New LTCC- hexaferrites by using reaction bonded glass ceramics

Karmazin[1] R., Dernovsek[1] O., Ilkov[1] N., Wersing[1] W., Roosen[2] A., Hagymasi[2] M.
[1]SIEMENS AG, Corporate Technology, Ceramics, Munich
[2]University of Erlangen-Nuremberg, Glass and Ceramics, Martensstr. 5, D-91054 Erlangen
Phone: +49 636 48039, Fax: +49 636 48131; E-mail: Process1-CTMM2@mchp.siemens.de

Hexaferrites are usually prepared according to the standard mixed oxide method with high sintering temperatures of up to 1350°C, which is not useful for LTCC technology. In this work, the sintering temperature of $BaFe_{12}O_{19}$ was reduced to 900°C by the development of reaction-bonded glass ceramics systems for LTCC-hexaferrites. Low amounts of reactive glasses (< 7 vol.%) based on boron and zinc oxide were used as sintering additive to achieve full densification at 900°C. The influence of variation in glass-ceramics compositions, different processing parameters, advanced powder preparation by using high-energy milling and the calcinations temperature on achieving high-μ ferrites at 900°C was study. The magnetic properties of these LTCC-hexaferrites were characterized by a coaxial airline method and impedance measurements in the frequency range of 0.1 to 10 GHz. The influence of phase composition and microstructure on magnetic properties was also discussed.

Keywords: LTCC, Ferrites, coaxial measurement, high permeability

1. Introduction

Advanced low temperature cofired ceramics (LTCC) including Ba-hexaferrites with the concept of reactive bonded glass ceramics are exceptional interesting for high frequency applications e.g. phase-shifter, circulator, antennas and wireless technologies for the next generation of miniaturized electronic modules. One of the favoured candidates who combine high permeability μ at high frequencies are the hexa-ferrites, which are usually prepared according to the conventional mixed oxide method with high sintering temperature up to 1350 °C in air.

Development trends of LTCC (low temperature cofired ceramics) magnetics using a small amount of additives and glass-ceramics systems, including low softening glasses and high melting magnetic ceramic. Typical additive for low temperature sintered ferrites, prepared with low cost mixed oxide method, is i.e Bi_2O_3 [1, 2]. Addition of lithium borosilicate glass [3] or B_2O_3-Sb_2O_3 [4] was also reported. The main problem with low temperature fired polycrystalline magnetic phases e.g. $Ba_{12}Fe_{19}$ is the high porosity. Due to a high content of an non-magnetic phase (> 10 vol.%) e.g. glass or pores the permeability are dramatic reduced. A novel technique to solve this problem and reach the densification of samples below 900 °C we developed using the sintering process of hexaferrites with addition of a small amount of reactive glasses which is based on Bi-B-Zn-O [4].

The influence of variation in glass-ceramics compositions, different processing parameters, advanced powder preparation by using high-energy milling and the calcinations temperature on achieving high-μ ferrites at 900°C was investigated in the present paper.

2. Experimental

Powder Preparation

M-Type modified hexaferrites with the phase composition $BaFe_{12}O_{19}$ were prepared using the mixed oxide method. The mixed oxide precursor was calcinated at temperature of 1200°C and than ball milled. Milled powder was mixed with low content of reactive glass frits based on boron and zinc-oxide (3, 5, 7 vol.%) and high energy milled using attritor mill (Dispermat SL-C, WMA-Getzmann, Germany). To achieve densification at temperature below 900 °C was necessary to reduce an average particle size of composite powder to 1.8 and 0.8 μm. As prepared powder was pressed into the pellets or tape-caste and sintered at temperature range 900°-1350°C/5 hours. Whole procedure is shown in the flow chart on the Fig. 1

