Li₂MoO₄-Based Composite Ceramics Fabricated from Temperature- and Atmosphere-Sensitive MnZn Ferrite at Room Temperature

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The first magnetic ceramic composites manufactured using the room temperature densification method are reported. The samples were prepared at room temperature using Li₂MoO₄ as a matrix and MnZn ferrite with loading levels of 10-30 vol-% followed by post-processing at 120 °C. The method utilizes the water solubility of the dielectric Li₂MoO₄ and compression pressure instead of high temperatures typical of conventional solid state sintering. Hence, composite manufacturing using temperature- and atmosphere-sensitive materials is possible without special conditions. This was demonstrated with MnZn ferrite, which is prone to oxidation when heat treated in air. Samples manufactured with room temperature densification showed no signs of reactivity during processing, whereas reference samples sintered at 685 °C suffered from oxidation and formation of an additional reaction phase. The densities achieved with different loading levels of MnZn ferrite with both methods were very similar. Measurements up to 1 GHz showed relatively high values of relative permittivity (21.7 at 1 GHz) and permeability (2.6 at 1 GHz) with 30 vol-% loading of MnZn ferrite in the samples manufactured by room temperature densification. In addition, pre-

granulation is proposed to improve the processability of the composite powders in room temperature densification.

I. Introduction

Composites with magnetic and dielectric properties are versatile and thus employed in microwave and RF applications, such as antennas¹⁻³ and electromagnetic wave absorbers.⁴⁻⁶ These composites are typically polymer- or ceramic-based soft ferrite composites.⁷⁻¹⁰ In this respect, the spinel-type MnZn and NiZn ferrites are popular choices, with a general formula of MFe₂O₄, where M represents a combination of the above-mentioned divalent cations. As oxides, the ferrites also exhibit good dielectric properties in addition to spontaneous magnetization due to magnetic Mn or Ni ions.¹¹ Depending on the valence of the cations and their distribution among different lattice sites, ferrite adopts different forms of the spinel structure. In a normal spinel, divalent M cations are located in tetrahedral A-sites and trivalent Fe cations in octahedral B-sites. In an inverse spinel, divalent cations occupy B-sites with trivalent cations distributed in both A- and B-sites. An intermediate cation arrangement is referred to as a mixed spinel.¹² As the cationic composition

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affects the spinel structure, it is an important factor in addition to porosity and grain size in determining the electrical and magnetic properties of these ferrites.¹²⁻¹⁴ To optimize the magnetic properties, an excess of iron oxide is often added.¹⁵ In the case of MnZn ferrites, their relative permeability (μ_r) remains high up to several MHz before it deteriorates, whereas NiZn ferrites have a high μ_r up to 100 MHz.¹³ However, these properties can be adjusted with a composite approach to meet the requirements of different applications.^{7,12} The properties of a composite are determined by its constituent phases, and thus the more abundant matrix phase dominates the effective properties of the final composite.⁹ Therefore, in the case of ceramic-based ferrite composites, relative permittivity (ϵ_r) always reaches greater values than the μ_r .

The general method for processing ceramic materials is the conventional solid state method which includes a high-temperature sintering step.^{10,12,16} During sintering, thermally assisted mass transport leads to densification of the compressed powder into a solid piece at temperatures relatively close to, but always below, the melting point of the ceramic material. Since ceramics are typically heat resistant, very high temperatures are required for sufficient sintering to occur. Besides the disadvantageous high energy consumption, the high temperature can also cause other challenges. Predictability and controllability of the final properties may decrease due to evaporation of volatile compounds and increased chemical reactivity. In addition, a possible thermal expansion mismatch between

different materials may lead to decreased durability, and sintering-related shrinkage complicates the preparation of products with complex shapes. Furthermore, compatibility with low-melting additive, conductor, and substrate materials is greatly restricted, which hinders further development of ceramic composites and components.¹⁶⁻¹⁸

