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Low temperature sintering behavior of La-Co substituted M-type strontium hexaferrites for use in microwave LTCC technology

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Abstract: The La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites with appropriate Bi_2O_3 additive were prepared by conventional sintering method and microwave sintering method at low sintering temperatures compatible with LTCC (low temperature co-fired ceramics) systems, and their sintering behavior was chiefly investigated, including the crystal structure, saturation magnetization M_s, magnetic anisotropy field H_a, intrinsic coercivity H_{ci}, and Curie temperature T_C. Experiment results clearly showed that the pure M-type crystal phase was successfully obtained when the La-Co substitution amount x did not exceed 0.3. However, the single M-type phase structure transformed to multiphase structure with further increased x, where the M-type phase coexisted with the non-magnetic phase such as α-Fe_2O_3 phase, La_2O_3 phase, and $LaCoO_3$ phase. Appropriate La-Co substitution improved the M_s (>62 emu/g), H_a (>1400 kA/m), and H_{ci} (>320 kA/m) for the ferrites with x varying from 0.1 to 0.3, but the T_C decreased with increasing substitution amount. Moreover, the microwave sintered ferrites could provide larger H_{ci} and similar M_s compared with the conventional sintered ferrites.

Keywords: M-type hexaferrites; $SrFe_{12}O_{19}$ ferrites; La-Co substitution; low temperature sintering; LTCC; rare earths

With rapid development of LTCC (low temperature co-fired ceramics) passive integration technology, some very compact inductors, capacitors, transformers, filters, and transmit/receive (T/R) modules have been demonstrated by LTCC technology[1–3]. However, the nonreciprocal components like isolators, circulators, and phase-shifters are difficult to be integrated by LTCC technology due to the absence of microwave LTCC ferrite materials[4–8]. The M-type hexaferrites ($BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ ferrites) can provide excellent permanent magnetic properties and gyromagnetic properties, which have been considered as the promising low temperature sintered materials for use in microwave and millimeter wave LTCC ferrite devices[9–12]. Because of high sintering temperature above 1200 ºC, the conventional hexaferrites cannot co-fire with the inner electrode metal Ag with a melting point of 961 ºC in LTCC systems. Interestingly, the sintering temperature of these hexaferrites can be reduced to 900 ºC by using some glass phase or metallic oxide as sintering aid, but their magnetic properties decrease accordingly[13–15]. Thus, how to improve the low temperature sintering characteristics of the hexaferrites is significant for the miniaturization of new microwave communication systems based on LTCC technology.

It is well known that the ion substitution is an important method to improve the magnetic properties of M-type Ba hexaferrites and Sr hexaferrites prepared at traditional high sintering temperatures, typically including the Al substitution, Gd substitution, rare-earth element (La, Nd, Gd, Pr, and Sm) substitution, Zn-Ti substitution, and La-Co substitution, etc.[6–12]. However, the effects of ion substitution on the sintering behavior and properties of M-type hexaferrites sintered at low temperatures are still undiscovered. In our previous work, the sintering temperature of $SrFe_{12}O_{19}$ ferrites was reduced to 900 ºC by using Bi_2O_3 as sintering aid, and the effects of Bi_2O_3 amount on their crystal structure and magnetic properties were studied[5]. In this work, the La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites with Bi_2O_3 additive were separately prepared by conventional sintering method and microwave sintering method at low sintering temperatures compatible with LTCC systems, and the effects of La-Co substitution amount on their crystal structure and magnetic properties were chiefly investigated.

1 Experimental

Starting materials of $SrCO_3$ (>98 wt.%), Fe_2O_3 (>99 wt.%),

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La_2O_3 (>99.99 wt.%), and Co_2O_3 (>99 wt.%) powders were weighed in composition of $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) for preparing the La-Co substituted ferrites. Mixed powders were calcinated at 1250 ºC for 2 h and then ball- milled at 400 r/min for 4 h with different amounts of Bi_2O_3 (>99 wt.%). Powders were pressed into disks with a diameter of 12 mm at 45 MPa, and prepared by conventional sintering method at 890 ºC for 2 h and microwave sintering method at 870 ºC for 30 min, respectively. Work frequency and output power of the microwave sintering furnace (GER-M2) are 2.45 GHz and 2000 W. Particle size of the powders was tested by a laser particle analyzer (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. Magnetization curves, magnetic hysteresis loops, and Curie temperature (T_C) were tested by a vibrating sample magnetometer (VSM, Versalab). Effective magnetic anisotropy constant and magnetic anisotropy field were calculated by the law of approach to saturation (LATS)[6].