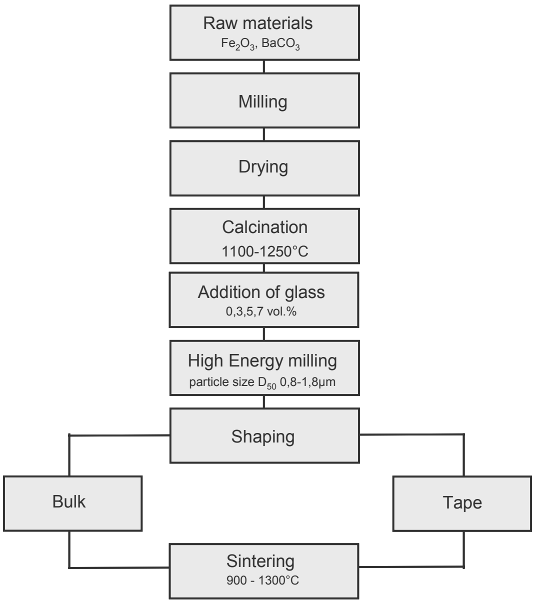

Fig. 1 Flow chart of synthesis of LTCC compatible hexaferrites

Characterization Method

Phase composition of calcinated hexaferritic powders was characterized by high-temperature x-ray-diffraction. Temperature and time-controlled sintering behaviour was investigated using dilatometer (Model STA 409C, Netzsch, Germany). Density of sintered hexaferrites was measured with helium pycnometry (Accupyc 1330, Micrometrics, Germany). Phase composition of glass-ceramic constituents was examined by X-ray analysis (Siemens Diffract 500, Siemens, Germany) and microstructure of sintered ceramic bodies was investigated with SEM (Jeol 840, Jeol, Japan).

Permeability Measurements

Permeability measurement based on broadband results up to 5GHz using a coaxial transmission - reflection (TR) was employed. The coaxial line had inner and outer diameter of 3 and 7 mm respectively. The thickness of the toroid of hexa-ferrites ranged from 3 to 4 mm. The test fixture of the TR measurement and prepared samples is at Fig. 2. The basic magnetic parameters were measured using an HP4291A analyzer in the range of 0,1…3 GHz.

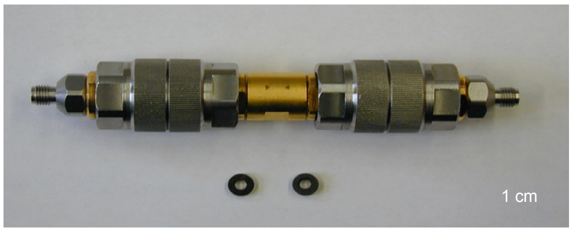

Fig. 2 Test fixture for transmission / reflection measurements of cylindrical hexaferrites.

3. Results and Discussion

Phase composition

High temperature X-RAY diffraction was employed to find the suitable temperature for the $BaFe_{12}O_{19}$ phase creation. . The resulting spectra is on the Fig. 3**Erreur! Source du renvoi introuvable.**. The first traces of the $BaFe_{12}O_{19}$ were observing at temperature around 1000°C, but pure hexaferrite phase was obtained at temperature 1200°C. Thus, this temperature was used for the calcination of the mixed oxide precursor.

Sintering behaviour of glass-hexaferrite composite

A dilatometer study of heat treatment of samples with different amount of BBSZ glass was done in order to determinate shrinkage on densification of reactive sintered ceramic-glass composites. The resulting diagram is on the Fig. 4. Increasing amount of the BBSZ glass means increasing of shrinkage up to the 22 % with 7 vol % BBSZ. Porosity is decreasing with increasing of shrinkage. Archimedes method was employed to measure the open porosity. Results are in the Tab. 1.

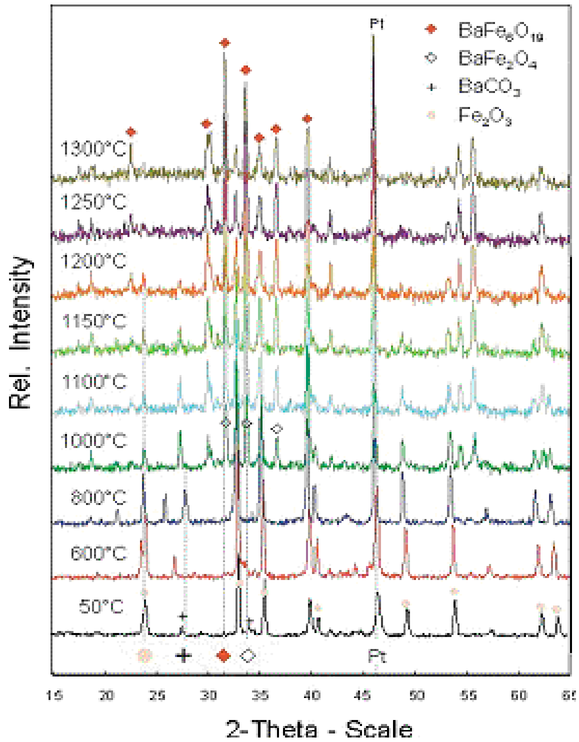

Fig. 3 High temperature x-ray analysis of mixed oxide process from $BaCO_3$ and Fe_2O_3 to determined the calcinations temperature of pure phases of $BaFe_{12}O_{12}$ at 1200°C.