Processing of ferrites by the conventional solid state method is challenging since ferrites with Mn and/or excess Fe generally suffer from oxidation depending on the sintering atmosphere at temperatures of 550-1000 °C.^{11,19,20} Even when higher temperatures are used, this phenomenon must be taken into account during cooling.¹⁹ Oxidation leads to deterioration of the magnetic properties as the spinel structure is changed or even decomposed,^{19,20} and to weight gain as extra oxygen atoms are incorporated into the material.¹⁹ The oxidation products that are formed depend on the applied temperature, annealing time, and oxygen partial pressure, whereas the rate of oxidation is inversely proportional to particle size.^{19,20} As Mn and Fe have various valences, they thus have the potential to undergo oxidation-reduction reactions.²⁰ Migration of oxidized Mn^{3+} cations with Fe^{3+} cations between A- and B-sites results in formation of a ferrite-manganite- $\gamma\text{-Fe}_2\text{O}_3$ solid solution within the spinel structure.¹⁹ After a critical degree of oxidation is exceeded, $\alpha\text{-Fe}_2\text{O}_3$ or even Mn_2O_3 precipitates as separate phases with body-centered cubic structures.^{19,20} In addition, formation of reduced Fe^{2+} cations at over 1000 °C and accompanying electrons and their migration within the lattice is detrimental

to the dielectric properties, as electrical resistivity decreases due to conduction by electron hopping.¹¹ To prevent these phenomena, an inert sintering atmosphere is required.^{11,19,20} Alternatively, the sample may be quenched in water after sintering stage.¹⁵ However, a completely oxygen-free atmosphere causes Zn to vaporize at high temperatures, deteriorating the magnetic properties.²¹ Therefore, prevention of oxidation and related side effects is essential and requires careful control of the sintering atmosphere and temperature.^{11,19,20}

During the past decades, attempts to overcome the problems related to the solid state method have led to the development of low- (LTCC) and ultra-low- temperature co-fired ceramic (ULTCC) technologies operating at sintering temperatures of < 950 °C and < 700 °C, respectively.^{16,17} These technologies rely on the use of glassy systems with low softening points or ceramic materials with originally low melting points, such as vanadates, tungstates, molybdates, tellurates, and borates,¹⁶⁻¹⁸ or the use of sintering aids.²² For example, Li_2MoO_4 , with a melting point of 704 °C, can be sintered at 540 °C.²³ However, this does not completely solve all the temperature-related problems.

Recently, an alternative fabrication method without the high-temperature sintering step has been presented for Li_2MoO_4 ceramics.²⁴⁻²⁶ This solution and pressure-assisted fabrication method has been referred to as room temperature densification (RTD). Taking advantage of the water solubility of Li_2MoO_4 , the method enables fabrication of dense Li_2MoO_4 -based ceramics at temperatures as low

as room temperature. Moderate moistening of Li_2MoO_4 powder with deionized water forms a small amount of aqueous phase; it is suggested that this phase transports material during uniaxial compression.²⁴ Subsequent evaporation of residual water leads to recrystallization of the previously dissolved Li_2MoO_4 . To promote this, post-processing at a mild temperature of 120 °C is suggested.²³ The post-processing temperature has been observed to mainly influence the time needed to remove residual water,²⁵ and can therefore be chosen to suit the other materials in use, such as the substrate or electrode materials. As a result, dense Li_2MoO_4 ceramics with relative permittivity of 5.1 and a $\tan \delta$ value of 3.5×10^{-4} at 9.6 GHz were achieved.^{24,25} In addition, the method has successfully been applied to composite manufacturing with 10-30 vol-% of TiO_2 and 10 vol-% of BaTiO_3 insoluble additives, enabling modification of the composite's dielectric properties.^{25,26} The measured dielectric properties were found to follow Lichtenecker's empirical logarithmic rule up to 20 vol-% loading. Beyond this level, the correspondence was observed to decrease due to increased porosity.²⁶

Because of the low processing temperature, RTD exhibits significant advantages over high-temperature solid state sintering. Undesirable reactions resulting in the formation of extra phases can be avoided as well as heat expansion and sintering-related shrinkage problems. This enhances the predictability and controllability of the product.^{25,26} Moreover, the samples maintain their dimensions after pressing, as no measurable changes in sample size have been

observed. This enables easy manufacturing of samples and components with complex shapes, since the final size of the product is defined by the mold's dimensions and the amount of powder.²⁶ In addition, RTD significantly extends the selection of usable additive, substrate, and electrode materials to temperature-sensitive ones. This is expected to enable fabrication of completely new kinds of composites and allow seamless integration of ceramics and polymers.²⁴ The method has also been proven feasible for Ag electrode integration.²⁶

