Journal of Alloys and Compounds 506 (2010) 347–350

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A new microwave absorber based on antimony-doped tin oxide and ferrite composite with excellent electromagnetic match

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 17 June 2010
Accepted 22 June 2010
Available online 13 July 2010

Keywords:
Permanent magnets
Composite materials
Complex permittivity
Complex permeability
Microwave absorber

ABSTRACT

Antimony-doped tin oxide ($Sn_{0.9}Sb_{0.1}O_2$, ATO) and W-type barium ferrite ($Ba_{0.9}Gd_{0.1}(Zn_{0.3}Co_{0.7})_2Fe_{16}O_{27}$) were synthesized by coprecipitation method and polymer adsorbent combustion method, respectively. The microstructures were studied using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the pure ATO with spherical morphology and the pure W-type barium ferrite with hexagonal flake shape were prepared. The complex permittivity and complex permeability of ATO, ferrite and ATO/ferrite composites were analyzed by Agilent 8722ET. It was indicated that ATO had strong dielectric property and ferrite showed superior magnetic performance. An appropriate electromagnetic match was established when the composite microwave absorber contained 50 wt% ATO and 50 wt% ferrite. For the optimized microwave absorber, the maximum reflection loss (RL) was about −19.4 dB at 14.8 GHz. Moreover, the absorption bandwidth reached 3.6 GHz when RL was −10 dB in the measured frequency range of Ku-band.

1. Introduction

With the rapid development of electric and electronic devices, electromagnetic pollution is becoming a serious problem. As a result, considerable interests have been attracted on microwave absorbers [1–4]. For the W-type barium ferrites, they are suitable for electromagnetic interference suppression and radar absorbent material (RAM) due to their strong magnetic losses at gigahertz frequency [5–7]. However, single conventional ferrite is hardly to satisfy the appropriate electromagnetic match which is essential for strong absorption behavior in wide frequency range. In recent years, a number of investigations have been well documented on the composite microwave absorbing materials based on ferrite [8–11]. For examples, carbon nanotube is compounded with ferrite due to its high complex permittivity [12], and polyaniline is compounded with ferrite because of its controllable resistivity [13]. It is well known that antimony-doped tin oxide (ATO) has low resistivity which may be useful to adjust the resistivity of ATO-based composites [14]. The electron hopping between Sb^{5+} and Sb^{3+} ions is expected to enhance the complex permittivity. To our knowledge, few studies have been focused on the microwave absorbing properties of ATO/ferrite composites.

In this work, the pure ATO, W-type barium ferrite and their composites were prepared to be used as microwave absorbers. In order to design better electromagnetic matching absorber, we investigated the effects of ATO/ferrite ratios on the resistivity and microwave electromagnetic properties. The capability and mechanism of microwave absorption were also discussed.

2. Experimental

2.1. Materials preparation

2.1.1. The preparation of antimony-doped tin oxide

Antimony-doped tin oxide ($Sn_{0.9}Sb_{0.1}O_2$, ATO) was synthesized by coprecipitation method. The calculated necessary amounts of $SnCl_4{\cdot}5H_2O$ and $SbCl_3$ were first dissolved in 2 mol·L^{-1} HCl solution. Then, $NH_3{\cdot}H_2O$ was added dropwise in the mixture solution until the pH of the solution reached 2.2 under vigorous stirring at 70 °C. The precipitate was collected by suction filtration method and washed with water and ethanol twice, respectively. The obtained precursor was dried at 80 °C for 5 h. Finally, the precursor was calcined at 800 °C for 3 h to prepare the ATO particles.

2.1.2. The preparation of barium ferrite

The W-type barium ferrite ($Ba_{0.9}Gd_{0.1}(Zn_{0.3}Co_{0.7})_2Fe_{16}O_{27}$) was synthesized by polymer adsorbent combustion method. A stoichiometric mixture solution was prepared by dissolving $Ba(NO_3)_2$, $Zn(NO_3)_2$, $Co(NO_3)_2$, $Gd(NO_3)_3$, $Fe(NO_3)_3$ and citric acid in deionized water. The mole ratio of total metal ions to citric acid was 1:1. Absorbent cotton was used as the polymer adsorbent to adsorb the mixture solution. The absorbent cotton/solution composites were then pretreated to combustion at 250 °C, and the dry precursor was obtained. Finally, the precursor was calcined at

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0925-8388/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.06.205

Table 1
Samples of microwave absorbers with different ratios of ATO to ferrite.

