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ARTICLE

Low Temperature Sintering Characteristics of Hot Press Sintered $SrFe_{12}O_{19}$ Ferrites for Use in Microwave LTCC Circulators

Peng Long, Li Lezhong, Wang Rui, Tu Xiaoqiang, Hu Yun

Sichuan Province Key Laboratory of Information Materials and Devices Application, Chengdu University of Information Technology, Chengdu 610225, China

Abstract: The $SrFe_{12}O_{19}$ ferrites with different amounts of Bi_2O_3 additive were prepared by a hot press sintering process at a low fired temperature of 870 ℃ in order to be compatible to the LTCC (low temperature co-fired ceramics) technology, and their low temperature sintering characteristics were investigated, including the crystal phase composition, sintering density, porosity, and magnetic properties. Results show that the addition of Bi_2O_3 promotes the formation of $SrFe_{12}O_{19}$ phase structure and increases the sintering compactness and magnetic properties of the ferrites fabricated at 870 ℃. The ferrites with Bi_2O_3 content from 2 wt% to 4 wt% exhibit a compact microstructure with sintering density higher than 4.65 g·cm^{-3} and porosity lower than 10%, which contributes to the enhanced saturation magnetization M_s and intrinsic coercivity H_{ci} above 252.4 kA·m^{-1} and 312.9 kA·m^{-1}, respectively. Moreover, the potentiality of the $SrFe_{12}O_{19}$ ferrites for use in microwave LTCC circulators was also discussed based on their low temperature sintering characteristics.

Key words: $SrFe_{12}O_{19}$ ferrites; LTCC; hot press sintering; circulators

Low temperature sintering of gyro-magnetic ferrites is a crucial problem for microwave LTCC (low temperature co-fired ceramics) ferrite devices[1-6]. Because of high sintering temperature, the traditional and commercial gyro-magnetic ferrite materials are unable to co-fire with the inner electrode metal Ag in LTCC systems. M-type hexagonal barium ferrites ($BaFe_{12}O_{19}$) and strontium ferrites ($SrFe_{12}O_{19}$) can be used in microwave and millimeter wave ferrite devices due to their relatively high saturation magnetization M_s, moderate intrinsic coercivity H_{ci}, large crystalline anisotropy field H_a, and appropriate resistivity ρ, which have been considered as the promising microwave LTCC ferrite materials[7-9]. Different additives were used as sintering aids to reduce the sintering temperature of the ferrites, typically including Bi_2O_3, BaCu (B_2O_5) and $Bi_2O_3·B_2O_3·SiO_2·ZnO$ (BBSZ), and their low temperature sintering characteristics were improved[10-12].

In the present paper, the $SrFe_{12}O_{19}$ ferrites with different amounts of Bi_2O_3 additive were prepared by a hot press sintering process at a low fired temperature in order to be compatible to the LTCC technology. The crystal structure and magnetic properties of the ferrites were mainly investigated, and their potential applications in microwave LTCC circulators were also discussed.

1 Experiment

High purity (≥99.99 wt%) $SrCO_3$ and Fe_2O_3 were weighed in composition of $SrFe_{12}O_{19}$ for preparing stoichiometric ferrites. Raw materials were mixed and ball-milled at 300 r/min for 6 h, then dried and calcinated at 1250 ℃ for 2 h. Powders were further ball-milled with different amounts of Bi_2O_3 additive from 0 to 5 wt% at 400

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Corresponding author: Peng Long, Ph. D., Associate Professor, College of Optoelectronic Technology, Chengdu University of Information Technology, Chengdu 610225, P. R. China, Tel: 0086-28-85966385, E-mail: penglong@cuit.edu.cn

r/min for 4 h, and then pressed into disks using a graphite mold and sintered at 870 ℃ under 60 MPa for 10 min. Particle size of powders was tested by laser particle analyser (JL-1178). Sintering density was measured by precision density balance (FA2004J) with resolution of 0.1 mg based on the Archimedes method. Crystal structure was detected by X-ray diffraction (XRD, DX-2700) with Cu Kα radiation. Direct-current resistivity was measured by precision power supply (Agilent, B2912A) from 0 to 200 V with resolution of 10 fA/100 nV. Magnetic hysteresis loops were tested by vibrating sample magnetometer (VSM, Versalab) to obtain the magnetic properties.

