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Microwave sintering of $(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$ microwave magnetic materials

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Abstract

Microwave sintering (ms) process is applied to efficiently densify the $(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$, Bi-CVG, materials, without inducing a deleterious effect on their microwave magnetic properties. A microwave sintering process can sinter the Bi-CVG materials to a density as high as 96.5%T. D., by firing the samples at 1030 °C (30 min). In contrast, it needs 1060 °C (6 h) to densify the materials to the same high density by a conventional sintering (cs) process. The ms-processed Bi-CVG materials possess pronouncedly smaller grain size (~1.2 μm), which markedly hinders their low frequency magnetization process (in a few tens of MHz frequency regime), resulting in larger coercive field (*Hc*) and smaller initial permeability (μ_i), as compared with the cs-processed large grain samples. But such a small grain characteristic insignificantly degrades the microwave magnetic properties, the resonance line width (ΔH), of the Bi-CVG materials.

Keywords: Bi-CVG; Microwave sintering; Microwave magnetic materials

1. Introduction

Yttrium-iron garnet (YIG, $Y_3Fe_5O_{12}$) materials possess the highest quality factor among the magnetic oxides in a microwave regime, viz. they posses the smallest linewidth (ΔH) in magnetic resonance.[1–4] These materials also own high saturate magnetization, which can be tailor designed by forming a solid solution with $Gd_3Fe_5O_{12}$ and $Y_3Al_5O_{12}$ etc. Yttrium-iron garnet materials, in ceramics or single crystal form, are thus widely used for magnetic microwave devices, such as circulators, oscillators and phase shifters.[5,6]

However, high sintering temperature (>1450 °C) and long soaking time (>10 h) are required to synthesize the YIG materials with a high enough density. Meanwhile, multilayer ceramic devices have attracted extensive attention owing to the necessity for the miniaturization of RF modules in a microwave communication system. Co-firing the ceramic materials, magnetic or dielectric, with the electrode materials, silver or gold, requires the development of low temperature sinterable materials. The Bi_2O_3 and $2CaO–V_2O_5$ incorporations were reported as being able to significantly lower the sintering temperature necessary for synthesizing high density samples, which were designated as Bi-CVG.[7–10] Moreover, the microwave sintering process was known to be capable of densifying the ceramic materials in a very rapid rate and at a substantially lower temperature.[11,12] Therefore, this technique was adopted in this work to prepare the microwave magnetic garnet.[13]

In this paper, we denesified the Bi-CVG materials using a microwave sintering technique and discussed how the microwave sintering process influences densification and magnetic characteristic for these materials.

2. Experimentals

$(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$, Bi-CVG materials were prepared by a conventional mixed oxide process. A mixture of Y_2O_3, Fe_2O_3, Bi_2O_3, V_2O_5 and $CaCO_3$ with nominated ratio was calcined at 925 °C for 3 h. The samples of toroidal geometry (20 mm I.D.×10 mm O.D.×5 mm high) were sintered in an electrical furnace or microwave sintering apparatus. In conventional sintering (cs) process, the toroids were sintered at 1020–1060 °C for 4–16 h (in air) with the heating and cooling rate controlled at 5 °C/min. In microwave sintering (ms)

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process, a 2.45 GHz microwave generated from a 5 kW magnetron (AsTex A50RH) was fed into an applicator made of WR284 waveguide. The samples were placed in a porous Al_2O_3–SiO_2 crucible, which contains SiC-rods as susceptors. The sintering temperature was measured using a B-type thermocouple placed touching the samples during the heating processing. The samples were heated at a rate of 30 °C/min, soaked at 950–1030 °C for 30 min (in air), and then cooled at a rate of 10 °C/min.