Samples	A	B	C	D	E
ATO (wt%)	0	20	50	80	100
Ferrite (wt%)	100	80	50	20	0

1250 °C for 5 h to make the ferrite powders. Compared with normal sol–gel method [15], the present method eliminated the process of evaporating solution to prepare the gel during the preparation of dry precursor.

2.1.3. The preparation of composite microwave absorbers

The composite microwave absorbers were prepared by uniformly mixing the synthesized ATO and ferrite in a two-roll mixing mill for 1–2 h. Table 1 lists the five samples of microwave absorbers with different ratios of ATO to ferrite.

2.2. Measurement

The X-ray diffraction (XRD) was carried out with an ARL X-ray powder diffractometer using Cu Kα radiation. Nature surfaces of ATO and ferrite were observed employing scanning electron microscopy (SEM, HITACHI S-4800 and JEOL JSM-5900). The electrical resistivity of composite microwave absorbers was determined using the two-probe technique. Network analyzer (Agilent 8722ET) was employed to measure the electromagnetic parameters (ε', ε'', μ', μ'') in the frequency range of Ku-band. The specimens were prepared by uniformly mixing 70 wt% composite absorbers with 30 wt% paraffin. Then these mixtures were pressed in a cylindrical mould (7.00 mm in outer diameter, 3.04 mm in inner diameter and 4.50–5.00 mm in thickness). The measured values of reflected and transmitted scattering parameters (S_{11}, S_{21}) were used to determine ε', ε'', μ', and μ'', [16]. Reflection loss of composite absorbers was measured by the software of YRCompute.

3. Results and discussion

3.1. Microstructure identification

Fig. 1 shows XRD patterns of the prepared ATO and ferrite, and it is confirmed that pure ATO and W-type barium ferrite are synthesized. Fig. 2 displays the SEM images of the prepared ATO and ferrite. It is indicated from Fig. 2(a) that ATO particles show the spherical morphology and the particle size is around 25 nm. Furthermore, it can be found from Fig. 2(b) that the prepared ferrite shows a hexagonal flake shape, which is beneficial for microwave absorption [15]. The average size of the ferrite flake is about 5 μm, and the thickness of the flake is about 1 μm.

3.2. Controllable resistivity of composites

To prepare an ideal microwave absorber in the desired frequency range, two fundamental conditions should be satisfied [17]. The first is that the incident wave can enter the absorber as much as possible, and the second is that the electromagnetic wave entering into the materials can be mostly attenuated. Thus, resistivity is an important factor due to the skin effect of absorbers. As shown in Fig. 3, the resistivity of ATO/ferrite composites varies inversely with

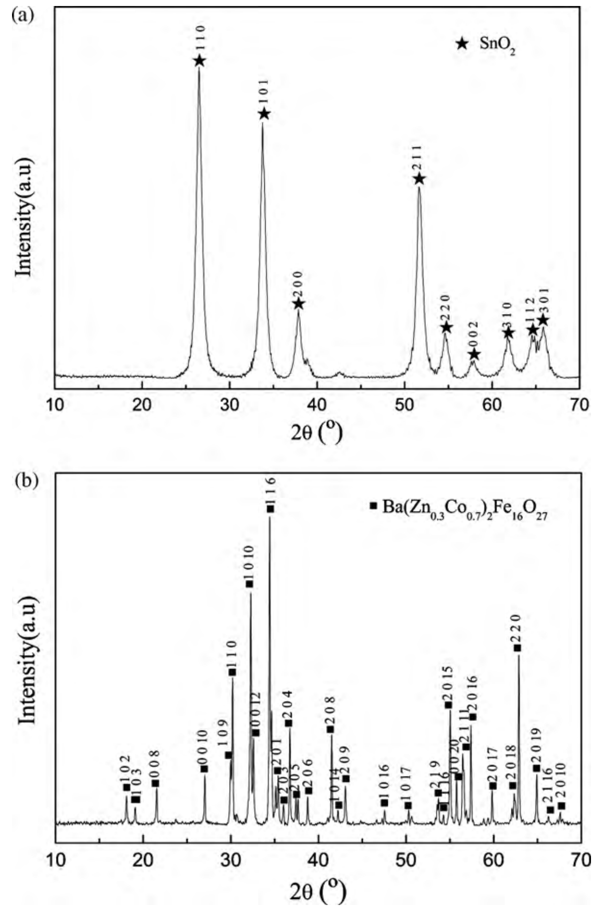

Fig. 1. XRD patterns of (a) antimony-doped tin oxide and (b) barium ferrite.

the content of ATO. Resistivity of sample A (pure ferrite) is about 10^7 Ω cm, but resistivity of sample E (pure ATO) decreases to about 10 Ω cm. As a result, electromagnetic wave can easily enter the ferrite but hardly access to the inner of ATO because of the skin effect. Therefore, electromagnetic wave can scatter and reflect repeatedly between interfaces of ferrite and ATO in sample C [18].