2 Results and Discussion

XRD patterns of the strontium ferrites with different Bi_2O_3 contents are shown in Fig.1. The $SrFe_{12}O_{19}$ phase with M-type hexagonal structure is formed in the ferrites with different Bi_2O_3 contents. For the ferrites without Bi_2O_3 additive, the $SrFe_{12}O_{19}$ phase coexists with the non-magnetic α-Fe_2O_3 phase and SrO_2 phase, where the diffraction peaks of α-Fe_2O_3 phase like (110), (020), (130) peaks and a weak (002) peak of SrO_2 phase are observed. This is in agreement with the formation mechanism of $SrFe_{12}O_{19}$ ferrites. The formation of $SrFe_{12}O_{19}$ ferrites prepared by a solid phase method is mainly based on the reaction as $SrCO_3+6Fe_2O_3=SrFe_{12}O_{19}+CO_2\uparrow$, and 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. When the content of Bi_2O_3 increases to 1 wt%, the crystal phase composition of the ferrites is still unchanged. It is worthwhile to note that the $SrFe_{12}O_{19}$ ferrites with single phase structure are successfully obtained when the Bi_2O_3 content increases to 3 wt%. The strength of (006) peak and (008) peak is obviously enhanced, suggesting an increased *c* axis preferred orientation in the ferrites. Redundant addition of Bi_2O_3 additive is observed in the ferrites when the Bi_2O_3 content further increases to 5 wt%, where a small amount of Bi_2O_3 phase with weak (112), (121), and (012) peaks is detected. Moreover, the inter-planer spacing d_{hkl} of most crystal faces is found to get a significant decrease, which is strongly correlated with the lattice constants *a* and *c*.

Lattice constants of the strontium ferrites are calculated from the values of d_{hkl} corresponding to (107) peak and (114) peak by the following equations:

$$d_{hkl} = \left(\frac{4}{3}\frac{h^2+hk+k^2}{a^2}+\frac{l^2}{c^2}\right)^{-1/2} \quad (1)$$

and the porosity *P* of the ferrites is obtained from

$$P = 1-\frac{d_s}{d_x} \quad (2)$$

$$d_x = (1-x)d_M + xd_A \quad (3)$$

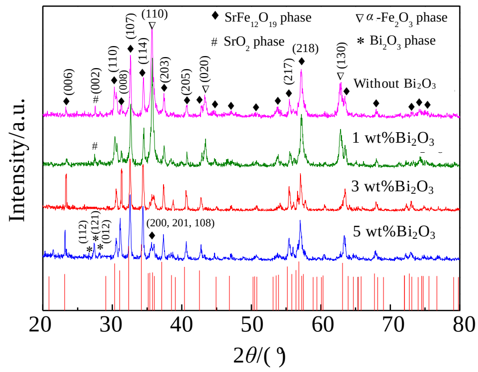

Fig.1 XRD patterns of the $SrFe_{12}O_{19}$ ferrites with different Bi_2O_3 contents

$$d_M = \frac{2M}{NV} \quad (4)$$

$$V = 0.8666a^2c \quad (5)$$

where *h*, *k*, and *l* are the Miller indices, d_x is the theoretical density of the ferrites, d_s is the sintering density of the ferrites, *x* is the amount of the additive, d_M is the X-ray density of $SrFe_{12}O_{19}$, d_A is the theoretical density of the additive, *M* is the molar mass of $SrFe_{12}O_{19}$, *V* is the lattice volume, and *N* is the Avogadro's number.

Evident effect of the Bi_2O_3 content on the lattice constants of the strontium ferrites is observed, as shown in Fig.2. The large lattice constant *a* from 0.5898 nm to 0.5922 nm is obtained with Bi_2O_3 content from 1 wt% to 4 wt%, which clearly exceeds the typical value of 0.588 nm. Correspondingly, the lattice constant *c* decreases to a range between 2.196 and 2.226 nm from a typical value of 2.307 nm. This indicates that the (001) face of the hexagonal structure is chiefly perpendicular to the pressure direction, leading to the lattice deformation.