The crystal structure and microstructure of the Bi-CVG materials were examined using an X-ray diffractometer (Rigaku D/max-II) and a scanning electron microscope (Joel JSM-840A), respectively. The density of the materials was measured using Archimedas method. The B–H hysteresis loops of the materials were evaluated by measuring the impedance of a coil wound on the toroidal samples, using magnetic hysteresis loops tracer (Walker AMH-20). The complex permeability measured by RF Impedance/ Material Analyzer (Agilent E4991A) from 1 MHz to 1 GHz and magnetic resonance properties measured by electron paramagnetic resonance (EPR) spectrometer (Bruker EMX-10) were used for evaluating the Q-factor in microwave regime.

3. Results and discussion

The as-calcined $(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$, Bi-CVG, powders are mainly garnet phase, but contain a small proportion of intermediated perovskite phase ($YFeO_3$, Fig. 1 a). The residual perovskite phase can be completely converted into the garnet phase, no matter whether the samples were sintered by the conventional sintering (cs) or microwave sintering (ms) process, which is illustrated in Fig. 1b and c, respectively. In the conventional sintering process, the density of Bi-CVG materials increases monotonously with sintering temperature, reaching a density as high as 98.0% T. D. when sintered at 1060 °C (6 h) (close symbols, Fig. 2). In contrast, the sintered density for these materials increases only moderately with the densification temperature when processed by the microwave sintering process. It requires only 950 °C (0.5 h) to achieve 96.5% T. D. (open symbols, Fig. 2).

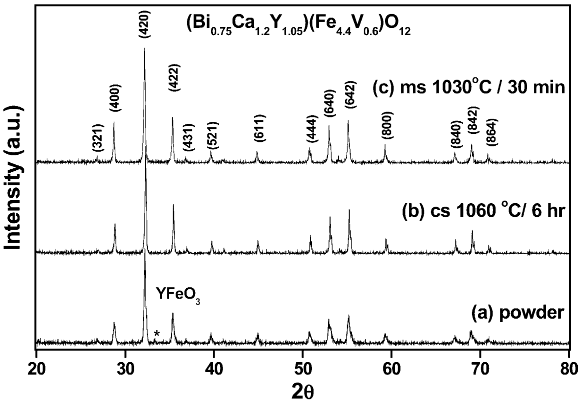

Fig. 1. X-ray diffraction pattern of Bi-CVG materials: (a) as-calcined, (b) conventionally sintered and (c) microwave sintered.

The microstructure of the Bi-CVG samples changes insignificantly with sintering temperature and soaking time. Typical SEM micrographs for the Bi-CVG materials are shown in Fig. 3 for the cs-sintered and ms-sintered samples, indicating that the grain size distribution is very uniform, regardless of sintering processes used. The grains are relatively large for the cs-sintered materials (4–6 μm, Fig. 3a) and are small for the ms-sintered materials (~1.2 μm, Fig. 3b). That the microwave-sintered samples possess pronouncedly smaller grains than the conventionally-sintered ones has also been observed in other materials system.[14] The probable explanation for this phenomenon is that, in the grain growth process, the ions jump from the convex to the concave side of the grain boundaries. The presence of a microwave does not facilitate such a process, as the jump of ions from one-site to another does not result in a change of polarity. The densification results by the interdiffusion between the vacancies and the adjacent cations or anions. Such a process is markedly enhanced in the presence of the microwave, since the vacancy-cation (or vacancy-anion) pairs are polar in nature. To reiterate, the microwave sintering process can preferentially improve the densification process without inducing the grain growth, resulting in a fine grain microstructure.