3.3. The relative complex permeability and permittivity

Electromagnetic properties of microwave absorber are usually characterized by complex permittivity ε (ε', ε'') and complex permeability μ (μ', μ''), which can be served to optimize the absorption of the incident wave [19]. The real (ε') and imaginary (ε'') parts of the complex permittivity spectra of microwave absorbers (sam-

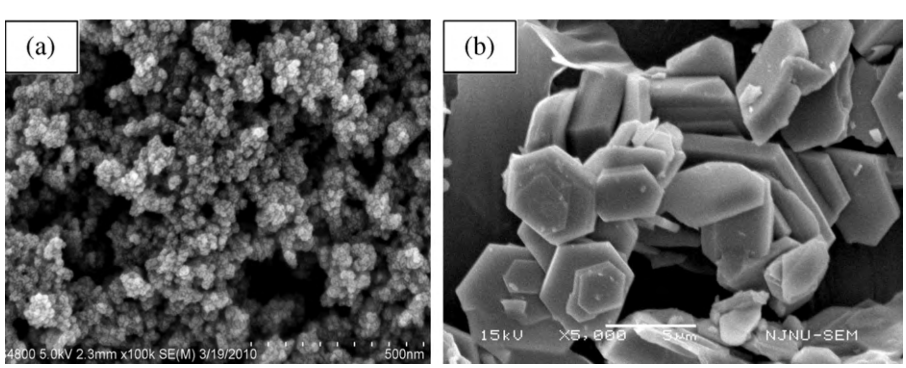

Fig. 2. SEM images of (a) antimony-doped tin oxide and (b) barium ferrite.

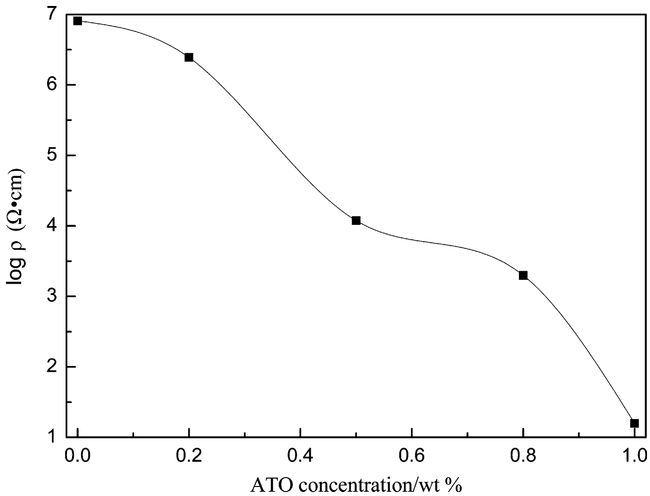

Fig. 3. Compositional variation of resistivity of ATO/ferrite composites.

ples A–E) are illustrated in Fig. 4. For samples A and B, ε' and ε'', are almost constant within the entire frequency range, and ε'', is about 0.4 as the ferrite is a magnetic loss material and its complex permittivity is low. By increasing the content of ATO in the ATO/ferrite composites (samples C–E), both ε' and ε'', significantly increase in the measurement frequency range due to the interfacial