However, some processing issues have existed with RTD due to the small particle size of Li_2MoO_4 .^{25,26} In the case of composite manufacturing, a Li_2MoO_4 particle size smaller than $45\text{ }\mu\text{m}$ was essential in order to achieve even distribution of a TiO_2 additive in the Li_2MoO_4 matrix.²⁶ Previously, when such Li_2MoO_4 powder was moistened, clay-like clumps were formed, resulting in uneven density and further warpage and cracking of the samples.¹⁵ With a larger particle size ($< 180\text{ }\mu\text{m}$), these problems were nonexistent. Therefore, the samples manufactured from Li_2MoO_4 powder with a larger particle size exhibited improved dielectric properties in comparison with those manufactured from the smaller particle size powder. In a recent study, the amount of aqueous phase was increased in an attempt to overcome the processing issues caused by the small particle size thereby enabling the manufacture of composites with even TiO_2 distribution.²⁶ However, this resulted in flashing of the material through the pistons during compression. On the other hand,

decreasing the pressure is not an adequate solution as pressure is considered to be the driving force responsible for densification.^{25,26} Hence, a larger Li_2MoO_4 particle size is considered more advantageous from the processing point of view.

In this study, the RTD method was applied to prepare magneto-dielectric composite ceramics from Li_2MoO_4 with insoluble temperature- and atmosphere-sensitive MnZn ferrite loadings up to 30 vol-% without the use of a controlled atmosphere. Furthermore, an additional process stage of pre-granulation is introduced to enhance the processability of Li_2MoO_4 composite ceramics. The effect of the MnZn ferrite volume fraction on the composite's relative permittivity and permeability was studied over a frequency range of 1 MHz to 1 GHz. The impact of the preparation method on these properties, as well as on the phase composition and microstructure, is discussed in contrast to sintering. Moreover, pressed toroids were prepared by RTD and their relative permeability and related losses were studied in comparison with corresponding discs that were drilled toroidal.

II. Experimental procedure

Li_2MoO_4 powder (99+ %, Alfa Aesar, Karlsruhe, Germany) was milled in ethanol with ZrO_2 milling media in a planetary ball mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany) to reduce particle size and to achieve suitable size distribution. After sieving with a mesh size of $< 45\text{ }\mu\text{m}$, the powder was analyzed with a laser diffraction particle size analyzer (Beckman Coulter LS13320, Brea, CA). At

least 99 % of the particles were observed to be smaller than the mesh size used, with a mean particle size of 15 μm . Similarly, the particle size distribution of as-received MnZn ferrite (Toda Kogyo, Hiroshima, Japan) was measured to be 100 % under 32 μm , with a mean particle size of 9.4 μm . To prepare the composite powders, predetermined amounts of MnZn ferrite corresponding to the desired ferrite loadings of 10, 20, and 30 vol-% were mixed with Li_2MoO_4 in ethanol, first with an ultrasonic mixer to break down possible agglomerates, and then with a mortar and pestle. The resulting slurries were dried out in an oven at 100 $^\circ\text{C}$, followed by sieving ($< 45 \mu\text{m}$).

As a difference from the previously reported RTD method of producing Li_2MoO_4 composite ceramics,²⁶ an additional process stage of pre-granulation²⁷ was carried out to reduce the fabrication problems related to the small Li_2MoO_4 particle size. Deionized water was sprayed on the composite powders while mixing with a spatula to achieve a thick uniform paste. Each paste was pressed uniaxially into a large disc ($\varnothing$ 25 mm) in a steel mold under a pressure of 40 MPa. The discs were then dried at 120 $^\circ\text{C}$ for 24 h to evaporate residual water and to recrystallize the dissolved Li_2MoO_4 . After grinding the discs by hand in a mortar with a pestle to a coarse powder, this pre-granulated powder was sieved with a mesh size of $< 180 \mu\text{m}$.