Variation of magnetic properties for the Bi-CVG materials with the sintering temperature are shown as B–H hysteresis curves in Fig. 4a and b, respectively, for those densified by the cs- and ms- processes. For the materials densified by the conventional sintering process, the sintering temperature imposes a very moderate effect on their magnetic properties. *Hc*-value decreases from 5.2 to 3.2 Oe, whereas *Br*-value was maintained at around 0.35–0.40 kG when sintering temperature increases from

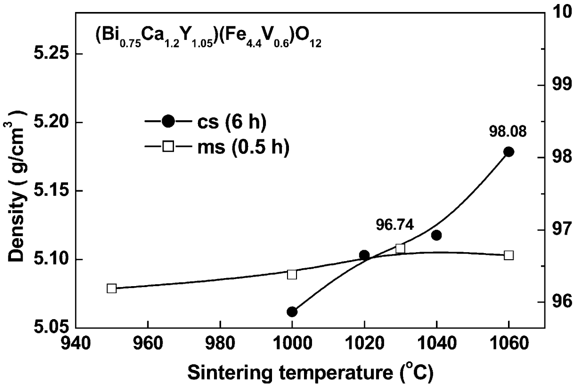

Fig. 2. Variation of fired density with sintering temperature for Bi-CVG materials processed by conventional or microwave sintering (solid symbols: fired by conventional sintering processes at 1000–1060 °C for 6 h; open symbols: fired by microwave sintering processes at 950–1030 °C for 0.5 h).

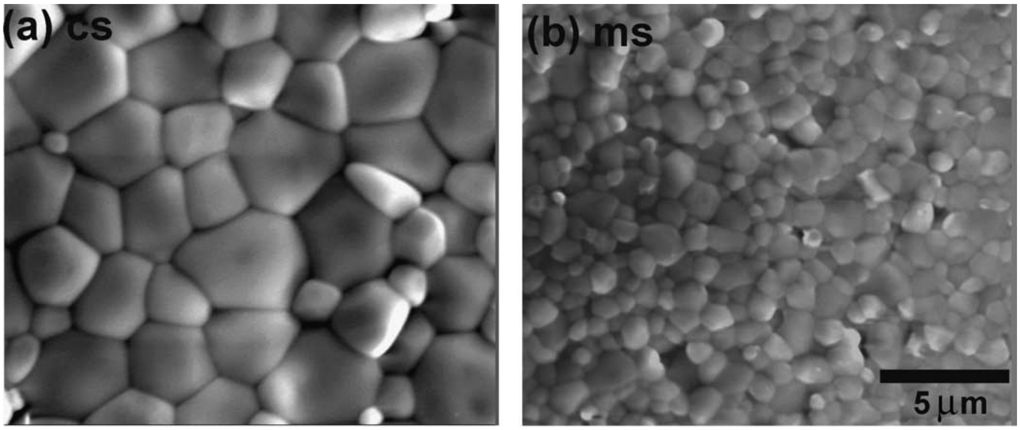

Fig. 3. Microstructure of Bi-CVG materials processed by (a) conventional sintering (1060 °C×6 h) and (b) microwave sintering processes (1030 °C×0.5 h).