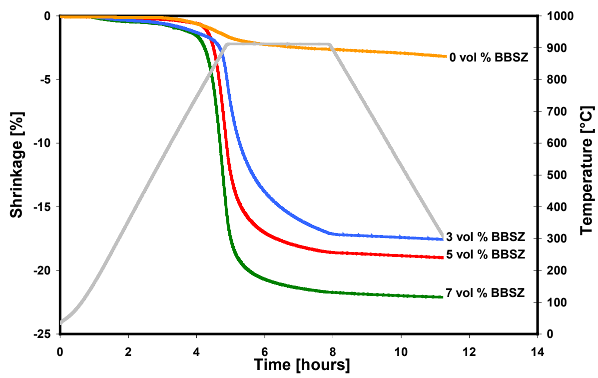

Fig. 4 Effect of the temperature and BBSZ-glass content on linear shrinkage of $BaFe_{12}O_{19}$

Tab. 1 Open porosity and shrinkage in dependence of amount of reactive glass

Glass [vol %]	Shrinkage [%]	Porosity [vol %]
0	3	>50
3	17	15
5	19	2,3
7	22	0,8

Microstructure of $BaFe_{12}O_{19}$ hexaferrites

Microstructure of the $BaFe_{12}O_{19}$ with 5 vol % BBSZ glass is shown at Fig. 5.

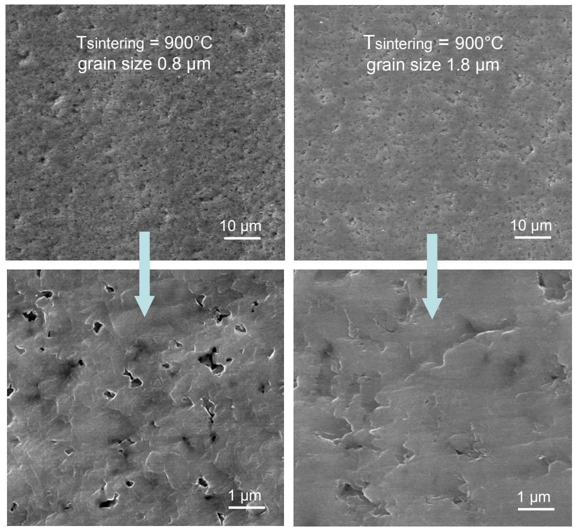

Fig. 5 Microstructure of reactive sintered $BaFe_6O_{12}$ in addition with 5 vol.% BBSZ glass at 900°C in dependency of grain size of starting powder 0.8 and 1.8 µm.

Reactive sintered hexaferrites with 5 vol % of BBSZ glass are relatively dense with the porosity of 2,3 vol % (Tab. 1). The porosity is decreasing with increasing of amount of the BBSZ glass. Increasing of the D_{50} of the starting powder to the 1,8 µm have lead to the increasing of the porosity up to the 6,3 vol %. Fig. 6 shows M-type hexaferrite sintered at 1350°C without addition of the BBSZ glass. High temperature is the reason of the big grain growth of $BaFe_{12}O_{19}$ grains. The grey matrix is $BaFe_2O_4$. Porosity of as sintered hexaferrite is 6 vol %.

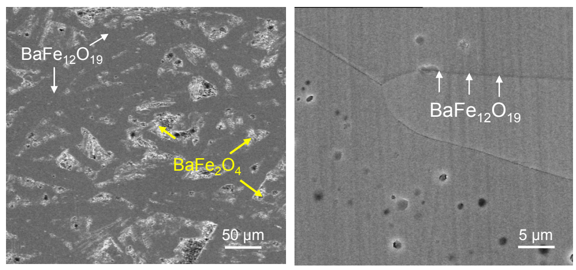

Fig. 6 $BaFe_{12}O_{19}$ without glass addition sintered at 1350°C

Reactive sintered hexaferrites do not show this grain growth. They have constant phase composition in whole sample. This is important for the permeability values. $BaFe_2O_4$ is decreasing value of permeability of the Barium hexaferrite.

