Integration of Ni-Cu-Zn and Hexagonal Ferrites into LTCC Modules: Cofiring Strategies and Magnetic Properties

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Abstract

We have studied the integration of Ni-Cu-Zn ferrite spinels as well as substituted hexagonal Co2Y- and M-type ferrites into LTCC (Low Temperature Ceramic Co-firing) modules. The cofiring behavior and the magnetic properties of these materials were investigated and evaluated for multilayer applications. Ni-Cu-Zn ferrites exhibit permeabilities of $\mu = 300 - 500$ for operating frequencies in the MHz range. Cu-substituted Y-type ferrites $\text{Ba}_2\text{Co}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Fe}_{12}\text{O}_{22}$ in combination with sintering additives display sufficient shrinkage and densification at 900°C. A permeability of $\mu = 10$ is observed; however, substituted Co2Y-type ferrites do not exhibit long-term stability at 900°C. Co/Ti-substituted M-type ferrites $\text{BaFe}_{12-2y}\text{Co}_y\text{Ti}_y\text{O}_{19}$ ($y = 1.2$) with planar magneto-crystalline anisotropy exhibit excellent soft magnetic behavior. Using sintering additives, complete densification is reached at 900°C and a permeability of $\mu = 15$ and a resonance frequency of larger than 1 GHz are observed. Integration of ferrite multilayer inductor components into LTCC modules using free and constrained cofiring technologies is demonstrated.

Key Words: Ferrites, Cofiring, LTCC modules, Permeability,

I. INTRODUCTION

Multilayer ceramic inductors, fabricated using the low-temperature ceramic cofiring technology (LTCC), have been available for many years. Typical ferrite materials for multilayer inductors include spinel ferrites of the Ni-Cu-Zn ferrite system with permeabilities typically in the range between $\mu = 100 – 400$ and operating frequencies up to the low to mid MHz range [1-5]. For high frequency applications substituted hexagonal ferrites of Z-, Y-, and M-types were proposed [6-8]. It has been shown that the thermodynamic stability of the different types of hexagonal ferrites varies with temperature. Whereas Z- and Y-type ferrites are stable at higher temperatures and show partial decomposition into other ferrites at 900°C [9], substituted M-type ferrites are compatible with a cofiring temperature of 900°C [10].

The integration of ferrite layers into LTCC multilayer modules has emerged as a new pathway in order to reduce the number of passives mounted on the surface of “simple” LTCC multilayer modules and is aimed at a further increase of packaging density in ceramic multilayer packages. The combination of ferrite multilayers with standard dielectric LTCC-tapes are of special interest. The effective integration of magnetic functions into LTCC-type multilayers enables applications like inductors, LC filters or transformers. Co-firing of multi-material laminates is challenging. Dense multilayers without microstructural defects as warpage, delamination and porosity are accessible only if a number of conditions are matched: (i) similar shrinkage curves of the individual materials are favorable for complete densification of all layers in multi-material laminates. Typically low-dielectric glass-ceramic LTCC tapes exhibit a shrinkage behavior different from that of a ferrite tape with a low content of glass or crystalline sintering additive only. (ii) Thermal expansion mismatch between the different materials, especially during cooling below the transformation points of the glass phases, causes stresses and cracks. Therefore matching of the coefficients of thermal expansion (CTEs) is required. (iii) Diffusion processes and phase reactions at the interfaces have to be controlled in order to not deteriorate the magnetic properties of the ferrite. It was shown that free cofiring of ferrite - LTCC laminates is possible, if shrinkage and thermal expansion mismatch is minimized [11]. Constrained sintering is another option for the preparation of ceramic multilayers. In-plane tensile stress, generated during constrained shrinkage in the x-y direction, might reduce the driving force of densification leading to residual porosity. However, sufficient densification is reached for most glass-rich standard LTCC materials by an increased shrinkage in z direction. Constrained sintering of ferrite multilayers which contain low additive
concentrations only, however, might result in insufficient densification. Therefore shrinkage matching is an important requirement for complete densification of multi-material modules including ferrite tapes. Uniaxial stress applied in the thickness direction is an alternative to matched shrinkage curves. It was already shown that dense Ni-Cu-Zn ferrite multilayers were sintered under constrained sintering conditions with alumina release tapes and uniaxial stress of 1-2 MPa at 900 °C [12, 13].

In this contribution we report on the fabrication and properties of monolithic Ni-Cu-Zn and hexagonal ferrite multilayer inductors. The integration of ferrite layers into low-k dielectric LTCC layers using free and constrained sintering technologies is demonstrated.

