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Microwave absorption properties of substituted $BaFe_{12}O_{19}/TiO_2$ nanocomposite multilayer film

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Abstract The nanocomposite multilayer film (NCMF) of substituted $BaFe_{12}O_{19}$ and TiO_2 was prepared using sol-gel method. $BaFe_{10.5}Al_{1.5}O_{19}$, $BaFe_{10.1}Al_{1.9}O_{19}$ and $BaFe_{11.4}Cr_{0.6}O_{19}$ with different absorption frequencies were selected to fabricate the multilayer film with TiO_2. The morphology, crystalline structure and microwave absorption property of the NCMF were investigated with an atomic force microscopy, X-ray diffraction and vector network analyses. The results show that the NCMF is uniform without microcracks and it is an ideal microwave attenuation material with a broad frequency range. Its maximum loss efficiency is about –40 dB. The frequency range with the loss above –10 dB is more than 7 GHz. The multilayer film assembles the achievements of each layer film. Moreover, the compounding of ferrites with TiO_2 is helpful to absorb more microwave energy. TiO_2 particles block the growth of ferrite grains and make most of their size within nanometers. TiO_2 also improves the dielectric loss efficiency of the NCMF.

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Introduction

Electromagnetic interference (EMI) has become a specific type of environmental pollution, due to the rapid growth in utilization of electrical and electronic devices in industrial, commercial and military applications. Electromagnetic attenuation materials have been commonly used to minimize EMI. M-type barium ferrite is an ideal material for the development of electromagnetic attenuation at microwave band, due to the high saturation magnetization, large anisotropy field, excellent chemical stability and high microwave magnetic loss [1–3]. In order to improve the magnetic and electromagnetic absorption properties of ferrites, some Fe^{3+} ions have been substituted with Co–Ti, Zn–Ti, Zn–Sn, Co–Sn, Ni–Zr and Co–Mo [4–9]. In another way, ferrites have been compounded with nonmagnetic materials such as SiO_2, Bi_2O_3 and Al_2O_3 [10–15]. In our previous work, the microwave absorption properties of a series of barium ferrites substituted with Al^{3+} and Cr^{3+} were studied [16]. We found that the locations of absorption peaks for the barium ferrites change regularly with the amount of substitution ions. We also compounded $BaFe_{12}O_{19}$ with TiO_2 when preparing the film, which not only eliminates the microcracks in film, but also improves its microwave absorption property. Based on these results, we suggested in this paper a method to broaden the absorption range of a film with different layers. $BaFe_{10.5}Al_{1.5}O_{19}$, $BaFe_{10.1}Al_{1.9}O_{19}$ and $BaFe_{11.4}Cr_{0.6}O_{19}$, having absorption peaks at different frequencies, are selected with TiO2 to prepare individual layers in the NCMF. In this way the absorption range of the NCMF can be broadened. The morphology, crystalline structure and microwave absorption property of NCMF are studied.

Experimental

The nanocomposite multilayer film was prepared using sol–gel method. The TiO_2 and ferrite sols were synthesized respectively first. The TiO_2 sol was obtained after adding tetrabutyl titanate, diethanolanine and a little of water to the absolute alcohol, with stirring for two hours. According to the composition of $BaFe_{10.5}Al_{1.5}O_{19}$, $BaFe_{10.1}Al_{1.9}O_{19}$ and $BaFe_{11.4}Cr_{0.6}O_{19}$ respectively, stoichiometric amount of barium nitrate, ferric nitrate, aluminum nitrate or chromium nitrate were dissolved in 60°C ethylene glycol with the addition of citric acid. After the ethylene diamine was added to adjust the pH value to 7.0, the ferrites precursor sols were formed. Depending on the weight ratio of ferrite to titanium dioxide for 3:5, three mixed sols were prepared. The mixed sol of $BaFe_{10.1}Al_{1.9}O_{19}$ and TiO_2 was first spin coated onto a quartz glass plate, which had been previously cleaned by deionized water and alcohol. The spin speed was 3,000 rpm and the spin time was 15 s. The composite film was dried at 60 °C for 30 min. Then the above spin process was repeated successively with the other two mixed sols containing $BaFe_{10.5}Al_{1.5}O_{19}$ and $BaFe_{11.4}Cr_{0.6}O_{19}$. Finally, three layer composite films were calcined at 850 °C for one hour.