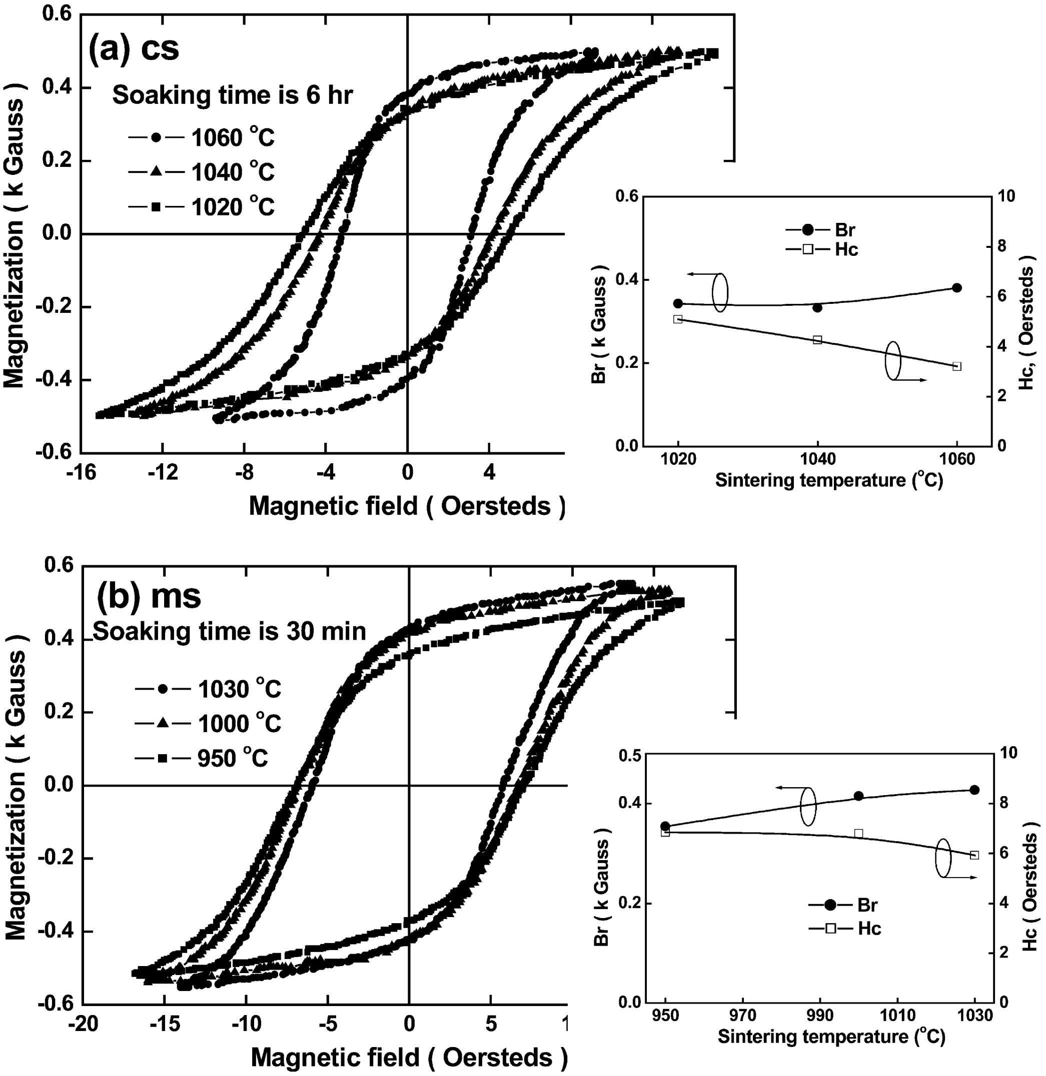

Fig. 4. Variation of B–H hysteresis loops with sintering temperature for Bi-CVG materials densified by (a) conventional sintering and (b) microwave sintering.

1020 to 1060 °C (6 h soaking time, Fig. 4a). When the materials were densified by microwave sintering (ms) process, both of the magnetic properties (*Br* and *Hc*) are essentially insensitive to the sintering parameters (Fig. 4b).

For the high density materials, which are the samples sintered at 1060 °C (6 h) by conventional sintering process or sintered at 1030 °C (30 min) by a microwave sintering process, the remanent magnetization (*Br*) is not sensitive to the sintering techniques used ($Br=6.5$–7 Oe), whereas the coercive force for cs-derived samples is pronouncedly smaller than that for ms-derived ones [$(Hc)_{cs}=3.2$ Oe and $(Hc)_{ms}=6.0$ Oe]. These results imply clearly that the *Br*-value is relatively insensitive to the microstructure of the samples, but the Hc-value is quite microstructurally dependent. Such a phenomenon is understandable, as the remanent magnetization (*Br*) stands for the density of magnetic dipole moments available in the materials, which is insignificantly influenced by the proportion of grain boundaries contained in the materials. In contrast, the coercive field (*Hc*) is related to the easiness for a magnetic dipole moment to switch with the external magnetic field, which is very sensitive to the presence of pinning sites, the grain boundaries. Therefore, the *Br*-value is insensitive to the size of the grains, whereas the *Hc*-value increases markedly as the grain size of the samples decreases.

