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ARTICLE

Characteristics Improvement of Low-temperature Sintered $SrFe_{12}O_{19}$ Ferrites in LTCC System Applications

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Abstract: In order to improve the sintering characteristics of the low-temperature sintered M-type hexagonal strontium ferrites ($SrFe_{12}O_{19}$) prepared by a solid phase method, the Bi_2O_3 additive was used as a sintering aid. The crystal structure, electrical properties, and magnetic properties of the ferrites were investigated. The results show that the single phase structural $SrFe_{12}O_{19}$ ferrites can be obtained even with a low sintering temperature of 900 ℃. The Bi_2O_3 additive is found to possess a significant effect on the electrical properties and magnetic properties for the ferrites sintered at low temperatures enhancing resistivity ρ, saturation magnetization M_s, intrinsic coercivity H_{ci}, and magnetic anisotropy field H_a. It is suggested that the low-temperature sintered $SrFe_{12}O_{19}$ ferrites with ρ of $0.42\times10^8\ \Omega\cdot$cm, M_s of 285.6 kA m^{-1}, H_{ci} of 347.3 kA m^{-1}, and H_a of 1546.6 kA m^{-1} provide an important potential application in nonreciprocal LTCC (low temperature co-fired ceramics) ferrite devices.

Key words: strontium ferrites; magnetic anisotropy field; LTCC technology; ferrite devices

M-type hexagonal strontium ferrites ($SrFe_{12}O_{19}$) can be used in microwave and millimeter wave ferrite devices due to their relatively high saturation magnetization, moderate intrinsic coercivity, large crystalline anisotropy field, and appropriate resistivity. To meet the demand of various ferrite devices, a lot of efforts have been put into the doping effect of different elements on the microstructure and magnetic properties of $SrFe_{12}O_{19}$ ferrites, which typically includes Al substitution, Cr substitution, rare-earth element (La, Nd, Gd, Pr and Sm) substitution, and La-Co combined substitution[1-5]. Some very compact inductors, capacitors, transformers, filters, and transmit/receive (T/R) modules have been demonstrated by low temperature co-fired ceramics (LTCC) technology[6-9]. However, the nonreciprocal components like isolators, circulators, and phase-shifters are difficult to be integrated by LTCC technology[10]. It is believed that the low-temperature sintering of gyromagnetic ferrite materials is a crucial problem for microwave LTCC ferrite devices[11-14]. Because of high sintering temperature, the traditional and commercial gyromagnetic ferrite materials are unable to co-fire with the inner electrode metal silver (Ag) providing a melting point of 961 ℃ in LTCC systems. In the present work, the stoichiometric $SrFe_{12}O_{19}$ ferrites were prepared by a solid phase method, and the Bi_2O_3 additive was used as a sintering aid to reduce the sintering temperature. Subsequently, the crystal structure, electrical properties, and magnetic properties of the ferrites were investigated.

1 Experiment

High purity (≥99.99%) $SrCO_3$ and Fe_2O_3 were weighed in the composition of $SrFe_{12}O_{19}$ for preparing stoichiometric ferrites. These raw materials were mixed and ball-milled at 300 r/min for 6 h, then dried and calcinated at 1250 ℃ for 2 h.

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The powders were further ball-milled with 5 wt% sodium dodecyl sulfate (SDS) as a dispersant at 500 r/min for 4 h. Subsequently, different content of Bi_2O_3 additive from 1 wt% to 5 wt% was added to the powders, and then ball-milled at 300 r/min for 6 h again. Powders were pressed into disks with a diameter of 10 mm using 8 wt% polyvinyl alcohol (PVA) as a binder at 18 MPa for 1 min, and sintered at temperatures from 800 ℃ to 1200 ℃ for 2 h. The particle size of powders was tested by a laser particle analyser (JL-1178). The sintering density was measured by precision density balance (FA2004J) with resolution of 0.1 mg based on the Archimedes method. The crystal structure was detected by X-ray diffraction (XRD, DX-2700) with Cu Kα radiation. The magnetic hysteresis loop and magnetization curve were tested by a vibrating sample magnetometer (VSM, Versalab) of Quantum Design. The room temperature direct-current resistivity was measured by precision power supply (Agilent, B2912A) with resolution of 10 fA/100 nV.

2 Results and Discussion

It is well known that the formation of $SrFe_{12}O_{19}$ ferrites prepared by the solid phase method mainly bases on the reaction as $SrCO_3$+ $6Fe_2O_3$=$SrFe_{12}O_{19}$+ CO_2↑, where the sintering temperature usually reaches above 1200 ℃. Generally, Fe_2O_3 can not fully participate in the reaction to produce $SrFe_{12}O_{19}$ at low sintering temperatures.