To prepare the disc samples, the pre-granulated powders were moistened again. Less water was now needed and a free-flowing powder was formed instead of a paste. The discs were pressed and dried ($\varnothing$ 20 mm, thickness 2.5

mm) as described above, except that the pressing pressure was increased to 150 MPa to achieve proper densification of the samples. Similarly, a set of toroidal samples was prepared using a steel mold equipped with hollow cylinder-shaped pistons accommodating a rod ($\varnothing$ 5 mm) in the middle. In addition, corresponding reference disc samples were prepared as described above, and then sintered at 685 $^\circ\text{C}$ for 2 h in air according to the sintering of $\text{Li}_2\text{MoO}_4\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composites.⁸ The surfaces of all samples were polished with a P1200 carborundum paper (EcoWet, KWH Mirka Ltd, Jeppo, Finland) to ensure even thickness and surface smoothness. The final thicknesses of the different samples varied from 1.9 to 2.4 mm.

The densities of the samples were calculated from their measured dimensions and masses. An X-ray diffractometer (XRD, Bruker D8 Discover X-Ray Diffractometer, Karlsruhe, Germany) with a sample spinner and a 1.2 mm secondary slit was employed to analyze the phase composition of the samples by using CuK_α radiation. The diffraction patterns were recorded at 10-70 $^\circ$ 2 θ with a 0.01 $^\circ$ step size and 0.10 s dwell time per step. Microstructural characterization of the samples was done with a field emission scanning electron microscope (FESEM, Zeiss ULTRA Plus, Karlsruhe, Germany) equipped with an energy dispersive spectrometer (EDS, Oxford Instruments X-Max^N, Abingdon, United Kingdom). Prior to the FESEM analyses, the sample surfaces were polished using water-free polycrystalline diamond suspensions (Akasel, Cloeren Technology GmbH, Wegberg, Germany) and

then coated with a thin layer of carbon to eliminate electrostatic effects. The relative permittivity and permeability of the samples were measured over a frequency range of 1 MHz to 1 GHz with an RF impedance/material analyzer (Agilent E4991A, Santa Clara, CA) equipped with test fixtures (16453A and 16454L for permittivity and permeability measurements, respectively). For the ϵ_r measurements, silver electrodes with diameters suitable for the test fixtures were sputtered on both sides of the disc samples. For the μ_r measurements, a hole ($\varnothing$ 5 mm) was drilled through the center of the disc samples to produce a toroidal shape. To study the effect of the processing temperature, thermogravimetric analyses and differential scanning calorimetric measurements (TGA-DSC) were performed with a thermal analyzer (Netzsch STA 449 F3 Jupiter, Selb, Germany) equipped with a silicon carbide furnace and alumina crucibles. A dynamic heating profile up to 700 °C and back to room temperature with a heating/cooling rate of 20 K/min was employed. The TGA-DSC measurements were carried out under concurrent flows of nitrogen as a protective gas

and either air or argon as a purge gas, all at a rate of 50 ml/min.

III. Results and discussion

The new processing stage of pre-granulation significantly improved the processability of composite powders by RTD, as earlier issues with processability^{25,26} were eliminated. Moistening with deionized water and mixing of the pre-granulated powders was easy without any clump formation. The resulting mass of free-flowing powder remained in the mold during compression, with some excess aqueous phase dripping through the pistons. The finished samples showed no signs of cracking or warpage.

The relative densities of the samples are reported in Table 1. The values achieved by RTD are similar to those of previously investigated $\text{Li}_2\text{MoO}_4\text{-TiO}_2$ composites with corresponding loading levels and fabrication method.²⁶ The sintered samples had slightly higher relative densities, even though no measurable change in sample dimensions was detected when the before and after sintering dimensions were compared. Regardless of the

Table 1. Relative densities and relative permeabilities, permittivities, and related losses, measured at 1 MHz and 1 GHz, of the samples manufactured by RTD and sintering

