Materials for inductive and microwave function integration in LTCC-technology multichip modules

V T Zaspalis¹,² M Kolenbrander² and J Boerekamp²

¹Laboratory of Inorganic Materials, Chemical Process Engineering Research Institute, 57001 Thessaloniki, Greece
²Ferroxcube GmbH, Department of Materials and Process Development, 22419 Hamburg, Germany

E-mail: zaspalis@cperi.certh.gr

Abstract. Low Temperature Cofired Ceramics Technology (LTCC) receives considerable industrial interest as a multichip module integration technology, particularly because its very good performance-cost combination. The integration potential of the LTCC technology will be significantly extended with the availability of LTCC-compatible low firing magnetic materials that will enable the integration of high frequency inductive functions. In this article the preparation of low firing cobalt containing hexagonal ferrite materials of the Z-structure (Ba₃Co₂Fe₂₄O₄₁, or Co-Z) is described using a PbO-WO₃ eutectic mixture as liquid phase sintering additive. Layers from the previous materials are prepared by the slip-casting technique and cofired with commercially available, low dielectric constant, LTCC tapes. Crack free multilayer structures are achieved after firing at 950-1000°C.

1. Introduction

Low Temperature Cofired Ceramics Technology (LTCC) is an important passive component integration technology for the manufacturing of multichip module substrates [1,2]. The LTCC substrates are usually multilayer structures consisting of a combination of resistive, dielectric or magnetic materials interconnected via a three dimensional conductor network. In this way, capacitive, resistive or inductive components and functions can be accommodated within the substrate, being thus eliminated from the surface, ultimately leading to better performance, reliability, miniaturization and cost reduction. Those multilayer structures are usually manufactured by a technique through which the designed conductor patterns are printed on the surface of the various ceramic layers that are subsequently accurately stacked on top of each other, laminated and finally fired to elevated temperatures (850-1100°C). A major processing challenge of the LTCC technology is the ability to control the sintering process. The various layers should exhibit comparable densification kinetics in order to minimize stress development and crack occurrence during the firing process.

High frequency magnetic ceramic materials consist an interesting material class that could be integrated in an LTCC substrate. In such a way a number of functions such as e.g. circulator function for receiving and transmitting antenna functions or isolator function, can be integrated within the multilayer ceramic substrate. The barium hexaferrites are particularly of importance since they exhibit
at high frequencies, even in isotropic structures, relative magnetic permeability higher than this exhibited by other ferrite materials e.g. of the other hexagonal types or of the cubic spinel structure [3]. A serious limitation is imposed by the usually high temperatures required during sintering of those materials (>1200°C) and the resulting incompatibility with low firing temperature dielectric materials [4].

In this article the synthesis of LTCC compatible Co-Z ferrite materials is described as well as the manufacturing of layers and their co-firing with dielectric layers towards crack free monolithic bodies [5].

2. Experimental

Hexagonal ferrite materials of the Z type structure (figure 1a) having the chemical formula \( \text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41} \) are synthesized by the mixed oxide method. The raw materials (BaCO\(_3\), CoO, Fe\(_2\)O\(_3\)) are initially proportioned by weighting according to the chemical formula and subsequently wet mixed. The mixed powder is then pre-fired at 900 °C for 3 hours under air atmosphere and milled (using distilled water 100wt.% in addition to the solids) for about 9 hours in ball-mills using stainless steel balls with diameter 13-16 mm. The milling process resulted to an average particle size diameter of 0.5-0.7 \( \mu \)m, as measured by laser scattering. Prior to milling 0.1 wt.% (on solid basis) of a PbO:WO\(_3\) mixture with molar proportions 5:1 respectively (figure 1b), is added to the powder. The milled powder suspension, after being separated from the balls, is concentrated to a solids content of 70 wt.% (dry basis) slurry. The slurry is then stabilized by adding 1wt.% stabilizer (Dispex A40). Finally 20 wt.% binder PVA (Merck, analytical grade, molecular weight 72000) is added to the slurry in the form of an aqueous solution.

![Figure 1. Left: The phase Fe\(_2\)O\(_4\)-BaO-CoO phase diagram indicating the position of the Z-structure materials prepared in this article. Right: The PbO-WO\(_3\) phase diagram indicating the position of the PbO-WO\(_3\) eutectic composition used as sintering additive.](image)

Foils are casted from the so prepared slip by the doctor blade method. The foils are then stacked on top of each other and pressed at about 50 °C towards a multilayer compact. No magnetic field is used during compaction in order to obtain pre-orientation of the easy magnetization planes of the Z-structure, so the specimens can be considered isotropic. For co-firing experiments, commercially available low dielectric constant LTCC foils are used (AT951, DuPont). All firing experiments took place under air atmospheres at heating and cooling rates of 1°C/min.

3. Results and Discussion

In figure 2 the real and imaginary part of the relative magnetic permeability is shown as a function of frequency for Co-Z specimens fired at 950, 1000 and 1050 °C. No magnetic properties could be
measured on specimens fired at the same temperature without the addition of PbO:WO₃ because of the very low densities.

**Figure 2.** Real (µ′, solid lines) and imaginary (µ″, dashed lines) parts of magnetic permeabilities for low firing Co-Z ferrite materials.

**Figure 3.** Series impedance (Z) as a function of frequency and firing temperature for low firing Co-Z materials.

In figure 3 the series impedance (defined as Z=ωL₀(µ′+µ″), where µ′ and µ″ as defined in figure 2, L₀ is the inductance without magnetic material under the same conditions and ω=2πf) as a function of the frequency is shown for three different sintering temperatures. The enhanced densification in the presence of PbO:WO₃ additions is probably because of the formation of a eutectic liquid phase (melting temperature 730°C) that promotes liquid phase sintering, however without disturbing the magnetic properties of the material.

In figure 4 the results of co-firing experiments at 950°C with dielectric material are shown, with and without the presence of PbO-WO₃ additions.

**Figure 4.** Dielectric-magnetic multilayer composites after firing at 950 °C without (left) and with (right) the presence of PbO-WO3 sintering additive in the magnetic phase.

As seen, in contradiction to the low firing dielectric material the densification of the Ba₃Co₂Fe₂₄O₄₁ magnetic material can only proceed sufficiently at 950 °C in the presence of PbO-WO₃ additions.
When PbO-WO₃ is not added then besides bad densification also cracking and bending of the layers occurs because of shrinkage mismatch between the dielectric and the magnetic layers. The chemical definition of the interface is very sharp and there is no significant penetration of chemical elements across the interface. Examinations with the energy dispersive analysis system of the scanning electron microscope (SEM-EDS) revealed that there is no diffusion layer greater than 5µm along either sides of the dielectric-magnetic material interface (figure 5). As a consequence the materials after co-firing maintain their individual dielectric and magnetic properties.

![Figure 5. Elemental mapping across the magnetic-dielectric layer interface, of Fe (characteristic element of the magnetic phase) and Al (characteristic element of the dielectric phase), indicating a chemically sharp interface without diffusion profiles on either side.](image)

4. Conclusions
Low firing hexagonal magnetic materials of the Z-structure and with the chemical formula Ba₃Co₂Fe₂₄O₄₁ are synthesized, with 0.1wt.% additions of PbO-WO₃. Relatively good magnetic permeabilities are measured up to 1GHz, after sintering at 950-1050°C isotropic structures. Foils casted from these materials are compatible with commercially available dielectric LTCC foils and can be cofired to continuous and rigid multilayer composites.

5. References
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