2 Results and discussion

Compared with the conventional sintering method, the microwave sintering method can promote the low temperature sintering of $SrFe_{12}O_{19}$ ferrites. Strong microwave coupling for the green compact ferrites with large dielectric loss and magnetic loss during microwave sintering process is propitious to increase the diffusion rate and reduce the activation energy for the ferrites, which is suggested to be responsible for the decreased sintering temperature and sintering time[16]. Moreover, the addition of Bi_2O_3 effectively decreases the sintering temperature of the ferrites, which is correlated with the formation of Bi_2O_3 liquid phase. But redundant non-magnetic Bi_2O_3 phase actually results in depressed magnetic properties for the ferrites[5]. Appropriate sintering process and Bi_2O_3 content are very important for preparing high performance M-type hexaferrites for use in LTCC technology. As to the $SrFe_{12}O_{19}$ ferrites prepared by conventional sintering method at 890 ºC and microwave sintering method at 870 ºC in our experiments, the optimal amount of Bi_2O_3 is found to be 3 wt.%. Therefore, the La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites are also prepared with 3 wt.% Bi_2O_3 additive.

Fig. 1 shows the XRD patterns of the La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites prepared by different sintering methods. Pure M-type crystal phase is successfully obtained when the La-Co substitution amount x does not exceed 0.3, indicating that a complete reaction occurs for producing the M-type hexaferrites by conventional sintering and microwave sintering at the low sintering temperatures. It is well known that the sintering temperature of M-type hexaferrites usually reaches above 1200 ºC, and Fe_2O_3 can not fully participate in the reaction to produce M-type crystal phase at low sintering temperatures. Appropriate addition of Bi_2O_3 promotes the formation of single M-type phase at low sintering temperatures. However, the multiphase structure is obtained when the substitution amount further increases to 0.4 and 0.5. For the ferrites prepared by conventional sintering method, the non-magnetic α-Fe_2O_3 phase and La_2O_3 phase are evidently observed to coexist with the M-type phase. Similarly, the coexistence of α-Fe_2O_3 phase and $LaCoO_3$ phase with M-type phase is also observed for the ferrites prepared by microwave sintering method. These results strongly suggest that the La^{3+}-Co^{2+} ions partially substitute the Sr^{2+}-Fe^{3+} ions even sintered at low temperatures for the ferrites prepared by conventional sintering method and microwave sintering method.

Fig. 2 presents the saturation magnetization (M_s) of the La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites prepared by different methods. As to the conventional sintered ferrites at 890 ºC, the M_s increases from 61.1 to 65.4 emu/g when the substitution amount x increases from 0 to 0.2. With x further increasing to 0.5, the M_s gradually decreases to 56.8 emu/g. For the microwave sintered ferrites at 870 ºC, the M_s firstly increases from

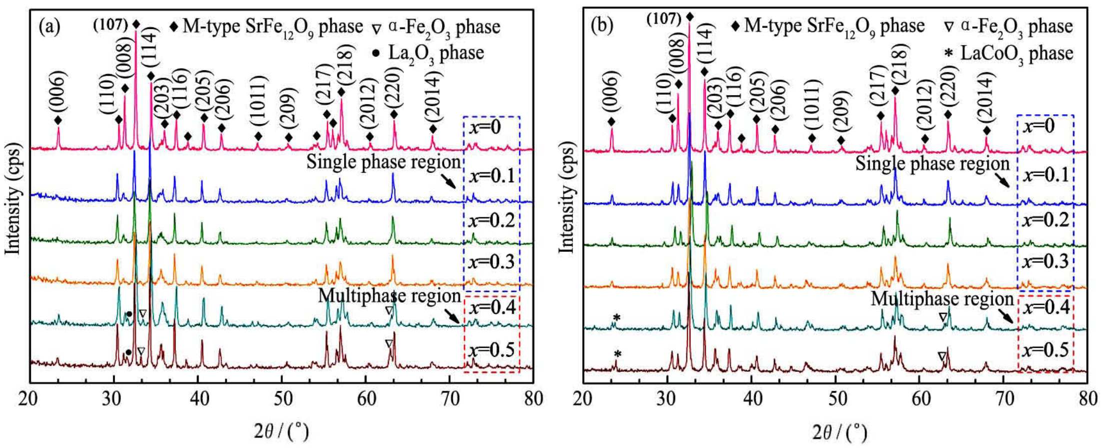

Fig. 1 XRD patterns of the La-Co substituted $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ (x=0–0.5) ferrites prepared by conventional sintering method (a) and microwave sintering method (b)