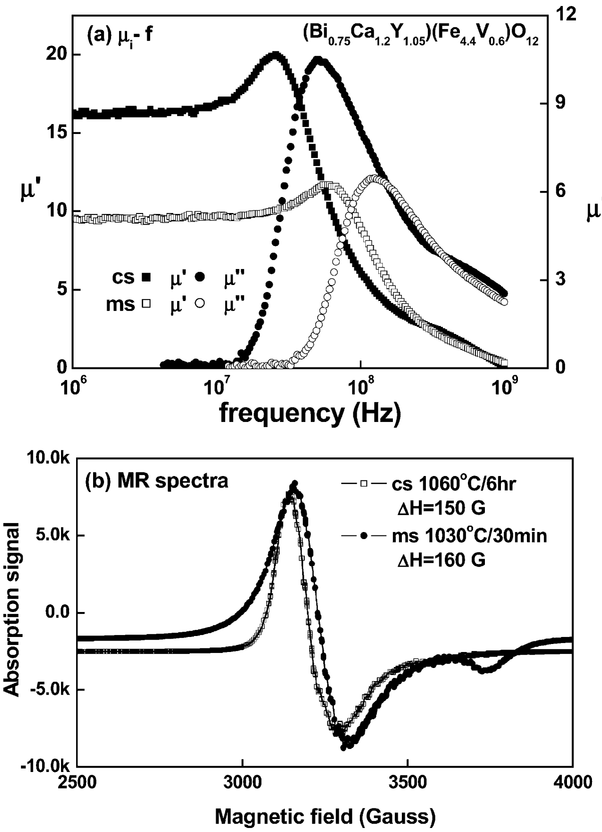

Fig. 5. Optimized (a) initial permeability and (b) gryo-magnetic resonance spectra for Bi-CVG materials densified by conventional sintering (1060 °C×6 h) or microwave sintering (1030 °C×0.5 h) processes.

Similarly, the initial permeability (μ_i) for the materials is also expected to be profoundly influenced by the microstructure of the samples, as the initial permeability (μ_i) represents the mobility of a magnetic domain wall in response to the small applied field.

Fig. 5a indeed reveals that the magnetic initial permeability (μ_i) of the large-grain samples (cs-processed) is markedly larger than the μ_i-value of the fine-grain ones (ms-processed). Moreover, Fig. 5a also reveals that the magnetic resonance phenomenon due to domain wall motion for ms-samples occurred at $(f_r)_{ms}=105$ MHz, which is slightly higher than that for cs-samples, $(f_r)_{cs}=70$ MHz. To reiterate, the magnetic phenomena related to the domain wall movement are significantly influenced by the presence of pinning sites, the grain boundaries.

However, the strong microstructural dependence of the magnetization process is true only in the low frequency regime. Fig. 5b shows that the gyro-magnetic resonance phenomenon measured by the electron-spin resonance (esr) apparatus for the ms-samples is essentially the same as those for the cs-samples. Both materials possess good gyro-magnetic properties, i. e., the line width for the magnetic resonance is, $\Delta H=150$–160 G. Such a phenomenon can be accounted for by the fact that in gyro-magnetic resonance process the magnetic dipoles interact with the electric and magnetic field of the microwave individually. Therefore, the presence of the grain boundaries totally unaffects the gyro-magnetic rotation of the individual magnetic dipoles. In contrast, in the permeability process, the magnetic dipoles in the vicinity of domain walls respond to the external magnetic field co-operatively and hence are significantly hindered by the existence of the grain boundaries.

The above-described results imply that microwave-sintering process, which induces small grain characteristics for the samples, does not degrade the microwave magnetic properties for the Bi-CVG materials, although they markedly influence the magnetic properties of the materials in low frequency regime (a few tens of MHz). Contrarily, the ms-process exhibits overwhelmingly advantages over the cs-process in the densification efficiency for these materials. The sintering temperature is markedly lower and the soaking time is pronouncedly shorter for microwave sintering (ms) process, as compared with those for conventional sintering (cs) process.