Permeability measurement

Permeability measurements show dependence of permeability on amount of non-magnetic BBSZ glass. Diagram permeability vs. frequency is on Fig. 7.

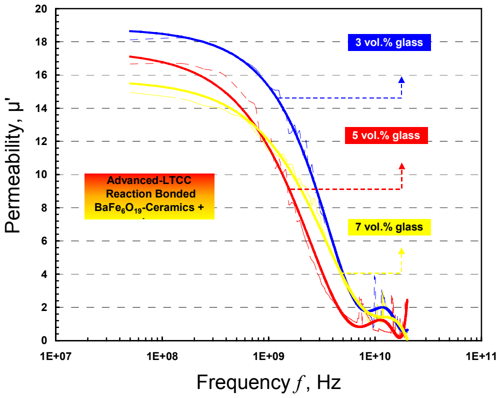

Fig. 7 Permeability vs. frequency for the reactive sintered $BaFe_{12}O_{19}$ with different amount of the BBSZ glass

Base of this diagram is clear, that low content of BBSZ glass used in composite do not affect strongly the value of permeability at high frequencies. The strong effect to the permeability brings the open porosity. Permeability of composite with 7 vol % of BBSZ glass with lowest porosity (Tab. 1) is dropping down not so fast like system with the highest porosity with 3 vol % BBSZ glass.

LTCC compatiblity

For LTCC applications are important compatibility of glass-ceramic composite and silver paste, which is use like standard screen printing paste. Fig. 8 shows SEM photo of interface between glass-ceramic composite and silver paste layer. The same picture shows EDX line scan spectra of the same interface.

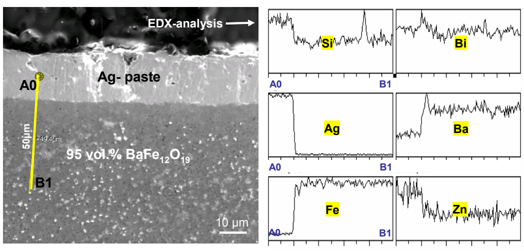

Fig. 8 LTCC compatibility of glass-ceramic composite and Ag-screen printing paste

There is good bonding between composite and paste after sintering, but EDX spectra show no diffusion of Ag to the composite.

6. Conclusion

Depending on glass-ceramic compositions, concentration, pre-processing parameters e.g. advanced powder preparation by high-energy milling, calcinations and sintering technique, dense hexa-ferrites at low temperature of 900 °C were obtain. This glass – hexaferrites composites shows value of permeability of around 10 at frequency of 1 GHz. Permeability is depend on amount of BBSZ glass added. Low content of additive does not affect strongly values of permeability, but strongly affect values of open porosity. Glass – ceramic composite shows good LTCC compatibility.

6. Acknowledgement

The authors are grateful for the financial support for this cooperation project of Kerafol GmbH, Siemens AG, University of Erlangen-Nuremberg for integration of magnetic components by LTCC under the StMWVT.

7. References

[1] Zhang, H., et al.: “Microstructure and Magnetic Characteristic of Low-Temperature-Fire Modified Z-Type Hexaferrite With Bi_2O_3 Additive”, *IEEE Trans. Magn.*, 2002, **38** (4), 1797-1802

[2] Drofenik, M., et al.: “Influence of the Addition of Bi_2O_3 on the Grain Growth and Magnetic Permeability of MnZn Ferrites”, *J.Am.Ceram.Soc.,* 1998, **81** (11), 2841-2848

[3] Hirota, K., et al.: “Microstructure and Magnetic and Electric Properties of Low-Temperature Sintering Mn-Zn Ferrites without and with Addition of Lithium Borosilicate Glass”, *J.Magn.Mag.Mat.,* 1999, **205**, 283-289

[4] Dernovsek, O., et al.: “LTCC Glass-Ceramic Composites for Microwave Application”, *J.Eur.Ceram.Soc,* 2001, **21**, 1693-1697

[5] Rezlescu, N., et al.: "$LiFe_5O_8$ and $BaFe_{12}O_{19}$ Fine
Particles Crystallised in a Glassy Matrix",
Cryst.Res.Techno.l, 1999, **34** (7), 829-836