Surface morphology of the multilayer film was analyzed with atomic force microscopy (AFM), which was performed on the UHV-SPM. The scanning area was 2 ×2 μm. The crystalline structures of multilayer film were determined with X-ray diffraction (XRD) carried out on a Bruker-AXS D8 Advanced diffractometer with Cu K_α radiation in the 2θ range from 10° to 90°, by steps of 0.02°. The microwave absorption property was expressed in microwave loss efficiency. The composite film was scraped off the quartz glass and collected together. The powders were filled into a 30 × 30 × 3 mm polytetrafluoroethylene box and pressed tightly. The transmission and reflection coefficients were measured with microstrip transmission line in 8722ES vector network analyzer in the frequency range from 5 GHz to 15 GHz. The microwave loss

A_{dB} was calculated according to Eq. 1.

$$A_{dB} = 10\log\frac{P_T}{P_I - P_R} \quad (1)$$

where P_T is the transmission wave power; P_I is the incident wave power and P_R is the reflection wave power. The microwave loss of the polytetrafluoroethylene box was subtracted.

Results and discussion

Morphology of multilayer film

The morphology of each layer film was investigated with AFM. The results are displayed in Fig. 1.

The Films have no microcracks and are individually consistent in color. It is known that the titanium dioxide film is achromatous and barium ferrite film is brown. The consistent in color of each layer film shows that the composite film is uniform. With the increase of layer, the color of composite film becomes heavier. The morphology of each layer film is different to others. The one layer film is looked not very even. Some cavities appear in it. The size of cavities changes from 60 to 180 nm. The grains in the one layer film are not homogeneous. The size changes from 30 to 120 nm. Compared with the one layer film, the surface of the two and three layer film is bettered. The cavity is few, and the grains are relative uniform in the two layer film. The size of grains changes from 30 to 60 nm. In the three layer film, some big grains appear, with the maximum size of 240 nm. The substrate and layer number are important factors to affect the growth of films. The first layer film grows on the quartz glass plate. The difference in structure makes the film to grow difficultly. So the defects easily appear and grains are unordered. However, the second layer film grows on the base of the first layer film. The growth conditions are improved for the second layer film. It can grow better under the direction of the first layer film. With the increase of layer number, some grains have chance to grow big in three dimensions. In the three layer film, some grains even grow to 240 nm. Additionally, the TiO_2 and ferrite grains can not be distinguished in the composite film.

Crystalline structure of multilayer film

In the course of preparing substituted $BaFe_{12}O_{19}$ using sol–gel method, the intermediate results including Fe_2O_3, $BaCO_3$ and $BaFe_2O_4$ will appear. If they react heavy with TiO_2 during the formation of multilayer film, the expected magnetic materials, substituted barium ferrites will not form. XRD is used to investigate the crystalline structure of composite film and its pattern is shown in Fig. 2. The composite film is composed of rutile titanium dioxide and M-type hexagonal barium ferrite. The diffraction peaks of Al_2O_3 and Cr_2O_3 are not found on the pattern, which shows that all of Al^{3+} and Cr^{3+} ions have entered the lattice of $BaFe_{12}O_{19}$. It is concluded that the mixed sols