Fig.3 gives the sintering density and porosity of the strontium ferrites with different contents of Bi_2O_3 additive. The addition of Bi_2O_3 is found to be conducive to increase the sintering density and to decrease the porosity of the ferrites, which is suggested to be strongly associated with the formation of Bi_2O_3 liquid phase during the sintering process. The ferrites can provide a relatively compact microstructure with sintering density higher than 4.65 g cm^{-3} and porosity lower than 10% when the Bi_2O_3 content varies from 2 wt% to 4 wt%. Low porosity can reduce the demagnetization field inside the ferrites and decrease the electromagnetic loss in high frequency applications.

Moreover, the enhanced saturation magnetization M_s and intrinsic coercivity H_{ci} are obtained for the ferrites due to the promoted low temperature sintering with appropriate amount of Bi_2O_3 additive, as shown in Table 1. To the contrary, the redundant non-magnetic Bi_2O_3 phase results in depressed magnetic properties, and there is a great

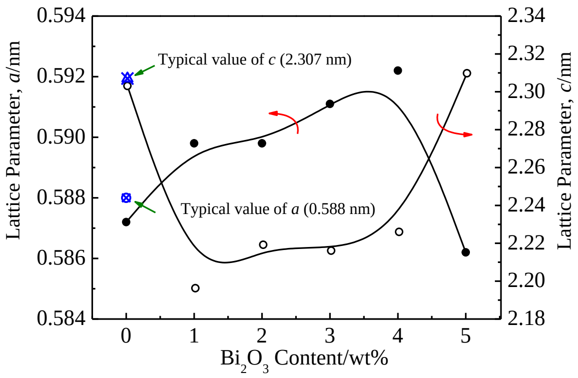

Fig.2 Effect of the Bi_2O_3 content on the lattice constants of the $SrFe_{12}O_{19}$ ferrites

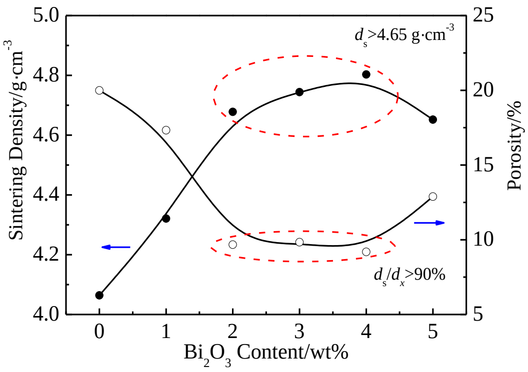

Fig.3 Sintering density and porosity of the $SrFe_{12}O_{19}$ ferrites with different contents of Bi_2O_3 additive

opportunity to observe the decreased M_s and H_{ci} in the ferrites with Bi_2O_3 content higher than 3 wt%. Interestingly, the hot press sintered ferrites with Bi_2O_3 content from 2 wt% to 5 wt% provide excellent M_s and H_{ci}, which typically ranges from 252.4 to 294.6 kA m^{-1} and from 312.9 to 353.2 kA m^{-1}, respectively.

The tensor permeability of magnetized gyro-magnetic ferrites is the important foundation for microwave ferrite circulators. The coefficients of tensor permeability μ and k are defined as

$$\mu = 1 + \frac{\omega_0 \omega_m}{\omega_0^2 - \omega^2} \tag{6}$$

and

$$k = \frac{\omega \omega_m}{\omega_0^2 - \omega^2} \tag{7}$$

where ω is the radian frequency and

$$\omega_0 = \gamma H_0 \tag{8}$$

$$\omega_m = \gamma M_s \tag{9}$$

Table 1 Sintering characteristics of the $SrFe_{12}O_{19}$ ferrites with different amounts of Bi_2O_3 additive

Bi_2O_3 content/ wt%	d_s/ g cm^{-3}	P/ %	M_s/ kA m^{-1}	H_{ci}/ kA m^{-1}
0	4.064	19.99	132.7	160.0
1	4.321	17.33	201.5	206.6
2	4.678	9.67	252.4	312.9
3	4.744	9.84	294.6	342.7
4	4.803	9.19	292.0	353.2
5	4.652	12.89	272.5	325.1

where H_0 is the applied magnetic field and γ is the gyro-magnetic ratio. The magnetic anisotropy field H_a contributes to the H_0 as

$$H_0 = H_{ext} + H_a - NM_s \tag{10}$$

where H_{ext} is the applied external field, and N is the demagnetization factor.

