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New LTCC-hexaferrites by using reaction bonded glass ceramics

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Abstract

Hexaferrites are usually prepared according to the standard mixed oxide method with high sintering temperatures of up to 1350 °C, which are not suitable for low temperature cofired ceramics (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 additives 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 calcination temperature on achieving high-μ ferrites at 900 °C was studied. The magnetic properties of these LTCC-hexaferrites were characterized by a coaxial airline method and impedance measurements in the frequency range of 0.1–10 GHz. The influence of phase composition and microstructure on magnetic properties was also discussed.

Keywords: LTCC; Ferrites; Glass ceramic; Magnetic properties

1. Introduction

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

Development trends in LTCC magnetics using a small amount of additives and glass–ceramics systems, including low softening glasses and high melting magnetic ceramic. A typical additive for low temperature sintered ferrites, prepared with low cost mixed oxide method, is 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 a non-magnetic phase (>10 vol.%), e.g. glass or pores the permeabilities are dramatically reduced. A novel technique to solve this problem and achieve the densification of samples below 900 °C at the same time was developed using the sintering process of hexaferrites with the addition of a small amount of reactive glasses which is based on Bi–B–Zn–Si–O (BBSZ).[5]

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

2. Experimental

2.1. Powder preparation

M-Type modified 0hexaferrites with the phase composition $BaFe_{12}O_{19}$ were prepared using the mixed oxide method. The mixed precursor was calcinated at 1200 °C and then ball milled. Milled powder was mixed with a low content of reactive glass frits based on boron and zinc-oxide (3, 5, and

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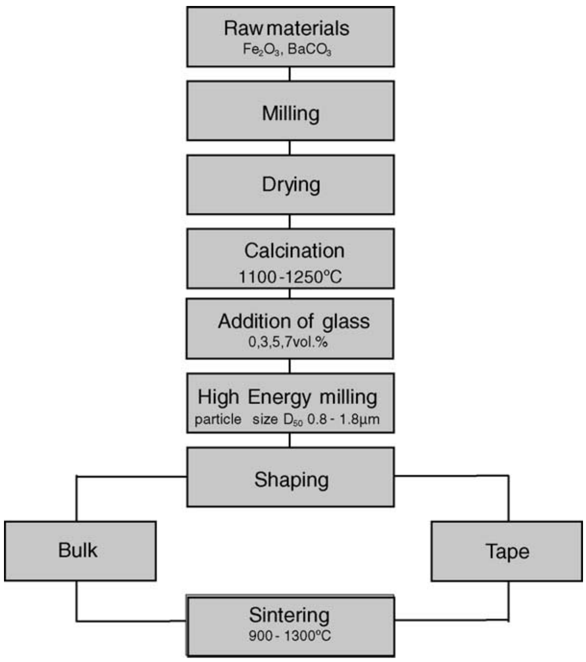

Fig. 1. Flow chart of synthesis of LTCC compatible hexaferrites.

7 vol.%) and then high energy milled using an attritor mill (Dispermat SL-C, WMA-Getzmann, Germany). To achieve densification at temperatures below 900 °C it was necessary to reduce the average particle size of the composite powder to 1.8 and 0.8 μm. The prepared powder was pressed into pellets or tape-casted and sintered at a temperature range of 900–1350 °C for 5 h. Fig. 1 displays the entire procedure.

2.2. Characterization method

Phase composition of calcinated hexaferritic powders was characterized by high-temperature X-ray diffraction. Measurements from 600 to 1300 °C with step 200 °C were done in order to describe evolution of hexaferritic phase in the mixture. Obtained diffractograms were compared with low temperature diffractogram (50 °C). Temperature and time-controlled sintering behaviour was investigated using dilatometer (Model STA 409C, Netzsch, Germany). The density of the sintered hexaferrites was measured using helium pycnometry (Accupyc 1330, Micrometrics, Germany). Phase composition of the glass–ceramic composites was examined by X-ray analysis (Siemens Diffract 500, Siemens, Germany) and the microstructure of the sintered ceramic bodies was investigated using a SEM (Jeol 840, Jeol, Japan).

2.3. Permeability measurements

Permeability measurements based on broadband results up to 5 GHz using a coaxial transmission–reflection (TR) was employed. The coaxial line had an inner and an outer diameter of 3 and 7 mm, respectively. The thickness of hexaferrites toroid ranged from 3 to 4 mm. The test fixture of the TR

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

measurement and prepared samples are shown in Fig. 2. The basic magnetic parameters were measured using an HP4291A analyzer in the range of 0.1–3 GHz.

3. Results and discussion

3.1. 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 are shown in Fig. 3. The first traces of $BaFe_{12}O_{19}$ were observed at temperatures around 1000 °C, but a pure hexaferrite phase was obtained at 1200 °C. Thus, this temperature was used for the calcination of the mixed oxide precursor.