Fabrication method	MnZn ferrite loading (vol-%)	Relative density (%)	f = 100 MHz				f = 1 GHz			
			ϵ_r	Tan $\delta(\epsilon)$	μ_r	Tan $\delta(\mu)$	ϵ_r	Tan $\delta(\epsilon)$	μ_r	Tan $\delta(\mu)$
RTD	10	88-90	9.4	0.015	1.5	0.030	9.2	0.025	1.6	0.149
	20	87-89	14.5	0.041	2.1	0.057	14.0	0.074	2.1	0.279
	30	84-87	22.7	0.081	2.8	0.091	21.7	0.173	2.6	0.411
Sintering	10	90-91	7.3	0.001	1.4	0.022	7.4	0.006	1.5	0.148
	20	88-89	7.9	0.003	1.8	0.036	8.1	0.012	1.9	0.240
	30	88	9.2	0.004	2.5	0.061	9.5	0.022	2.4	0.357

fabrication method, the relative densities were observed to decrease with increasing MnZn ferrite loading. In the previous case of $\text{Li}_2\text{MoO}_4\text{-TiO}_2$ composites processed with RTD, a similar observation was made, likely due to increased formation of finely distributed very small pores when the amount of insoluble additive was increased.²⁶ The higher loading level incorporates an increasing amount of aqueous Li_2MoO_4 phase, which is needed to fill the spaces between the insoluble particles during compression. Thus, more residual water remains in the sample after compression, which then evaporates during post-processing, leaving very small pores behind.²⁶ Similar results with $\text{Li}_2\text{MoO}_4\text{-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composites sintered at 685 °C have been explained by disturbed

interaction between each developing Li_2MoO_4 grain due to the increased content of ferrite particles.⁸

Figure 1 shows back-scattered electron (BSE) images as well as the mix images of $\text{Li}_2\text{MoO}_4\text{-MnZn}$ ferrite samples with 30 vol-% MnZn ferrite loadings prepared using both methods. Increasing porosity was observed with increasing MnZn ferrite loading, which is in line with the measured densities. The size of the pores in the samples prepared by RTD was smaller than in the sintered samples (Fig. 1 a and b), while their characteristic shape appeared to be the same. The larger rounded pores are clearly caused by the sintering. The surrounding material appeared more granular in the case of the RTD samples in contrast to the more

Figure 1. Backscattered electron images and mix images of the composites with 30 vol-% MnZn ferrite loadings prepared (a and c) by room temperature densification (RTD), and (b and d) by sintering, respectively. The colors in the mix images denote Mo (cyan), superimposed Mn, Zn, and Fe (brown), and superimposed Mo and Mn (dark blue)

uniform material in the sintered ones. However, due to the similar relative atomic masses of the Li_2MoO_4 and MnZn ferrite phases, no gray scale variation between the phases was detected from plain BSE images. Therefore, to investigate the MnZn ferrite particle distribution in the Li_2MoO_4 matrix, X-ray elemental mapping was additionally employed with EDS. The resulting mix images (Fig. 1 c and d) reveal that the distribution is quite uniform, which further supports the feasibility of the pre-granulation stage for RTD processing of composite powders. In addition, the mix images of the sintered samples indicate that an additional phase containing at least Mn and Mo has formed during sintering, with increasing amounts corresponding to MnZn ferrite loading.

Figure 2 shows the X-ray diffraction patterns of the composite samples prepared by RTD with different MnZn ferrite loadings. The only phases observed were Li_2MoO_4 and MnZn ferrite with increasing intensity of the MnZn ferrite signals respective to its loading. As the EDS analyses showed no indication of additional phases, it is therefore suggested that no reaction takes place at the RTD process stages. This is consistent with previous composite studies with the RTD method.^{25,26} The diffraction patterns of the corresponding sintered samples appeared similar to those of the RTD-processed samples, with no distinguishable signals of Mn- or Mo-based extra phases. However, minor differences were detected in the MnZn ferrite-related signals in the patterns of the 30 vol-% samples (Fig. 3). This indicates that the ferrite has undergone

Figure 2. X-ray diffraction patterns of the composites manufactured with room temperature densification (RTD) with a stick column pattern of Li_2MoO_4 (powder diffraction file 12-0763) and X-ray diffraction pattern of MnZn ferrite powder

Figure 3. X-ray diffraction pattern of the composites with 30 vol-% MnZn ferrite loading manufactured with both methods. Two differing MnZn ferrite-related signals have been pointed out as examples

some structural changes during sintering, probably as a consequence of oxidation. Due to the intensity and complexity of the diffraction pattern of the Li_2MoO_4 matrix and the resulting possibility of overlapping, detailed identification of the supposed oxidation products by XRD is restricted. Similarly, no Mn- and Mo-based reaction phase was detected by XRD due to its expectedly low amount, and thus the low intensity of the corresponding diffraction pattern in addition to plausible overlap with that of Li_2MoO_4 .