II. EXPERIMENTAL

Ni-Cu-Zn ferrite Ni_{0.30}Cu_{0.20}Zn_{0.52}Fe_{1.98}O_{3.99}, hexagonal Y-type ferrite Ba_{2}Zn_{1.6}Cu_{0.4}Fe_{12}O_{22}, and M-type Ba_{2}Co_{1-y}Zn_{y}Fe_{12-y}O_{19} were prepared by the standard mixed-oxide route. The oxides were wet mixed for 12 hours in a polyethylene container. Powder mixtures were calcined at 750°C in the case of Ni-Cu-Zn ferrite and at 1000°C for the hexagonal ferrites, respectively. Subsequently, the powders were milled to a mean particle size of about d_{50} = 0.6 µm using a planetary ball mill and zirconia grinding media. Sintering aids were added during the fine milling step. The powders were compacted using polyvinyl-alcohol as binder to give pellets for sintering studies or toroids for permeability measurements. Ferrite tapes of thickness 100 µm were prepared by the doctor blade method. A low-k dielectric LTCC tape (BAM474) designed to have similar shrinkage and thermal expansion behaviors as Ni-Cu-Zn ferrite was used for cofiring experiments [11]. Hexagonal M-type ferrite was cofired with a different low-k dielectric LTCC tape (KFM23) consisting of crystalline Zn-Ti-O phases with <2% glass addition. Multilayer laminates were prepared by lamination with a pressure of 25 MPa at 80°C. For permeability measurements, the green laminates were cut in the shape of ring cores and cofired. All samples were sintered or cofired at 900°C for 2 hours in air.

The phase formation of the materials was evaluated by XRD (Bruker AXS, D8). Shrinkage measurements were made with a Netzsch DIL402 dilatometer during heating with 4 K/min heating rate. The bulk density of sintered samples was determined from the dimensions and weight. The powder morphology and the microstructure of the sintered samples were studied with a scanning electron microscope (SEM, Zeiss DSM940A). The permeability was measured using an Agilent E4991A impedance/materials analyzer (static permeability taken as real part of permeability at 1 MHz).

III. RESULTS AND DISCUSSION

Ni-Cu-Zn ferrite multilayer laminates were sintered without and with 0.5 wt% Bi_{2}O_{3} as liquid-phase sintering aid. The density of both samples is 5.2 g/cm³, i.e. the densification is almost complete. The grain size of the additive-free sintered sample is 2 µm and the addition of 0.5 wt% Bi_{2}O_{3} leads to abnormal grain growth resulting in a microstructure with large grains of about 20 µm. This is reflected in the permeability (Fig. 1): whereas the additive-free Ni-Cu-Zn ferrites exhibit a permeability of about µ = 300-350, the Bi_{2}O_{3}-containing ferrite multilayer has a larger permeability of µ = 500.

![Fig. 1](image1.png)

**Fig. 1** Complex permeability (real part µ_r: solid line; imaginary part µ_i: dashed line) vs. frequency f of Ni-Cu-Zn ferrite multilayers with/without additive.

![Fig. 2](image2.png)

**Fig. 2** Complex permeability (real part µ_r: solid line; imaginary part µ_i: dashed line) vs. frequency f of substituted M- and Y-type ferrite multilayers.
Multilayers of Y-type ferrite $\text{Ba}_2\text{Zn}_{1.6}\text{Cu}_{0.4}\text{Fe}_{12}\text{O}_{22}$ were sintered at 900°C using 5 wt% of $\text{Bi}_2\text{O}_3$ as liquid-phase sintering aid. Dilatometric measurements proved that the temperature of the maximum shrinkage rate of the ferrite is $T_{\text{MSR}} < 900°C$. The permeability of the Y-type ferrite material is $\mu = 10$ (Fig. 2). However, it was shown that sintering the Y-type ferrite at 900°C results in partial decomposition of the ferrite. SEM and XRD analysis showed that minority spinel and perovskite phases appear besides the ferrite main phase after firing at 900°C. This heterogeneous phase assemblage as a result of firing at 900°C is believed to be the reason for the permeability reduction compared to the single-phase Y-type ferrite sintered at 1200°C (which has a $\mu = 30$ [14]) and for the appearance of another dispersion process at lower frequency. Multilayers of M-type $\text{BaCo}_{1.2}\text{Ti}_{1.2}\text{Fe}_{9.6}\text{O}_{19}$ ferrite were prepared using 5% of a glass as a sintering additive. They exhibit a permeability of $\mu = 15$ (Fig. 2). This is considerably less than the same ferrite sintered at 1300°C without additive, however, the liquid-phase sintering additive enables cofiring at low temperature. The permeability of the ferrite sintered at 900°C is smaller due to smaller grain size and dilution by a nonmagnetic glass phase. According to XRD and SEM the samples are single-phase M-type after sintering at 900°C. Different to Y-type ferrites, the substituted M-type ferrites are stable at the cofiring conditions at 900°C and represent a promising material for LTCC integration [10].