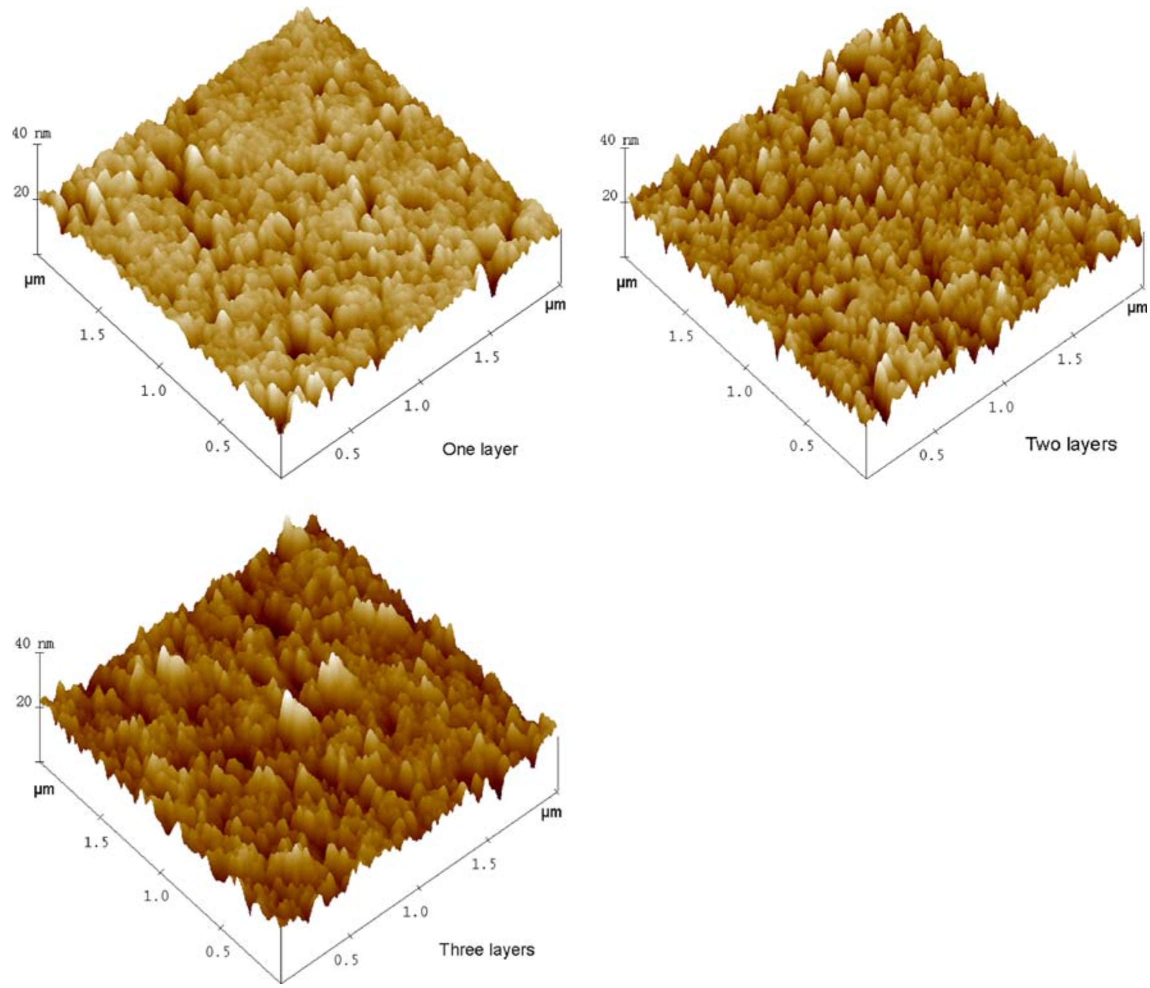

Fig. 1 AFM Photographs of composite multilayer film

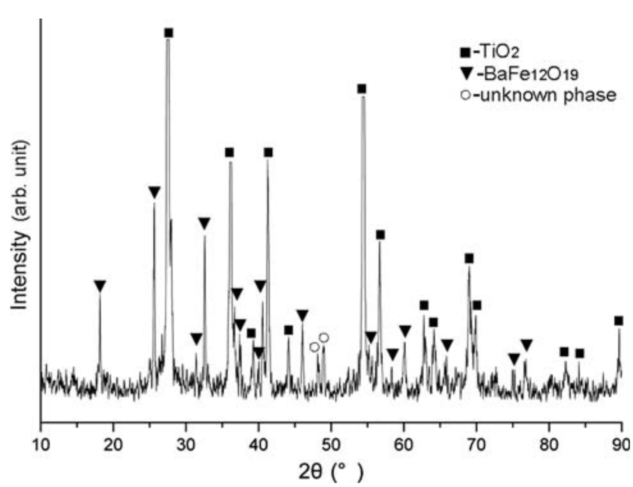

Fig. 2 XRD pattern of composite multilayer film

basically react into the substituted $BaFe_{12}O_{19}$ and TiO_2 during the calcination process. The substituted barium ferrite can be synthesized via titanium dioxide as a matrix using sol–gel method. In addition, there are two unknown weak diffraction peaks on XRD pattern, which can not be recognized by standard cards. Maybe, a little part of Fe, Ti and O elements still reacted into an unstoichiometric compound.

Microwave absorption property of multilayer film

Microwave attenuation materials are required to absorb microwave energy in a broad frequency range. Single material is not easy to realize it. Substituted barium ferrites are selected to prepare composite multilayer film with TiO_2. These films are arranged according to the frequencies of their microwave absorption peaks. The absorption frequencies of $BaFe_{10.1}Al_{1.9}O_{19}$ are the highest, so the composite layer containing $BaFe_{10.1}Al_{1.9}O_{19}$ is treated as the first layer nearby the substrate. The absorption frequencies of $BaFe_{11.4}Cr_{0.6}O_{19}$ are the lowest, and then the composite layer containing it is on the top. The composite layer containing $BaFe_{10.5}Al_{1.5}O_{19}$ is in the middle. This arrangement can make more microwave energy to enter the multilayer film and to be absorbed. The microwave loss spectrum of composite multilayer film is shown in Fig. 3. The microwave loss spectra of $BaFe_{10.1}Al_{1.9}O_{19}$, $BaFe_{10.5}Al_{1.5}O_{19}$ and $BaFe_{11.4}Cr_{0.6}O_{19}$ powders are simultaneously displayed as a comparison.

