

Preparation, thermal stability and permeability behavior of substituted Z-type hexagonal ferrites for multilayer inductors

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Abstract Co₂Z-type hexagonal ferrites with iron excess Ba₃Co_{2-x}Fe_{24+x}O₄₁ (0 ≤ x ≤ 0.8) and deficiency Ba₃Co_{2+y}Fe_{24-y}O₄₁ (0 ≤ y ≤ 0.6) were prepared by an oxalate coprecipitation technique. This synthesis route leads to almost single phase Z-type ferrites for x=0 after calcination and sintering at 1330 °C. The Z-type formation is enhanced for x>0 and single phase ferrites are obtained for 0.4 ≤ x ≤ 0.8. The permeability of Z-type ferrites varies with composition x: Maximum permeability of μ' = 28 is observed for 0.4 ≤ x ≤ 0.6 for samples sintered at 1330 °C. The frequency dispersion shows broad peaks of μ'' stretching from 200 MHz to >1 GHz. For iron deficient samples 0 ≤ y ≤ 0.6 multi-phase mixtures were obtained. For Ag-based multilayer inductor applications sintering at 950 °C is required. Co₂Z ferrites with Fe excess are not stable at this temperature as demonstrated by XRD. The permeability of samples sintered at 950 °C is drastically reduced to μ' = 3. This demonstrates that these materials are not able to provide sufficient permeability for multilayer inductors for high-frequency operations since they are not compatible with the low temperature ceramic cofiring technology.

Keywords Soft ferrites · Co₂-Z hexagonal ferrites · Permeability

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1 Introduction

Hexagonal ferrites with Z-type structure are soft magnetic materials with potential application to multilayer ferrite inductors (MLFI) at operating frequencies up to the lower GHz range [1]. The magnetic properties of Co₂Z ferrite as a member of the ferroxplana family of ferrites are peculiar [2]: At room temperature the preferred plane of magnetization is perpendicular to the c-axis and the magnetization may easily rotate within that plane. The resonance frequency of this compound has been shown to be at f = 1–4 GHz [1, 2].

The structure of Z-type hexagonal ferrites may be described as a stacking of close-packed oxygen/barium layers along the hexagonal c-axis with an ordering sequence of S-, R- and T-blocks. S is a two-layer building unit (Fe₆O₈)²⁺, R a three-layer block of composition (BaFe₆O₁₁)²⁻ and T consists of the four-layer unit Ba₂Fe₈O₁₄. Combinations of R and S or T and S result in M-type ferrite BaFe₁₂O₁₉, or Y-type hexagonal ferrite Ba₂Me₂Fe₁₂O₂₂, respectively, whereas a sequence of RSTS (or MY) gives the typical structural motif of the Z-type structure [3, 4].

Due to the structural complexity, the preparation of single phase Co₂Z ferrite is not straightforward. A variety of different synthesis techniques have been reported, e.g. the standard ceramic oxide route [5] with a typical sintering temperature of 1250–1300 °C. A citrate precursor route was reported to give Co₂Z at around 1200 °C [6]; a sol-gel process was used to synthesize Z-type ferrite at 1350 °C [7] and a self-propagating synthesis was reported to give single phase Co₂Z already at 1200 °C [8]. However, many of the synthesized materials shown in the literature (and often claimed to be single phase) contain various amounts of additional phases. Endo and Nakano [1] have already

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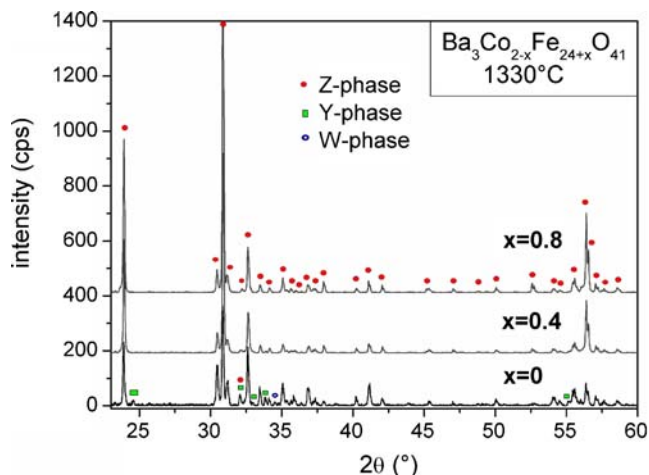