However, the identity of the Mn- and Mo-based reaction phase can be speculated. Investigation of the Mn-Mo-O phasediagram²⁸ reveals two tentative candidates: MnMoO_4 and $\text{Mn}_2\text{Mo}_3\text{O}_8$. These phases were found to match the diffraction pattern of the sintered 30 vol-% sample, MnMoO_4 with both α and wolframite structures. In addition, different hydrates of MnMoO_4 also produced a match. Previously, both MnMoO_4 and $\text{Mn}_2\text{Mo}_3\text{O}_8$ have been prepared from stoichiometric amounts of Mn oxides and MoO_3 by using a solid state reaction.^{29,30} A temperature of 580 °C and an open crucible were used to produce MnMoO_4 , whereas a temperature of 980 °C and a closed ampoule were used to produce $\text{Mn}_2\text{Mo}_3\text{O}_8$.²⁹ Another sealed solid state sintering of MnMoO_4 at 1000 °C produced an α -structure, whereas a wolframite structure was obtained under additional pressure of 65 kbars.³⁰ Therefore, taking into account the conditions prevailing both during and after sintering, the most probable candidate is α - MnMoO_4 , which also is the most stable MnMoO_4 polymorph under STP conditions.³⁰ In addition, formation of MnMoO_4

hydrates is unlikely as water evaporates during post-processing at 120 °C for 24 h prior to sintering. Moreover, even constitutional water is absent, since Li_2MoO_4 and MnZn ferrite do not form hydrates, as has been shown previously²⁴ and is shown later in this article.

Reported solid state preparations of α - MnMoO_4 ^{29,30} suggest a requirement of some MoO_3 , which incongruent melting of Li_2MoO_4 ³¹ could provide. Previously, Li_2MoO_4 - $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composites were observed to melt at 690 °C,⁸ which is only 5 °C higher than the sintering temperature used in this study. Therefore, the proposed partial melting of Li_2MoO_4 at the sintering temperature used is plausible even though the reported melting points of 698 °C³² and 705 °C³¹ for pure Li_2MoO_4 are not exceeded.

To acquire supplementary information on the elemental composition of the Mn-Mo-based phase, point analyses were conducted with EDS. The analyses showed a Mn-Mo-O atomic ratio of 1:2.3:10.6, for which neither MnMoO_4 nor $\text{Mn}_2\text{Mo}_3\text{O}_8$ gives a match. However, it is noted that EDS detection of light elements is unreliable at best. Therefore, the above-reported atomic percentage of O is only a tentative approximation, and the possible coexistence of Li in the Mn- and Mo-based reaction phase cannot be observed at all.

To get further insight into the proposed oxidation of the MnZn ferrite during sintering, TGA-DSC analysis was performed for the pre-granulated composite powder with a MnZn ferrite loading level of 30 vol-% in air. The composite powder showed no changes in the DSC graphs (Fig. 4 a) until the appearance of an

Figure 4. TG (red line) and DSC (black line) graphs of (a) pre-granulated 30 wt-% Li_2MoO_4 -MnZn ferrite composite powder measured in air and (b) pure MnZn ferrite powder measured in air (solid line) and in argon (dotted line)

endothermic peak in the DSC graph at 660-700 °C, which is attributed to the Li_2MoO_4 melting. Respectively, a strong exothermic signal at 640-660 °C was observed upon cooling, which is related to the Li_2MoO_4 recrystallizing and the formation of the Mn- and Mo-based phase previously detected by EDS (Fig. 1 d). In the TG graph, only a slight increase (about 0,3 %) in mass during heating was detected. This would result from addition of oxygen due to the proposed MnZn ferrite oxidation.¹⁹