4. Conclusion

Characteristics of Bi-CVG materials prepared by the microwave sintering (ms) process are compared to those prepared by the conventional sintering (cs) process. The microwave sintering process can densify the Bi-CVG materials to a density as high as 96.5%T. D., by sintering at 1030 °C (30 min), whereas the conventional sintering process needs 1060 °C (6 h) to densify the materials to the same high density. The ms-processed Bi-CVG materials possess a pronouncedly smaller grain size (~1.2 μm), as compared with the cs-processed samples (4–16 μm). Small grain size was observe to hinder pronouncedly the low frequency magnetization process (⩽tens of MHz), resulting in a large coercive field (Hc) and a smaller initial permeability (μ_i), but insignificantly degrades their microwave magnetic properties, the resonance line width (ΔH), for the samples.

Acknowledgements

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References

1. Warin, D., Mage, J. C. and Simonet, W., Ferrimagnetic relaxation in YIG versus frequency and temperature. *IEEE Trans. Magn., Mag*., 1984, **20**, 1216–1218.
2. Patton, C. E., Effect of grain size on the microwave properties of polycrystalline Yttrium Iron garnet. *J. Appl. Phys*., 1970, **41**, 1637–1641.
3. Dionne, G. F., Effect of porosity on the ferrimagnetic resonance linewidth. *Mater. Res. Bull*., 1970, **5**, 939–946.
4. Gokarn, S. G., Palkar, V. R. and Mulatni, M. S., Sub-micro YIG microstructure and ferrimagnetic resonance linewidth. *Mater. Res. Bull*., 1980, **17**, 957–962.
5. Murthy, V. R. K., Sundaram, S. and Viswanathan, B., *Microwave Materials*. Narosa Publishing House, 1994 164–199.
6. Hudson, A. S., Molecular engineering in the design of microwave ferrimagnetic garnets. *J. Phys. D: Applied Physics*, 1970, **3**, 251–268.
7. Geller, S., Espinosa, G. P., Williams, H. J., Sherwood, R. C. and Nesbitt, E. A., Ferrimagnetic garnets containing Pentavalent Vanadium. *Appl. Phys. Lett*., 1964, **35**, 570–572.
8. Hodges, L. R. Jr, Rodrigue, G. P., Harrison, G. R. and Sanders, A. D., Magnetic and microwave properties of calcium vanadium-substituted garnets. *J. Appl. Phys*., 1966, **37**, 1085–1086.
9. Tsay, C. Y., Liu, C. Y., Liu, K. S., Lin, I. N., Hu, L. J. and Yeh, T. S., Low temperature sintering of microwave magnetic garnet materials. *J. Magn. Magn. Mater*., 2002, **239**, 490–494.
10. Popma, T. J. A., Van Diepen, A. M. and Bongers, P. E., Magnetic properties of the garnets $Bi_{0.8}Ca_{2x}Y_{2.2\text{-}2x}Fe_{5\text{-}x}V_xO_{12}$. *J. Phys. Chem. Solids*, 1974, **35**, 201–205.
11. Krage, M. K., Microwave sintering of ferrites. *Ceramic Bulletin*, 1981, **60**, 1232–1234.
12. Sutton, W. H., Microwave processing of ceramic materials. *Ceramic Bulletin*, 1998, **68**, 376–386.
13. Oakada, F., Tashiro, S. and Suzuki, M., Microwave sintering of ferrites, ICF4. *Advances in Ceramic*, 1984, **15–16**, 205–210.
14. Chang, H. Y., Chen, H. W., Hu, C. T. and Lin, I. N., High Tc PTCR $(Pb_{0.6}Sr_{0.3}Ba_{0.1})TiO_3$ materials prepared by microwave sintering. *Ferroelectrics*, 1997, **195**, 65–68.