Fig. 1 XRD plots of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with $x=0$; 0.4 and 0.8 after calcination at 1330 °C

stressed that the optimum synthesis temperature is at 1300 °C with the maximum amount of Z-type ferrite in the reaction product. In a previous communication we have shown that multiple sintering at 1330 °C leads to almost single phase Co_2Z with minor Y-type impurities [9].

Co_2Z ferrites with excess of iron, i.e. the substitution of Co by Fe to yield $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$, were suggested as a new family of Z-type materials that could be prepared as single phase materials for $x=0.4$ and 0.6 at 1300 °C in air and reduced oxygen pressure [10]. The permeability of Fe excess ferrites was shown to be increased compared to the stoichiometric Co_2Z ferrite and the cation distribution was determined by neutron diffraction [11]. More complex Fe-deficient compositions have also been proposed [12], but no XRD analysis was performed in order to control the phase composition.

For MLFI fabrication, a Low Temperature Ceramic Cofiring (LTCC) process is used: a stack of ferrite tapes with screen printed Ag metallization is cofired at $T \leq 950$ °C. Sintering additives reduce the temperature of substantial shrinkage down to 950 °C: Bi_2O_3 [1, 9, 13] or lead-containing glasses [14] are commonly used. However, the permeability is usually decreased to $\mu' = 2-4$ in the MHz range and decays at around 1 GHz.

In this contribution we report on investigations on the formation conditions, permeability and phase stability of Co_2Z -type hexaferrites with substitution of Fe for Co (Fe-excess) $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) and Co for Fe (Fe-deficiency) $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ ($0 \leq y \leq 0.6$). Single phase Z-type ferrites are formed at 1330 °C using an oxalate precursor process for Fe-excess samples with $0.4 \leq x \leq 0.8$. Fe-deficient samples always result in mixtures of various hexagonal ferrites. The permeability of ferrites with $x=0.6$ reaches $\mu' = 28$ when sintered at 1330 °C. This is a significant increase compared to the standard material ($x=0$). The ferrite is sintered at 950 °C to sufficient density with the

addition of 3 wt% Bi_2O_3 , but the permeability is reduced to $\mu' = 3$. It is shown that this permeability reduction is caused by thermal decomposition of the Z-type material at 950 °C.

2 Experimental

Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) and $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ ($0 \leq y \leq 0.6$) were prepared by an oxalate precursor route. Metallic iron powder was dissolved in an acetic acid solution in Ar atmosphere to give a clear solution of ferrous acetate. Next, cobalt acetate and barium acetate were dissolved in water and added to the Fe^{2+} solution; hence a clear cation solution was obtained. An oxalic acid solution was added dropwise and a yellow-colored precipitate was immediately formed. After drying the oxalate precursor was calcined at 1330 °C for 4 h. Next, the powders were wet milled in a planetary ball mill with zirconia balls of 3 mm diameter down to a grain size of $d_{50} = 0.8$ μm . Flat compacts for sintering studies or toroids for permeability measurements were prepared by uniaxial pressing with polyvinyl-alcohol as binder. The specimens were sintered at 1330 °C for 4 h.