As the amount of MnZn ferrite is relatively low in the composite, its contribution to the behavior of the composite was clarified by a similar analysis of the pure ferrite powder. Contrary to that of the composite powder, the DSC graphs of MnZn ferrite (Fig. 4 b) demonstrated two mild exothermic signals, at

360-400 °C and at 580-620 °C, respectively. Simultaneously, the TG graph showed a 2 % increase in mass starting at 360-400 °C with a moderate rise until 700 °C. No signals appeared upon cooling in either the TG or DSC graphs. An equivalent analysis in an inert argon atmosphere (Fig. 4 b) showed that the two exothermic signals in the DSC graph were now absent. In addition, no mass change was observed, whatsoever. Therefore, it was concluded that oxidation of MnZn ferrite is evident during sintering of the reference composite samples. However, the behavior of pure MnZn ferrite powder should not be considered identical to its behavior as a constituent phase of a composite. In this particular case, the total degree of oxidation is assumed to be relatively low, since the MnZn

ferrite particles are protected by the surrounding Li_2MoO_4 matrix. Furthermore, the composite has already been compacted with RTD prior sintering to a density of at least 84 % (Table 1), which further decreases the opportunity for interaction with air. However, the MnZn ferrite particles on the sample surfaces are exposed to more severe oxidation.

Furthermore, the possibility of MnZn ferrite hydrate formation was studied with TGA-DSC, in air. A sample of pure MnZn ferrite was now moistened with deionized water and then dried at 120 °C for 3 h, imitating RTD processing of the composite. The following analysis produced a TG-DSC graph identical to that of non-moistened MnZn ferrite. Since no signals related to hydrate decomposition were observed, the formation of MnZn ferrite-related hydrates was excluded.

The relative permittivity and permeability of the samples over the frequency range of 1 MHz to 1 GHz are presented in Figure 5 and the corresponding values at 100 MHz and 1 GHz

are given in Table 1. The composites exhibit relatively larger values of ϵ_r and μ_r as the loading level of MnZn ferrite increases. Also the properties of the RTD samples exhibit values about 2-3 times higher than the sintered ones which were observed to suffer from oxidation and thus related degradation of MnZn ferrite. For example, the value of ϵ_r is about the same for the RTD sample with 10 vol-% MnZn ferrite loading as for the 30 vol-% sintered sample (Fig. 5 a, Table 1). In the case of μ_r , both of the 10 vol-% samples showed similar values (Fig. 5 b, Table 1). However, with higher MnZn ferrite loading levels, the increase in μ_r is faster with the RTD samples. Thus, the lower the MnZn ferrite loading level, the better the ferrite particles are protected by the Li_2MoO_4 matrix which lowers the effect of oxidation on the composite properties. Furthermore, it should be noted that the sample surfaces that experience the highest oxidation were polished before the measurements.

Figure 5. (a) Relative permittivity and dielectric loss tangents, and (b) relative permeability and magnetic loss tangents of the samples manufactured by room-temperature densification (RTD) and sintering

In general, a higher processing temperature enhances the material's dielectric and magnetic properties as its density improves and grain size increases with decreasing grain boundary area.^{33,34} With the RTD method, it is clear that no grain growth occurs, whereas with sintering the density is slightly increased and somewhat larger Li_2MoO_4 particles were observed (Table 1, Fig. 1). In the case of MnZn ferrite no grain growth is expected according to its significantly high sintering temperature of about 1200-1300 °C.^{14,35} Based on the measurements, the effect of the slightly increased Li_2MoO_4 grain size cannot cancel out the impairing effect of MnZn ferrite oxidation on the ϵ_r and μ_r of the sintered samples.

The frequency dispersion of the ϵ_r and μ_r (Fig. 5 a) resembles the corresponding behavior of polypropylene-MnZn ferrite composites prepared from the same MnZn ferrite composition.⁹ The dielectric losses appear to decrease with increasing frequency until a rapid increase occurs near 1 GHz. Previously, such a decrease in $\tan \delta(\epsilon)$ towards higher frequencies was explained by dielectric relaxation of the MnZn ferrite powder.⁹ However, it is noted that near the 1 GHz region, the resonance of the measurement system interferes with the actual dielectric loss behavior of the samples, thus complicating interpretation of the results. When the amount of MnZn ferrite increases, the dielectric losses are also observed to increase rapidly, especially with the RTD samples. A similar observation was explained by percolation in the case of polypropylene-based samples.⁹ In the current case, the percolation limit is not expected to be exceeded since the

loading levels of MnZn ferrite are only moderate.