Fig.1 shows the XRD patterns and lattice constants calculated by a cell refinement method for the strontium ferrites sintered at 900 ℃ with different Bi_2O_3 contents. Coexistence of α-Fe_2O_3 phase with $SrFe_{12}O_{19}$ phase is observed in the ferrites without additives, which is in well agreement with the above formation mechanism. However, the α-Fe_2O_3 phase is hardly detected when the addition of Bi_2O_3 reaches 3 wt%, and the $SrFe_{12}O_{19}$ ferrites with single phase structure are obtained. This indicates that the reaction process is significantly improved by adequate addition of Bi_2O_3 for the $SrFe_{12}O_{19}$ ferrites sintered at low temperatures, which is suggested to be correlated with the formation of Bi_2O_3 liquid phase during the sintering process. In addition, the precise lattice constants of the ferrites are calculated by the cell refinement method. It is worthwhile to note that the lattice constant c nearly stabilizes at a value over 2.3011 nm when the Bi_2O_3 content does not exceed 3 wt%, but it rapidly decreases to 2.2932 nm with the Bi_2O_3 content further increasing to 5 wt%. Bi^{3+} is extremely possible to get into the lattice of $SrFe_{12}O_{19}$ structure for the ferrites with an exorbitant Bi_2O_3 content. Due to the large ionic radius of 0.103 nm, Bi^{3+} preferentially occupies the hexahedron site (2b↑) or the octahedral site (2a↑, 12k↑, and $4f_2$↓) of Fe^{3+} (0.064 nm), leading to the lattice deformation. Simultaneously, the substitution of Fe^{3+} by Bi^{3+} more or less changes the binding energy of $SrFe_{12}O_{19}$ structure, which also makes contribution to the lattice deformation.

Current-voltage curves and resistivity-voltage curves of the strontium ferrites sintered at 900 ℃ with different Bi_2O_3 contents are shown in Fig.2, and the inset also gives the sintering density of the ferrites. Linear relationship of current-voltage curves is observed for the ferrites with different Bi_2O_3 content without the unstable low field region, providing an almosts constant resistivity ρ. When the Bi_2O_3 content increases from 0 to 5 wt%, the ρ gradually increases from 0.18×10^8 to 0.61×10^8 Ω·cm. Formation of Bi_2O_3 liquid phase can promote the low temperature sintering for the ferrites, resulting in enhanced sintering density d_s. The d_s is raised to 4.76 from 3.95 g/cm^3 when the Bi_2O_3 content increases from 0 wt% to 5 wt%. It is suggested that the elevated sintering density is preferably responsible for the increased resistivity in the low temperature sintering ferrite systems. Interestingly, the ferrites sintered at low sintering temperatures can still provide a compatible resistivity for use in microwave and millimeter wave bands.

Effect of the Bi_2O_3 content and sintering temperature on the magnetic properties of the strontium ferrites are shown in Fig.3. The Bi_2O_3 additive is found to possess a significant effect on the magnetic properties of the ferrites sintered at 900 ℃. The saturation magnetization M_s quickly increases from 33.2 A m^2 kg^{-1} to 60.7 A m^2 kg^{-1} when the Bi_2O_3 content increases from 0 wt% to 3 wt%, and then it slightly decreases to 59.6 A m^2 kg^{-1} with the Bi_2O_3 content further increasing to 5 wt%. Similar dependence of the intrinsic coercivity H_{ci} on the Bi_2O_3 content is observed too, and the maximal H_{ci} of 347.3 kA m^{-1} is obtained in the ferrite with

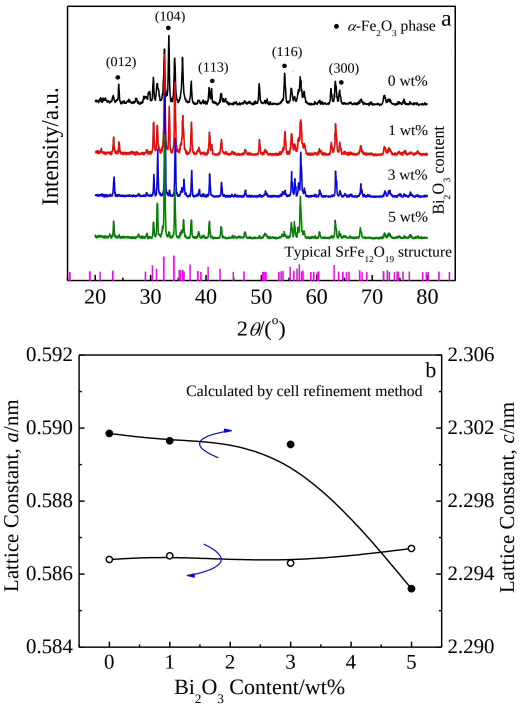

Fig.1 XRD patterns (a) and lattice constants (b) of the strontium ferrites with different Bi_2O_3 contents sintered at 900 ℃