The phase composition was evaluated by X-ray powder diffractometry XRD (Cu- K_α radiation, Siemens D5000). XRD-scans were recorded for the determination of lattice constants from $15 \leq 2\theta \leq 80$ with a step size of 0.02° and a step time of 8 s and were analyzed using the TOPAS R software. The powder particle size was measured using a laser diffraction system (Malvern Mastersizer 2000). The bulk density of sintered samples was determined from the dimensions and weight. The microstructure of the samples was studied with a scanning electron microscope (Zeiss DSM940A). The permeability of toroids (13 mm outer diameter, 6.5 mm inner diameter, 3 mm thickness) was measured up to 1 GHz with an Agilent E4991A impedance/materials analyzer in connection with a magnetic materials

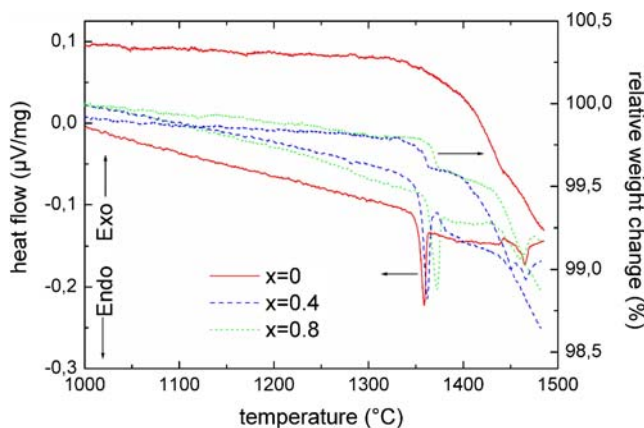


Fig. 2 DTA/TG curves of Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with $x=0$, 0.4 and 0.8 heated in air (heating rate 4 K/min)

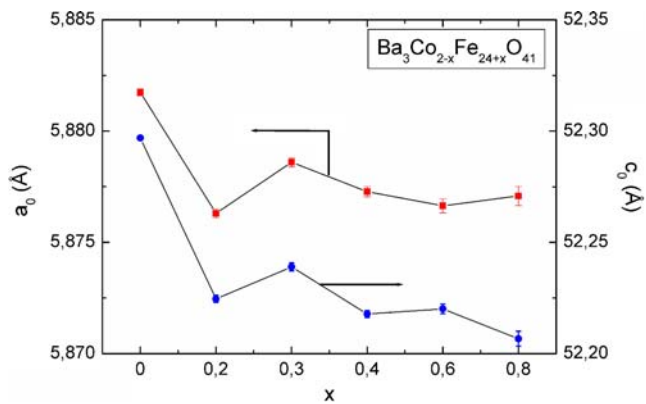


Fig. 3 Unit cell parameters of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with $0 \leq x \leq 0.8$ prepared at 1330°C

test fixture (16454A). Magnetization (as M vs. T) was measured on powdered samples with a VSM magnetometer in a field of 5 kOe.

3 Results and discussion

The thermal decomposition of an oxalate precursor is a convenient synthesis route for Co_2Z ferrites. The oxalate thermal decomposition and details of the preparation of stoichiometric $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ have been reported elsewhere [9]; it was shown that the optimum preparation temperature is 1330°C , lower calcination temperatures increase the concentrations of Y- or M-type phases and higher temperature favors the formation of W-type ferrite. Substitution of Fe for Co in $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) leads to an enhanced formation of Z-type ferrite. While the synthesis protocol for $x=0$ and 0.2 results in almost single phase samples after calcination at 1330°C with minor

concentrations of Y-type, attempts to prepare fully single-phase ferrites were successful for $0.4 \leq x \leq 0.8$. As examples the XRD plots of the calcined powders with $x=0$ (with Y-type impurities) and $x=0.4$ and 0.8 (single phase Z) are shown in Fig. 1. Powders prepared via the reported oxalate route require a synthesis temperature of 1330°C for a complete formation of the Z-phase. Reduction of the synthesis temperature down to 1250 or even 1150°C , as frequently reported in the literature, gave increased concentrations of impurity phases. Experiments to prepare Fe deficient ferrites with $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ ($0 \leq y \leq 0.6$) were not successful. The XRD analysis of samples calcined at 1330°C reveals substantial concentrations of Y- and W-type ferrites.

The thermal decomposition behavior of the Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) was monitored by thermal analysis. The decomposition of Co_2Z is indicated by an endothermic reaction at $T > 1350^\circ\text{C}$ with simultaneous mass loss is (shown here for $x=0, 0.4$ and 0.8 in Fig. 2). The decomposition temperature (T_{onset}) shifts from 1350°C for $x=0$ to 1370°C for $x=0.8$. The second endothermic effect at 1460°C might indicate the formation of a liquid phase.