3.2. Sintering behaviour of glass–hexaferrite composite

A dilatometric study of heat treatment of samples with different amounts of BBSZ glass was done in order to determinate shrinkage on densification of the reactive sintered ceramic–glass composites. The results are shown in a graph (Fig. 4). The shrinkage increases with the increase of the amount of BBSZ glass. The porosity, evalu-

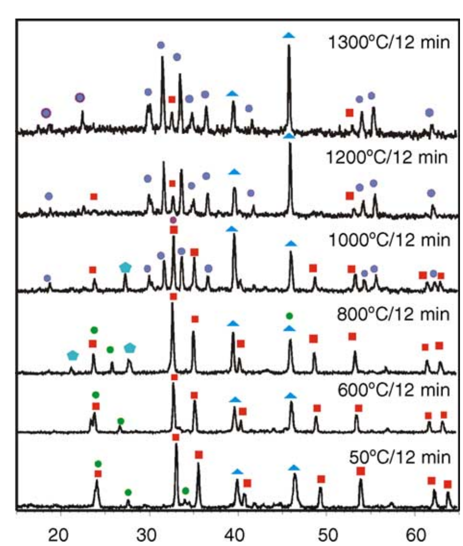

Fig. 3. High temperature X-ray diffractogram of heat treatment of mixture of $BaCO_3$ and Fe_2O_3.

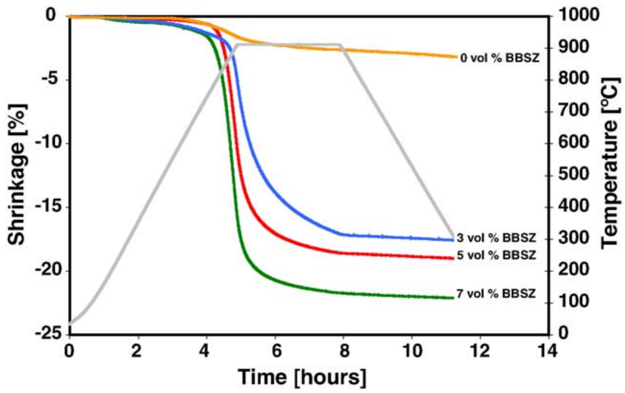

Fig. 4. Effect of the BBSZ–glass content on linear shrinkage of $BaFe_{12}O_{19}$.

Table 1
Effect of the amount of reactive glass on the open porosity and shrinkage

Glass (vol.%)	Shrinkage (%)	Porosity (vol.%)
0	3	>50
3	17	15
5	19	2.3
7	22	0.8

ated using Archimedes method, decreases with increasing amount of BBSZ glass. Detail values of shrinkage and porosity in dependence on amount of BBSZ glass are listed in Table 1.

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

Microstructure of the $BaFe_{12}O_{19}$ with 5 vol.% BBSZ glass is shown in Fig. 5. Reactive sintered hexaferrites with 5 vol.% of BBSZ glass are relatively dense with the porosity of

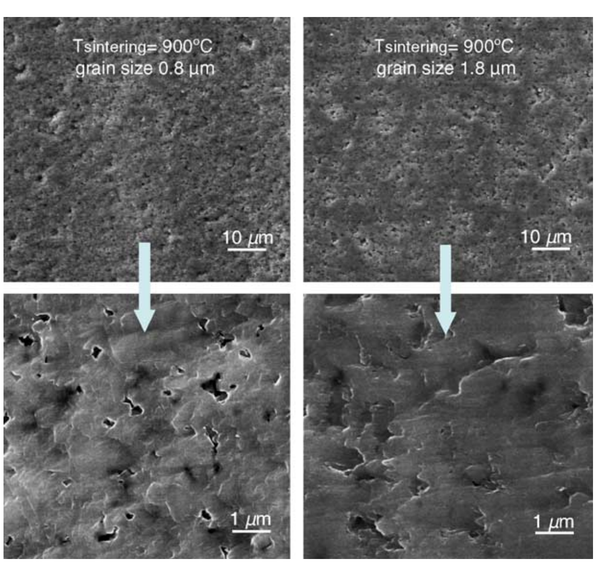

Fig. 5. Microstructure of reactive sintered $BaFe_6O_{12}$ with 5 vol.% BBSZ glass sintered at 900 °C. Two types of grain size of the starting powders are shown.

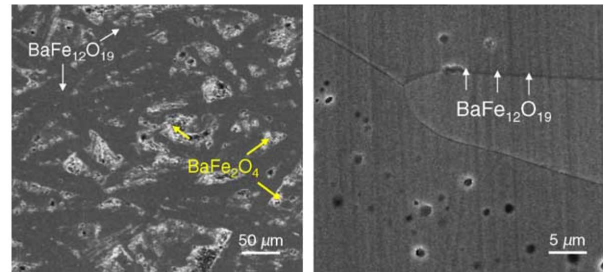

Fig. 6. $BaFe_{12}O_{19}$ without glass addition sintered at 1350 °C.