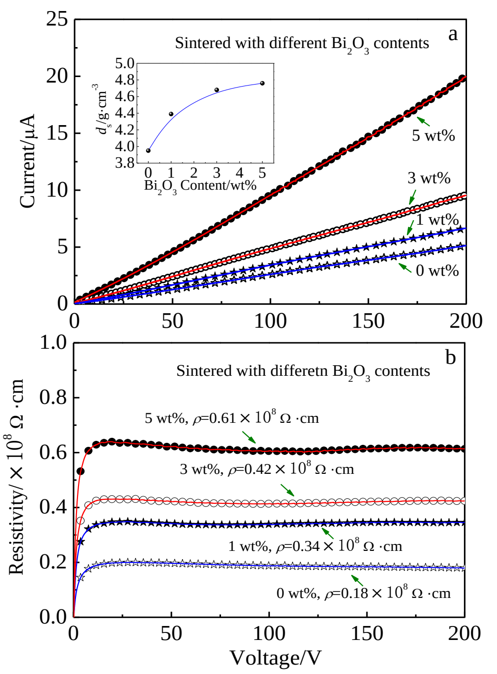

Fig.2 Current-voltage curves (a) and resistivity-voltage curves (b) of the strontium ferrites sintered at 900 ℃ with different Bi_2O_3 contents

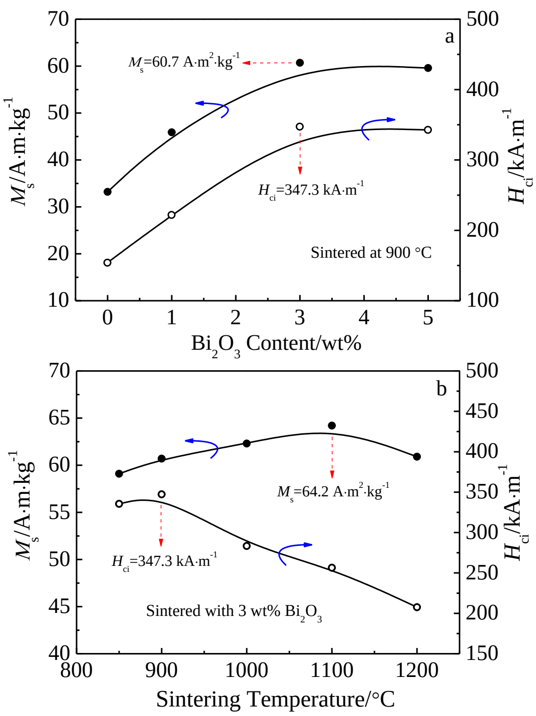

Fig.3 Magnetic properties of the strontium ferrites versus Bi_2O_3 content (a) and sintering temperature (b)

3 wt% Bi_2O_3. Moreover, the elevated sintering temperatures are certainly beneficial to the saturation magnetization improvement. When the sintering temperature increases to 1100 ℃, the M_s of the ferrites with 3 wt% Bi_2O_3 increases to 64.2 A·m^2·kg^{-1}, but the H_{ci} decreases to 256.5 kA·m^{-1} simultaneously. Promoted sintering of the ferrites using Bi_2O_3 additive as a sintering aid is suggested to be responsible for the enhanced magnetic properties. To the contrary, the redundant non-magnetic Bi_2O_3 liquid phase results in the depressed magnetic properties. Moreover, if Bi^{3+} occupies the 2b↑ site, 2a↑ site, or 2k↑ site of Fe^{3+}, the magnetic moment of $SrFe_{12}O_{19}$ phase will be weakened, and then there is a great opportunity to observe the decreased saturation magnetization.

Magnetic hysteresis loop and magnetization (*M-H*) curve of the $SrFe_{12}O_{19}$ ferrites sintered at 900 ℃ with 3 wt% Bi_2O_3 are shown in Fig.4, and the inset gives the susceptibility (d*M*/d*H*-*H*) curve accordingly. It can be seen that the ferrites provide an unsatisfactory remanence ratio under 0.6, which can be improved by applying magnetic field during the moulding process. With a sintering density d_s of 4.68 g·cm^{-3}, the saturation magnetization M_s transforms from 60.7 A·m^2·kg^{-1} to 285.6 kA·m^{-1}. The fully saturation is not observed from the *M-H* curve, even when the external magnetic field *H* reaches 1600 kA·m^{-1}, where the d*M*/d*H* arrives at a minimum value of 17.8%. Hence, the paramagnetic susceptibility can be still negligible. Similar magnetic hysteresis loops and *M-H* curves are observed in other ferrites sintered at 900 ℃ with different contents of Bi_2O_3 additive.