The lattice constants of the Co_2Z ferrites were refined in space group $\text{P}6_3/\text{mmc}$ (No. 194). The refined unit cell parameters for $x=0$ are $a_0=5.8817(2)$ and $c_0=52.297(2)$ Å. A slight decrease in a_0 and c_0 is observed with increasing x (Fig. 3). A small deviation from that trend is found for $x=0.2$ which could be caused by the fact that compositions with $x < 0.4$ are not single phase and contain additional ferrite phases. The decrease of unit cell parameters with x might be interpreted by the fact that the ionic radius of Fe^{2+} is slightly smaller than that of Co^{2+} [15]. A model for the substitution of Fe^{2+} for Co^{2+} mainly on the Me-1 site has

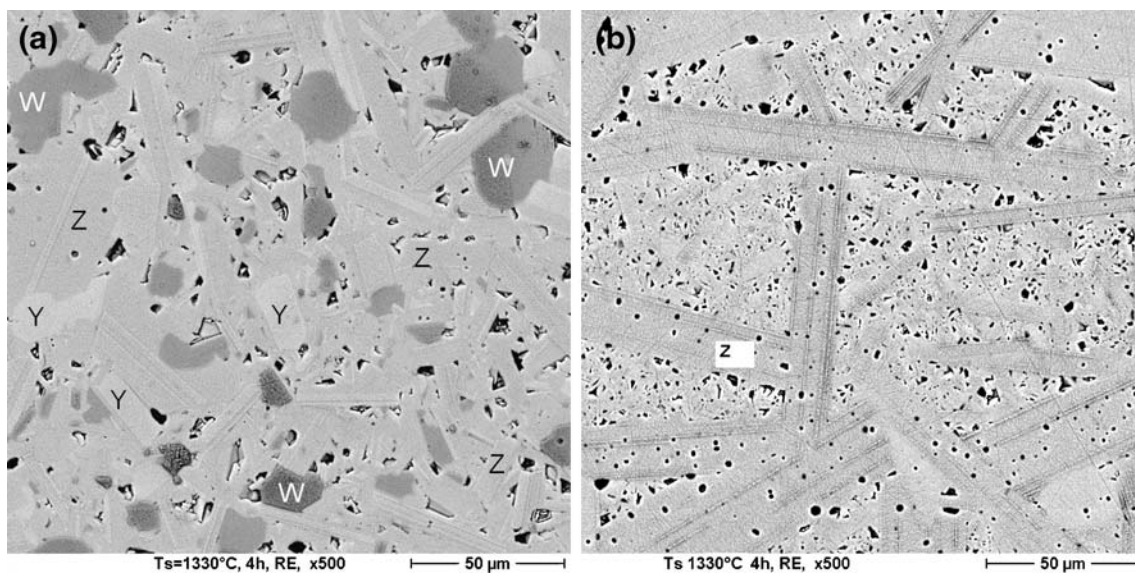


Fig. 4 SEM micrographs of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with $x=0$ (a) and $x=0.8$ (b) sintered at 1330°C for 4 h

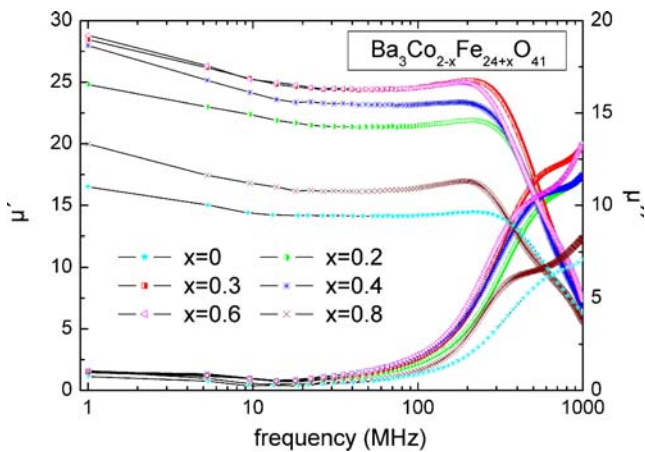


Fig. 5 Frequency dispersion of permeability μ' and μ'' for Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) calcined and sintered at 1330°C

been derived by Tachibana et al. [11] based on X-ray and neutron powder diffraction analysis.