The value of k/μ is an important parameter for the microwave ferrite circulators, which is strongly correlated with the working frequency. Fig.4 presents the relationship between the value of k/μ and working frequency for self-biased circulators (H_{ext}=0) based on the hot press sintered $SrFe_{12}O_{19}$ ferrites with 3wt% Bi_2O_3, which gives suitable saturation magnetization M_s of 294.6 kA m^{-1}, intrinsic coercivity H_{ci} of 342.7 kA m^{-1}, and magnetic anisotropy field H_a of 1584.0 kA m^{-1}. The ferromagnetic resonance frequency f_0 is calculated as 45.1 GHz for the ferrites. More importantly, the value of k/μ gradually goes into the resonance domain after 40 GHz. It can be suggested that the $SrFe_{12}O_{19}$ ferrites provide a significant potential application in the self-biased LTCC circulators from 34 GHz to 40 GHz with k/μ from 0.28 to 0.46 accordingly.

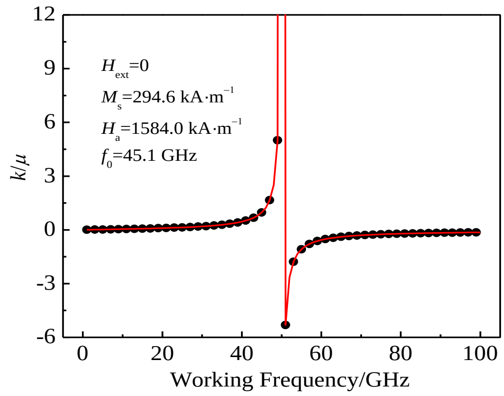

Fig.4 Relationship between the value of k/μ and working frequency for self-biased circulators (H_{ext}=0) based on the hot press sintered $SrFe_{12}O_{19}$ ferrites with 3 wt% Bi_2O_3

3 Conclusions

1) Compact microstructure of the hot press sintered ferrites $SrFe_{12}O_{19}$ with large sintering density and low porosity is observed with Bi_2O_3 content above 2 wt%, where the sintering compactness reaches a value higher than 90%.

2) When the Bi_2O_3 content varies from 2 wt% to 5 wt%, the M_s and H_{ci} are enhanced to a range from 252.4 to 294.6 kA m^{-1} and from 312.9 to 353.2 kA m^{-1}, respectively.

3) Typically, the $SrFe_{12}O_{19}$ ferrites with 3 wt% Bi_2O_3 are suggested to be suitable for use in the self-biased LTCC circulators from 34 to 40 GHz, which possess excellent sintering characteristics including d_s of 4.74 g cm^{-3}, M_s of 294.6 kA m^{-1}, H_{ci} of 342.7 kA m^{-1}, H_a of 1584.0 kA m^{-1}, and ρ of 0.45×10^8 Ω·cm.

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微波 LTCC 环行器用热压烧结 $SrFe_{12}O_{19}$ 铁氧体的低温烧结特性

彭　龙，李乐中，王　瑞，涂小强，胡　云

(成都信息工程学院 四川省信息材料及器件化应用高校重点实验室，四川 成都 610225)

摘　要：为了与低温共烧陶瓷（LTCC）技术兼容，采用热压烧结工艺在 870 ℃制备了添加不同 Bi_2O_3 含量的 $SrFe_{12}O_{19}$ 铁氧体材料，着重研究了材料的晶相组成、烧结密度、气孔率和磁性能等低温烧结特性。研究结果表明，材料在 870 ℃烧结时，Bi_2O_3 的添加促进了 $SrFe_{12}O_{19}$ 晶相结构的形成，提高了材料的烧结致密度和磁性能。当 Bi_2O_3 的添加量 (质量分数) 为 2%～4%，材料可以获得致密的结构，烧结密度达到 4.65 g cm^{-3} 以上，气孔率低于 10%，材料的饱和磁化强度 M_s 和内禀矫顽力 H_{ci} 较高，分别达到 252.4 kA m^{-1} 和 312.9 kA m^{-1} 以上。此外，基于 $SrFe_{12}O_{19}$ 材料的低温烧结特性讨论了该材料在微波 LTCC 环行器当中的应用。

关键词：$SrFe_{12}O_{19}$ 铁氧体；LTCC；热压烧结；环行器

作者简介：彭　龙，男，1980 年生，博士，副教授，成都信息工程学院光电技术学院，四川 成都 610225，电话：028-85966385，E-mail: penglong@cuit.edu.cn