Subsequently, the effective magnetic anisotropy constant K_{eff} and magnetic anisotropy field H_a of the strontium ferrites sintered at 900 ℃ with different Bi_2O_3 contents are

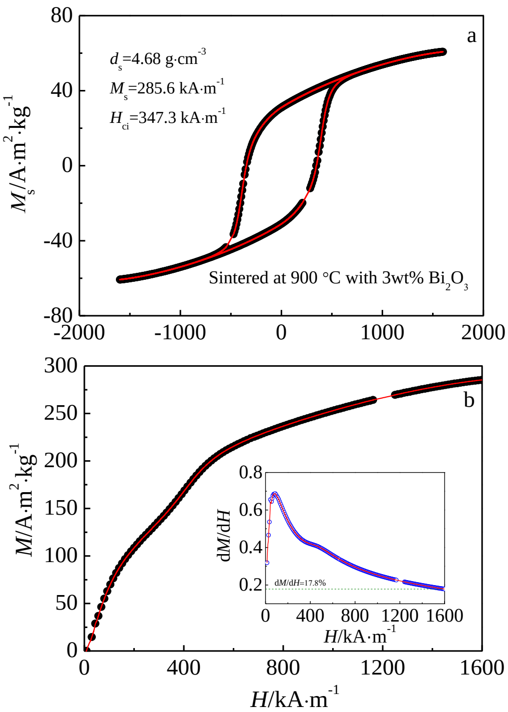

Fig.4 Magnetic hysteresis loop (a) and magnetization curve (b) of $SrFe_{12}O_{19}$ ferrites sintered at 900 ℃ with 3 wt% Bi_2O_3

Table 1 Effective magnetic anisotropy constant K_{eff} and magnetic anisotropy field H_a of the strontium ferrites sintered at 900 ℃

Bi_2O_3 content/wt%	$K_{eff}/10^5 \times J \cdot m^{-3}$	H_a/kA·m^{-1}
0	1.26	1526.3
1	1.99	1562.8
3	2.82	1546.6
5	2.75	1463.2

calculated based on the law of approach to saturation (LATS) within a external magnetic field region of 1200 kA·m^{-1} to 1600 kA·m^{-1} [15,16], which are listed in Table 1 accordingly. It is worthwhile to note that the M_s, H_{ci}, and H_a of the ferrites sintered with 3 wt% Bi_2O_3 reaches 285.6 kA·m^{-1}, 347.3 kA·m^{-1} and 1546.6 kA·m^{-1}, respectively, which provide a potential application in nonreciprocal devices like the self-biased LTCC isolators and circulators. Large coercivity effectively counteracts the influence of shape-dependent demagnetization field on the magnetic hysteresis loop, and then the ferrites can be self-biased with a large magnetic anisotropy field.

3 Conclusions

1) The Bi_2O_3 additive possess a significant effect on the crystal structure, electrical and magnetic properties for the strontium ferrites prepared by solid phase method.

2) When the Bi_2O_3 content reaches 3 wt%, the single phase structural $SrFe_{12}O_{19}$ ferrites are obtained even with a low sintering temperature of 900 ℃.

3) The sintering characteristics of the low-temperature sintered ferrites are improved with appropriate addition of Bi_2O_3 additive, including d_s, ρ, M_s, H_{ci}, K_{eff}, and H_a.

4) The M_s, H_{ci}, H_a, and ρ of the ferrites sintered at 900 ℃ with 3 wt% Bi_2O_3 reaches 285.6 kA·m^{-1}, 347.3 kA·m^{-1}, 1546.6 kA·m^{-1} and 0.42×10^8 Ω·cm, respectively, providing compatible characteristics for use in microwave LTCC technology.

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LTCC 系统用低温烧结 $SrFe_{12}O_{19}$ 铁氧体性能的改善研究

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摘 要：采用固相法制备 M 型六角锶铁氧体($SrFe_{12}O_{19}$)材料，利用 Bi_2O_3 作为烧结助剂以改善材料的低温烧结特性，系统研究了材料的晶体结构、电学性能和磁学性能。结果表明：当烧结温度降低至 900 ℃时可以获得单相的 $SrFe_{12}O_{19}$ 铁氧体材料。Bi_2O_3 的添加对低温烧结材料的电学性能和磁学性能影响显著，可以提高材料的电阻率 ρ、饱和磁化强度 M_s、内禀矫顽力 H_{ci} 和磁晶各向异性场 H_a。低温烧结材料的 ρ、M_s、H_{ci} 和 H_a 分别可以达到 0.42×10^8 Ω·cm、285.6 kA·m^{-1}、347.3 kA·m^{-1} 和 1546.6 kA·m^{-1}，在非互易 LTCC（低温共烧陶瓷）铁氧体器件领域具有重要的应用前景。

关键词：锶铁氧体；磁晶各向异性场； LTCC 技术；铁氧体器件

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