The microstructure of the samples calcined at 1330°C , milled and sintered at 1330°C reflects the results of the phase formation studies. The SEM micrograph of a sample $x=0$ shows a microstructure based on a matrix of Co_2Z -type crystals with preferential growth in one direction and with inclusions of both Y- and W-type ferrites (Fig. 4(a)). As an example of a single phase Z-type microstructure the micrograph of the sample with $x=0.8$ consists of gray Z-type grains only (Fig. 4(b)). The densities of samples sintered at 1330°C were 4.93 g/cm^{-3} (92%) for $x=0$ and between 5.0 and 5.1 g/cm^{-3} (93–95%) for $0.2 \leq x \leq 0.8$.

The permeability of Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) sintered at 1330°C is shown in Fig. 5. For $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ ($x=0$) a permeability of $\mu'=15$ is measured in the MHz range. The real part of permeability μ' has a plateau up to about 300 MHz where it starts to decrease; at

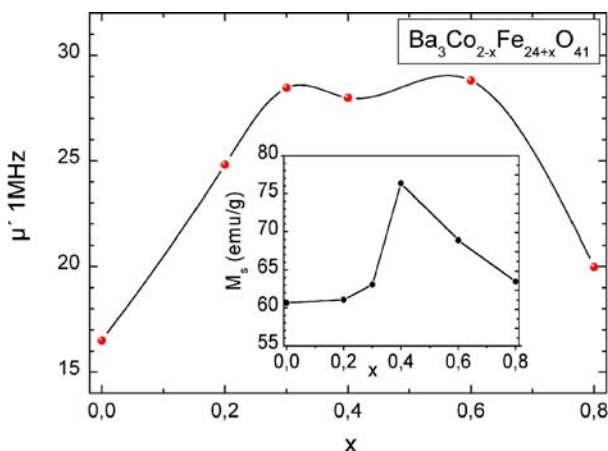


Fig. 6 Permeability μ' (at 1 MHz) of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) sintered at 1330°C as function of substitution x , inset: saturation magnetization at 5 K as function of x for $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) synthesized at 1330°C

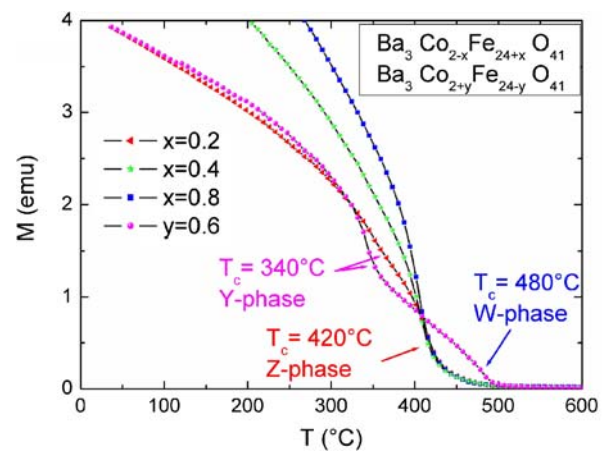


Fig. 7 Magnetization as function of temperature for Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($x=0.2; 0.4$ and 0.8) and $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ with $y=0.6$ synthesized at 1330°C

