 1, whereas in samples 2 and 3 the first peak gradually vanishes. In both samples the volume fraction of spinel phase is large enough to somewhat disrupt the domain pattern in the hexaferrite phase and thus affect the permeability. This would also explain the poorer matching of the calculated and measured permeabilities at lower frequencies. The match is better when we used samples 1 and 3 as the input parameters for the calculations because the domain pattern of the matrix (hexaferrite) does not differentiate as much.

In Table 2 the mass or volume fractions of the spinel phase in the samples 1–3 are listed. As explained previously, the mass and volume fractions are, in this particular case, the same. If we take into an account the experimental error of the XRD methods, which is 1–3 wt.%, depending on the sample, nearly all the data are in agreement. A significant discrepancy can be observed for the mass fraction determined with the Rietveld method for sample 2. The Rietveld method is based on the structure model

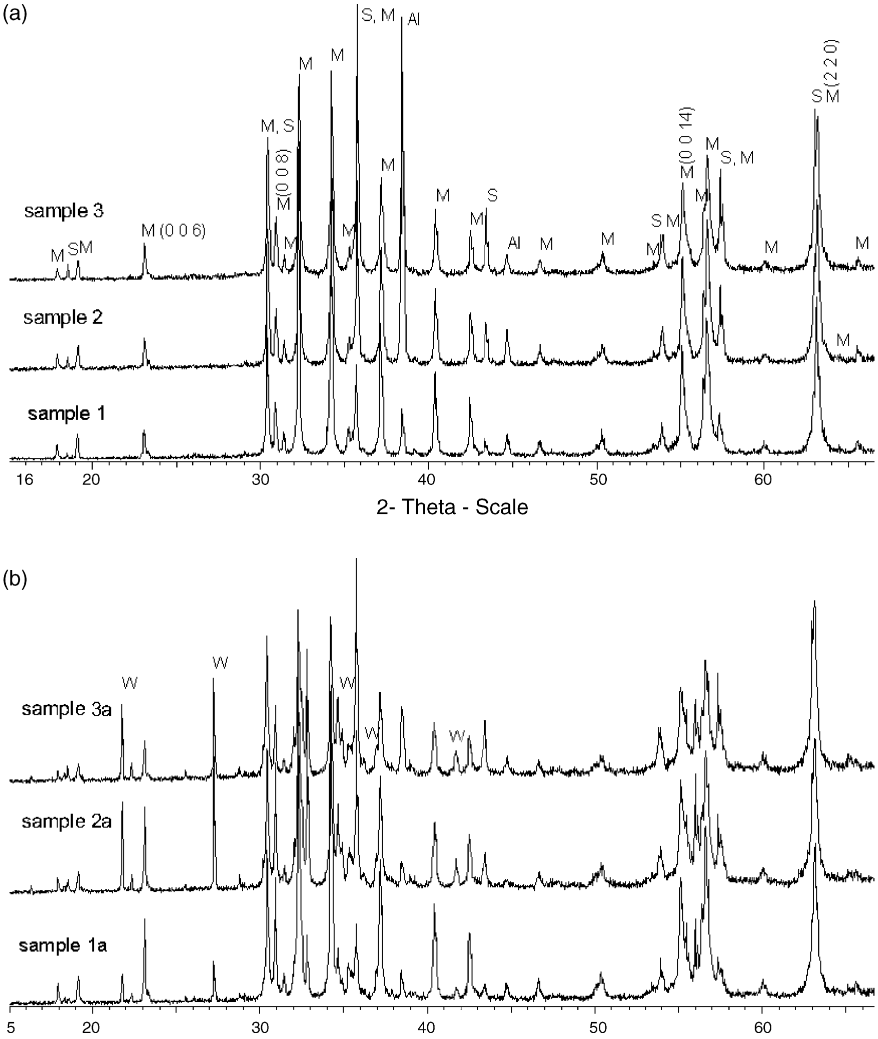

Fig. 6. X-ray diffractograms of the samples 1–3, sintered at 1228 and 1296 °C. S, M and W denote spinel, M- and W-hexaferrite, respectively. Al stands for Al from a sample holder.

and the peak intensities are fitted with respect to the structure and the mass ratios of the crystalline compounds in the sample. However, in the case of the hexagonal M-hexaferrite crystallites preferential orientation can be induced during the sample preparation for the XRD analysis and cannot be avoided or controlled. As a consequence the intensities of the (0 0 l) peaks (see Fig. 6) are influenced also by the degree of preferential orientation. In contrast, the Pawley method is based on decomposition of the whole pattern and the peaks intensities are irrelevant and depend only on the mass ratios of the crystalline compounds in the sample. When the Pawley method was used, the (0 0 l) peaks of M-hexaferrite structure were omitted from the calculation, and the calculated mass fractions are therefore more reliable in this particular case. Nevertheless, also when the Pawley method was used for sample 1a lower mass fraction of the spinel was determined compared to the other methods. This could be explained on the basis of the spinel and M-hexaferrite structures. Namely, the M-hexaferrite structure is composed of two types of structural blocks, the so-called S and R. The S block represents a spinel-type arrangement of the atoms. Conse-

Table 2
wt.%/vol.% of spinel for different ceramic composites

	Nominal composition (wt.%)	EMT (vol.%)	EMT (vol.%) sample 1 + sample 3	Pawley method (wt.%)	Rietveld method (wt.%)
Sample 1	10	10		7	11
Sample 2	20	21.5	21	19	16
Sample 3	30	30.5		29	30
Sample 1a	10	5			
Sample 2a	20	12			
Sample 3a	30	23			

quently, some of the diffraction peaks of the spinel overlap with those of the M-hexaferrite. When the amount of spinel phase is low, like in sample 1, the overlapped peaks present a significant contribution to the overall intensity of the spinel peaks and consequently a significantly lower amount of the spinel was determined.

6. Conclusions

We applied mixing rules to ceramic composites in order to determine their phase composition. With our experiments we showed that by using the effective-medium theory calculation we could not only determine the volume fractions of the constituent phases in a ceramic composite but also detect the formation of new phases. By sampling composites sintered at different temperatures we could roughly determine the reaction temperature. Since the presented method of applying mixing rules is simple and fast, it could be used for controlling the sintering process.

Comparing the XRD and EMT data we can conclude that the EMT quantitative phase determination of magnetic composites is at least as reliable as the XRD methods. The EMT method represents a simple and fast complementary alternative to XRD quantitative phase analysis in the case of magnetic samples, and by knowing the limitations of each method one can choose the most appropriate.

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