2.3 vol.% (Table 1). The porosity decreases with increasing amounts of the BBSZ glass. Increasing the D_{50} of the starting powder to 1.8 µm caused an increasing of the porosity up to 6.3 vol.%. Fig. 6 shows M-type hexaferrite sintered at 1350 °C without the addition of the BBSZ glass. Grain growth of $BaFe_{12}O_{19}$ grains in the grey matrix of $BaFe_2O_4$ is observed due to high temperature treatment. Porosity of as sintered hexaferrite is 6 vol.%. Reactive sintered hexaferrites do not show this grain growth (Fig. 5). They have a constant phase composition throughout the whole sample. This is important for the permeability values. $BaFe_2O_4$ presented in the system is decreasing the value of the permeability of the barium hexaferrite.

3.4. Permeability measurement

Permeability measurements show the dependence of permeability on the amount of non-magnetic BBSZ glass. A diagram of permeability versus frequency is shown in Fig. 7. The permeability is strongly affected by the amount of BBSZ at low frequencies. The increase of the amount of BBSZ glass causes a decrease of the permeability. Permeability is decreasing down with increasing frequency. The effect of BBSZ glass is at high frequencies not so significant. The

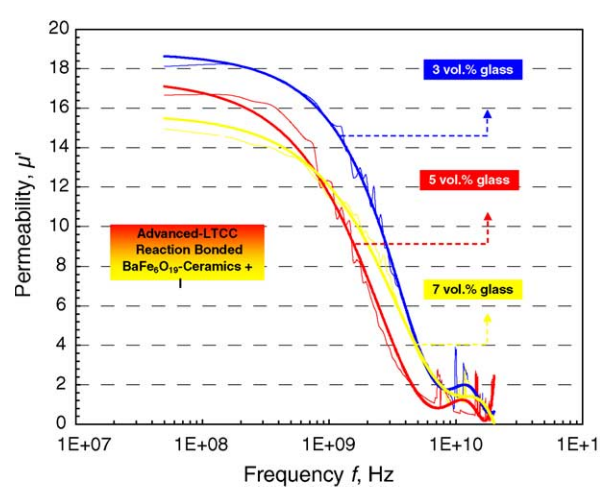

Fig. 7. Permeability vs. frequency for the reactive sintered $BaFe_{12}O_{19}$ with different amount of the BBSZ glass.

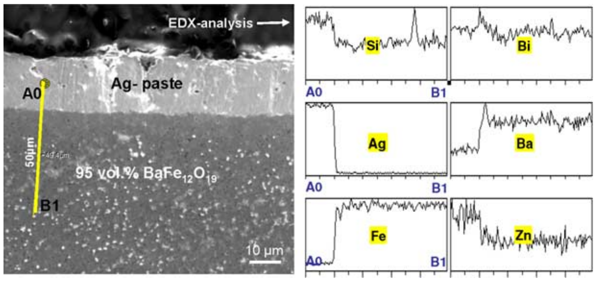

Fig. 8. LTCC compatibility of glass–ceramic composite and Ag-screen printing paste.

value of permeability is over 100 MHZ affected more by open porosity. Thus, the permeability of composite with 7 vol.% of BBSZ glass with lowest porosity (Table 1) is decreasing slower than composite with the highest porosity with 3 vol.% BBSZ glass. At 1 GHz permeabilities of composites with 5 and 7 vol.% of BBSZ are similar.

3.5. LTCC compatibility

Silver-based paste is used in LTCC technology for printing of integrated electronic circuits. Thus, the compatibility between glass–ceramic composite and silver paste is necessary. There must be no diffusion and no leaks observed between paste and composite.

Fig. 8 shows a SEM photo of an interface between the glass–ceramic composite and the silver paste layer. Analog with picture shows EDX line scan spectra of the same interface. No leaks are observed between the glass–ferrite composite and the paste after sintering. EDX spectra show sharp interface between Ag from paste on one side and Ba and Fe from tapes on the other side. This is means no diffusion between paste and tape. Signal of Si, Bi and Zn are coming from BBSZ glass which is added in very low amount, thus they are not significant for interpretation.

4. Conclusions

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 obtained. These glass–hexaferrite composites show values of permeability of around 10 at frequency of 1 GHz. Permeability is dependent on the amount of BBSZ glass added. Low content of additive does not strongly affect values of the permeability, but does strongly affect values of open porosity. Glass–ceramic composite shows good LTCC compatibility.

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