1 GHz the permeability is 7; simultaneously a broad peak of the imaginary part of permeability μ'' with its maximum at around the upper measuring frequency of 1 GHz is seen. Substitution of iron for cobalt causes significant changes in the permeability behavior: (1) the permeability μ' at the plateau first increases from $\mu'=15$ for $x=0$ to $\mu'=25$ at $x=0.3$, then remains constant at $\mu' \approx 25$ for $0.3 \leq x \leq 0.6$ until it starts to fall to $\mu'=17$ for $x=0.8$. (2) the frequency where μ' starts to decrease is almost independent on x at 300 MHz and (3) the imaginary part μ'' has a broad peak around 1 GHz, but it becomes more obvious with increasing x that at least two mechanisms contribute to that loss peak: one peak appears in the upper MHz region (200–800 MHz) which is due two domain wall resonances; the second peak is centered at >1 GHz (that is above the measured frequency range shown here) which is caused by spin rotation as suggested in Tachibana et al. [11]. The variation

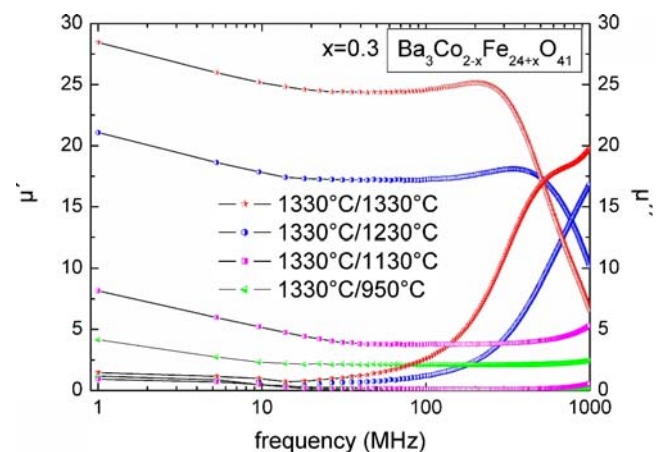


Fig. 8 Frequency dispersion of permeability μ' and μ'' for $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with $x=0.3$ calcined at 1330°C and sintered at 1330, 1230, 1130 or 950°C

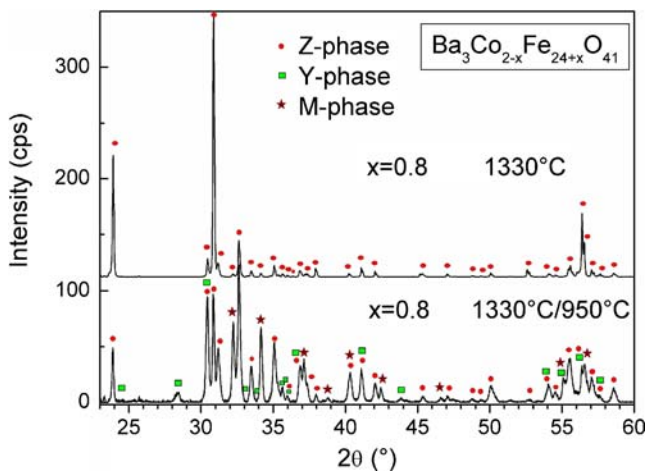


Fig. 9 XRD plots of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ powder ($x=0.8$) prepared at 1330 °C for 4 h and fired at 950 °C for 24 h

of permeability μ' as a function of x is shown in Fig. 6; maximum permeability is obtained at $0.4 \leq x \leq 0.6$. Since all samples with $x \geq 0.4$ are single phase according to XRD (and contain only minor traces of other ferrites according to SEM) the maximum permeability in that compositional range is compatible with the fact that single phase Co_2Z ferrites have large μ . For $x < 0.4$ additional ferrite phases (Y and W) tend to reduce the permeability. These results are different from those of Tachibana et al. [11] who report on a maximum μ' of 20 for $x=0.2-0.4$ and drastically reduced values for $x=0.6$. The saturation magnetization of $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) has a maximum of M_s at $x=0.4$ and then decreases for $x > 0.4$ (Fig. 6, inset). Since the permeability of hexagonal, polycrystalline ferrites

$$(\mu - 1) = \frac{8\pi M_s}{3H_a} \quad (1)$$

is proportional to the saturation magnetization M_s [2] (H_a —anisotropy field) the reduction of M_s for $x=0.8$ could account for the small permeability of that composition, assuming that micro-structural parameters as grain size and density are comparable.