The slightly declining behavior of the relative permeabilities (Fig. 5 b) resembles that of the polypropylene-MnZn ferrite samples.⁹ It represents the relaxation-type permeability spectra also observed for polyphenylene sulfide resin-MnZn ferrite composites.¹³ In addition, μ_r decreases at higher frequencies when the loading level of MnZn ferrite is decreased, similar to what was observed for polypropylene and polyphenylene sulfide resin composites.^{9,13}

Furthermore, it is noted that the pressed and drilled toroids, both prepared with RTD, represent convergent behavior of μ_r and $\tan \delta(\mu)$, thus ensuring feasible preparation of toroids by pressing.

Mixing rules are widely used to predict the properties of a product composite material. Various mixing rules have been developed for different applications concerning the amount, morphology, and/or alignment of the additive particles in relation to the matrix phase, for example.^{7,8} Two commonly used mixing rules for a two-phase system are the Maxwell-Garnett rule (Eq. 1), which is applied when additive particles below the percolation threshold are randomly distributed in the matrix, and Lichtenecker's logarithmic rule (Eq. 2) for randomly aligned spherical particles that are uniformly distributed in a continuous matrix,⁷⁻

9,24-26

$$\epsilon_{eff} = \epsilon_m + \epsilon_m \left[\frac{\left(\frac{V}{3}\right) \frac{\epsilon_a - \epsilon_m}{\epsilon_m + \frac{1}{3}(\epsilon_a - \epsilon_m)}}{\left(1 - \frac{V}{3}\right) \frac{\epsilon_a - \epsilon_m}{\epsilon_m + \frac{1}{3}(\epsilon_a - \epsilon_m)}} \right] \quad (1)$$

$$\log \epsilon_{eff} = V \log \epsilon_a + (1 - V) \log \epsilon_m \quad (2)$$

where ϵ_{eff} , ϵ_m , and ϵ_a are the effective permittivities of the composite, matrix, and additive materials, respectively, and V is the additive volume fraction. In calculating permeability, ϵ is replaced by μ . The ϵ_{eff} and μ_{eff} calculated using these mixing rules with the measured properties of the samples are provided in Figure 6. In the case of the sintered samples, the measured values of ϵ_r appear to be only slightly lower than the calculated ones, probably due to porosity or the additional Mn- and Mo-based reaction phase (Fig. 6 a). On the contrary, the measured values of μ_r are somewhat higher than what could have been expected based on the mixing rules (Fig. 6 b). Correspondence between the measured and calculated ϵ_r and μ_r values is extremely poor in the case of the RTD samples. This is an interesting observation since previously,

Figure 6. Experimental (solid line) and calculated (dashed line) (a) relative permittivities and (b) relative permeabilities at 100 MHz and at 1 GHz

$\text{Li}_2\text{MoO}_4\text{-TiO}_2$ composites manufactured by RTD were found to be in good agreement with Lichtenecker's rule below the loading level of 20 vol-%, beyond which correspondence decreased due to increased porosity.²⁶ However, the values available for pure MnZn ferrite, given without the measurement frequency or any information on sample processing (hence the possibility of oxidation) on the data sheet, might be inapplicable. Additionally, the measurement accuracy of the relative permeability is low.

IV. Conclusions

The first magnetic composites manufactured by the RTD method were prepared from Li_2MoO_4 and temperature- and atmosphere-sensitive MnZn ferrite. Reference samples sintered at 685 °C in air suffered from formation of a small amount of additional Mn- and Mo- based reaction phase in addition to MnZn ferrite oxidation. All this was avoided with the RTD method without a need for special atmospheric conditions during sample processing. As a result, the measured relative permittivity and permeability values of the RTD samples were relatively higher compared with the sintered samples. Furthermore, additional processing stage of pre-granulation was introduced to enhance the processability of composite powders with a small particle size. In addition, the RTD method was successfully applied in manufacturing samples with a more complex toroidal shape.

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