Integration of Ni-Cu-Zn ferrite layers into a LTCC-tape BAM474 was already demonstrated [11]. This low-k dielectric LTCC tape was designed to have the shrinkage maximum and the CTE similar to that of the ferrite. However, the use of $\text{Bi}_2\text{O}_3$ additive in the ferrite tape lead to an inhomogeneous Bi-distribution and a gradient of grain sizes in the integrated ferrite layers [11]. As a result the permeability of the ferrite integrated into a LTCC multilayer module was reduced compared to the permeability of the monolithic ferrite multilayer of the same material [11]. In order to overcome this severe limitation of $\text{Bi}_2\text{O}_3$-containing ferrite tapes, we investigated the integration of highly sinter-active Ni-Cu-Zn ferrites in LTCC modules. In this study, additive-free Ni-Cu-Zn ferrite multilayers were cofired with low-k dielectric LTCC tape (BAM474). Multilayers of Ni-Cu-Zn ferrite $\text{Ni}_{0.30}\text{Cu}_{0.20}\text{Zn}_{0.52}\text{Fe}_{1.98}\text{O}_{3.99}$ were laminated with BAM474 and cofired at 900°C. The shrinkage behavior of BAM474 is well adapted to that of the Ni-Cu-Zn ferrite of that particular composition with 0.5% $\text{Bi}_2\text{O}_3$ as well as additive-free ferrite. The shrinkage rate peaks at about 880°C for both ferrites, but the shrinkage rate peak of the Bi-containing ferrite is much larger and sharper. The sintered multilayers are dense and no microstructural defects were observed. A SEM micrograph of a multilayer is shown in Fig. 3. The permeability of the ferrite layers is $\mu = 330$, i.e. it has the same permeability as the pure Ni-Cu-Zn ferrite material. This shows that cofiring of this ferrite LTCC multilayer module did not change the ferrite microstructure. As a consequence, the permeability of the ferrite remains unaffected. It was shown by SEM that the ferrite microstructure is homogeneous with grains of about 2 µm. It is demonstrated that pressure-less cofiring of additive-free Ni-Cu-Zn ferrite layers within a LTCC multilayer module might be successfully performed if the shrinkage and thermal expansion mismatch between the materials is minimized.

![SEM micrograph of cross-section of multilayer LTCC modul containing NiCuZn ferrite (NiZn100) and low-k dielectric (BAM474) layers.](image1)

![Complex permeability (real part $\mu'$: solid line; imaginary part $\mu''$: dashed line) of substituted M-type ferrite multilayer integrated in low-k dielectric (KFM23) layers. (inset: SEM micrograph).](image2)
Another example illustrating this cofiring strategy is the integration of M-type BaCo_{1.2}Ti_{1.2}Fe_{9.6}O_{19} ferrite into a LTCC multilayer structure. A different low-k dielectric LTCC material (KFM23) which has been especially designed to fit to the shrinkage behavior and the CTE of the M-type ferrite layers was used for this experiment. This LTCC tape is based on crystalline Zn-Ti-O phase in combination with a low concentration of a glass additive identical in composition with the one used to tailor the shrinkage of the substituted M-type ferrite. Consequently, this LTCC material (KFM23) does not represent a glass-ceramic composite, but a crystalline ceramic with a small concentration of liquid-phase sintering additive. A multilayer module with substituted M-type ferrite layers integrated into low-k dielectric layers (KFM23) and Ag metallization was cofired at 900°C. No structural defects, camber and delaminations were observed (inset Fig. 4). The permeability of the integrated ferrite layer is $\mu = 15$ (Fig. 4). The resonance frequency is at $f > 1$ GHz; thus this integrated ferrite multilayer can be operated up to high frequency. The permeability of the Co/Ti-substituted M-type ferrite layers integrated into LTCC multilayers (Fig. 4) has the same value as in the monolithic ferrite multilayers (Fig. 2). This demonstrates the successful integration of the ferrite layers into a LTCC multilayer module without significant chemical interaction and permeability deterioration.

The two reported examples of ferrite integration in LTCC modules document the usefulness of the concept of pressure-less cofiring of functional materials and low-k dielectrics with matched shrinkage and thermal expansion properties. Detailed investigations on the cofiring of additive-free spinel ferrites, substituted M-type hexagonal ferrites as well as different functional ceramics (high-k dielectrics, thermistors) with low-k dielectric LTCC tapes will be presented in forthcoming publications.

REFERENCES