The permeability of the Fe deficient compositions $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ ($0 \leq y \leq 0.6$) is drastically reduced to e.g. $\mu'=5$ for $y=0.6$ due to the multiphase nature of these materials; significant concentrations of Y- and W-type ferrites tend to decrease μ .

Measurements of the magnetization $M(T)$ also reveal the phase composition of the studied samples (Fig. 7). Ferrites with $x=0.4$ and 0.8 display a regular $M(T)$ curve with a $T_c=420$ °C typical of a Z-type ferrite. The sample with $x=0.2$ has a small hump at 320 °C signaling the existence of a second phase which was identified as Y-type by XRD. The $M(T)$ curve of the ferrite with $y=0.6$ (substitution of Co for Fe) clearly demonstrates the multi-phase state of that composition: besides the T_c of the Z-type ferrite, two strong

components are visible at $T_c=320$ °C for the Y-type and at $T_c=480$ °C for the W-type ferrite.

If Co_2Z hexagonal ferrites are to be used for multilayer inductors the cofiring temperature of the LTCC fabrication process is limited to 950 °C. It was shown in a previous paper that the densification and shrinkage behavior of Co_2Z ferrite can be modified by additives (e.g. Bi_2O_3); sufficient density after sintering at 950 °C was obtained [9]. Therefore, Co_2Z with $x=0$ and with 3 wt% Bi_2O_3 addition appeared as promising candidate for LTCC-type multilayer processes. However, the permeability of these materials was only $\mu'=3$ which was shown to be due to the instability of the Z-type phase below 1300 °C [9]. The permeability of substituted Co_2Z ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ sintered at various temperatures is shown for $x=0.3$ as an example in Fig. 8. The samples were calcined at 1330 °C and then sintered at 1330, 1230, 1130 or 950 °C for 4 h. Reduction of the sintering temperature drastically reduces the permeability and $\mu'=3$ was obtained after sintering at 950 °C. XRD studies confirm that the Z-type is unstable at 950 °C: Co_2Z powder (here for $x=0.8$) synthesized at 1330 °C and subsequently annealed at 950 °C for 24 h transforms from a single phase Co_2Z sample into a multiphase mixture with Y- and M-type ferrite as main constituents (Fig. 9). These results demonstrate that Co_2Z hexagonal iron excess ferrites $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ with substitution of iron for cobalt are not suited for the fabrication of multilayer inductors for high-operating frequency via LTCC technology. The ferrites are not compatible with the LTCC processing temperature of 950 °C for cofiring with internal Ag metallizations. This also shows that the large scattering of permeabilities for Z-type ferrites in the literature is caused by different firing conditions. Many studies report permeabilities of $\mu'=3-5$ for “single phase Z-type ferrites” after firing at 900–950 °C without any control of the phase composition. Further work is needed to develop compositions for inductors for high operating frequency which are compatible with the LTCC processing conditions.

4 Conclusions

We have shown that the synthesis of $\text{Co}_2\text{-Z}$ hexagonal ferrites with substitution of Fe for Co (Fe-excess) $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($0 \leq x \leq 0.8$) and Co for Fe (Fe-deficiency) $\text{Ba}_3\text{Co}_{2+y}\text{Fe}_{24-y}\text{O}_{41}$ ($0 \leq y \leq 0.6$) leads to single phase Z-type ferrites at 1330 °C via an oxalate precursor process for Fe-excess samples with $0.4 \leq x \leq 0.8$. Fe-deficient samples decompose into mixtures of various hexagonal ferrites. The permeability of ferrites with $x=0.6$ reaches $\mu'=28$ which is a significant increase compared to the standard material ($x=0$). Sintering at 950 °C as characteristic temperature for the LTCC-type multilayer fabrication process gives a reduced permeability of $\mu'=3$. XRD

studies show that substituted Co_2Z phases are not stable at $T < 1300$ °C hence these materials are not the preferred high-permeability material for the LTCC-compatible fabrication of MLFI for high operating frequencies.

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