The microwave absorption property of the composite multilayer film is excellent. The largest loss efficiency is close to –40 dB. The frequency range with the loss above –10 dB is more than 7 GHz. It is an ideal microwave absorption material. Because of the variable absorption frequency, each layer film can absorb microwave energy in different frequency band. The multilayer film assembles the achievements of each layer. Moreover, the compounding of ferrites with TiO_2 is helpful for the microwave absorption. Barium ferrite is a magnetic material, and TiO_2 is a nonmagnetic material. After they are compounded together, electromagnetic properties of magnetic material can be changed. It is known that almost all of ferrites have little dielectric loss. Now the compounding with TiO_2 can improve the dielectric losses of substituted barium ferrites. Additionally, the size of most grains in multilayer film belongs to nanometer scope, which is attributed to the surround of TiO_2 particles. The ferrite grains with single magnetic domain structure can not grow big and convert into multi-domain structure, due to the block of TiO_2 particles, which also increase the microwave absorbing.

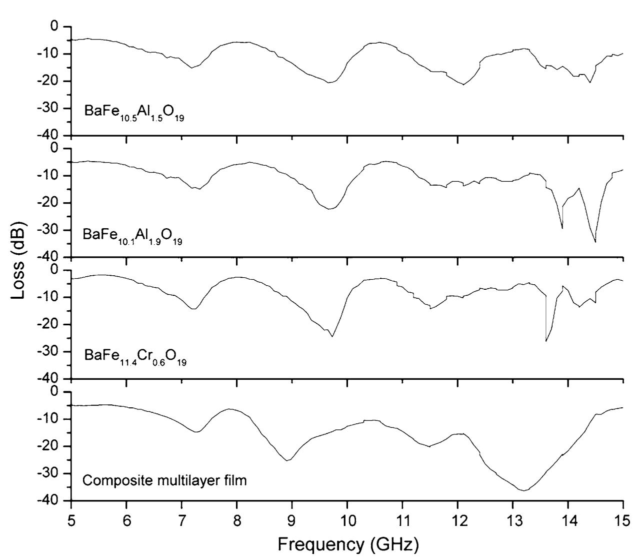

Fig. 3 Microwave loss spectra of composite multiplayer film and substituted $BaFe_{12}O_{19}$

Conclusions

The nanocomposite multilayer film composed of substituted $BaFe_{12}O_{19}$ and TiO_2 was prepared using sol–gel method. The multilayer film is arranged according to the frequencies of microwave absorption peaks for each layer film. The composite film with the highest absorption frequency is on the bottom. This arrangement makes more microwave energy to enter the multilayer film and to be absorbed. The microwave absorption property of composite multilayer film is excellent. The maximum loss efficiency almost reaches –40 dB. The frequency range with the loss above –10 dB is more than 7 GHz. It is much broader than those of substituted barium ferrites powders. The composite multilayer film is relatively uniform and even. Most grains belong to nanometer scope. The compounding with TiO_2 and the nanometer effect also result in the improvement of microwave absorption property of the multilayer film.

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References

1. Li ZW, Chen L, Ong CK (2002) J Appl Phys 92:3902
2. Kim YJ, Kim SS (2002) IEEE Trans Magn 38:3108
3. Kwon HJ, Shin JY, Oh JH (1994) J Appl Phys 75:6109
4. Kubo O, Ogawa E (1994) J Magn Magn Mater 134:376
5. Agresti DG, Shelfer TD, Hong YK (1989) IEEE Trans Magn 25:4069
6. Zhou XZ, Morrish AM, Yang Z (1994) J Appl Phys 75:5556
7. Wang CS, Wei FL, Lu M (1998) J Magn Magn Mater 183:241
8. Hong YK, Jung HS (1999) J Appl Phys 85:549
9. Rane MV, Bahadur D, Kulkarni SD (1999) J Magn Magn Mater 195:L256
10. Abe M, Kuroda J, Matsumoto M (2002) J Appl Phys 91:373
11. Nakamura T, Hankui E (2003) J Magn Magn Mater 257:158
12. He XH, Zhang QQ, Ling ZY (2003) Mater Lett 57:3031
13. Wu YP, Li ZW, Chen LF, Wang SJ, Ong CK (2004) sJ Appl Phys 95:4235
14. Mekala SR, Ding J (2000) Alloy Compd 296:152
15. Zhang HG, Zhou J, Wang YL, Li LT, Yue ZX, Gui ZL (2002) IEEE Trans Magn 38:1797
16. Qiu JX, Gu MY, Shen HG (2005) J Magn Magn Mater 295:263