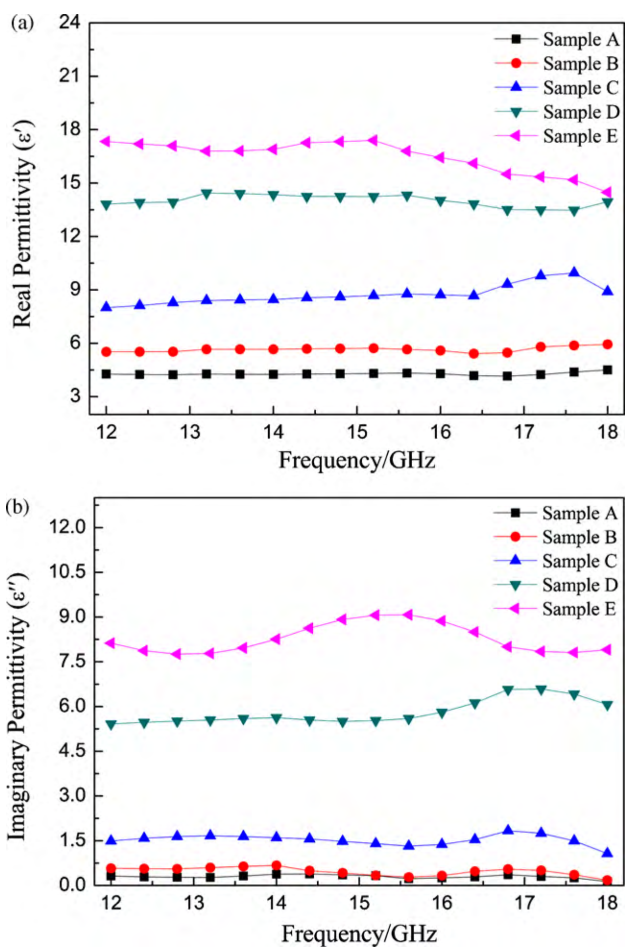

Fig. 4. Complex permittivity measurements of samples A–E, (a) real part of permittivity and (b) imaginary part of permittivity.

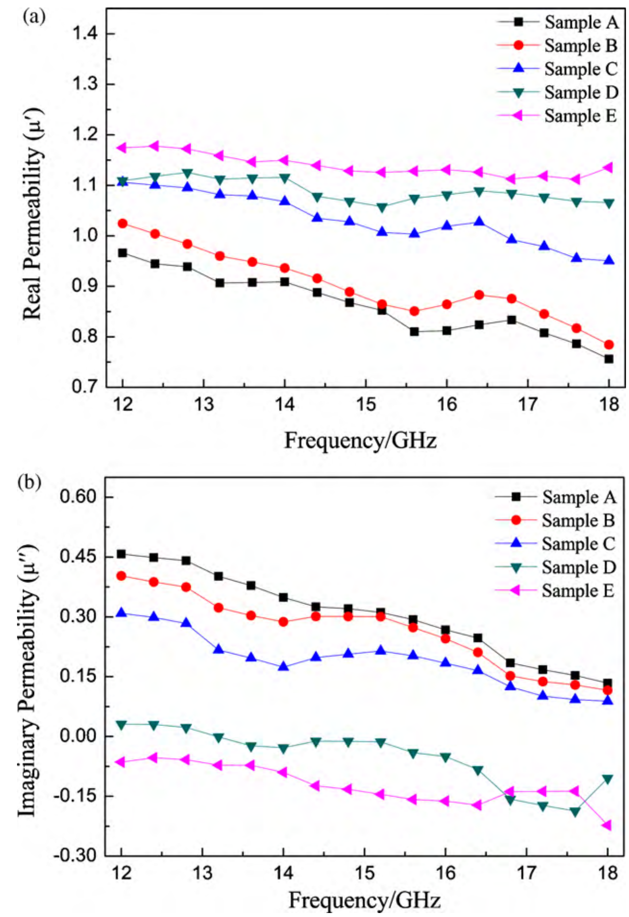

Fig. 5. Complex permeability measurements of samples A–E, (a) real part of permeability and (b) imaginary part of permeability.

polarization and intrinsic electric dipole polarization. The interfacial polarization absorption comes from the interaction of the electromagnetic wave with multipoles at the interfaces between different absorbents [12]. In the present composite absorbers, interfaces between ATO and ferrite are beneficial to the interfacial polarization absorption. The mechanism of intrinsic electric dipole polarization is strongly correlated with hopping electrons due to the replacement of ions with different valences [20]. The substitution of Sb^{5+} for Sn^{4+} leads to a change of Sb^{5+} to Sb^{3+} in order to balance the electrical valence [21,22]. This replacement directly affects the hopping process ($Sb^{3+} \Leftrightarrow Sb^{5+} + 2e$), which results in the polarization, causing the high values of ε' and ε'', [5,23].

Fig. 5 displays the frequency dependence of the complex permeability μ (μ', μ'') of different samples. As shown in Fig. 5(a), μ' rises with increasing the content of ATO in the composites and the value fluctuates between 0.7 and 1.2 in the measured frequency range. It is indicated in Fig. 5(b) that μ'' increases with the increasing content of ferrite. According to the equation of $\mu'' = M_s/(2H_A\alpha)$ (where M_s, H_A and α are magnetization, anisotropy field and extinction coefficient, respectively), complex permeability μ'' is in direct proportion to M_s. In the case of W-type barium ferrite, the electromagnetic properties of ferrite depend on the distribution of basic metal ions. Unpaired 3d electrons of Fe^{3+} and unpaired 4f electrons of Gd^{3+} can afford 5 μ_B and 8 μ_B (spin magnetic moment), respectively, causing the large M_s of the ferrite. Therefore, ferrite has high value of μ'' and the magnetic properties of ATO/ferrite composites can be improved by increasing the ratio of ferrite.

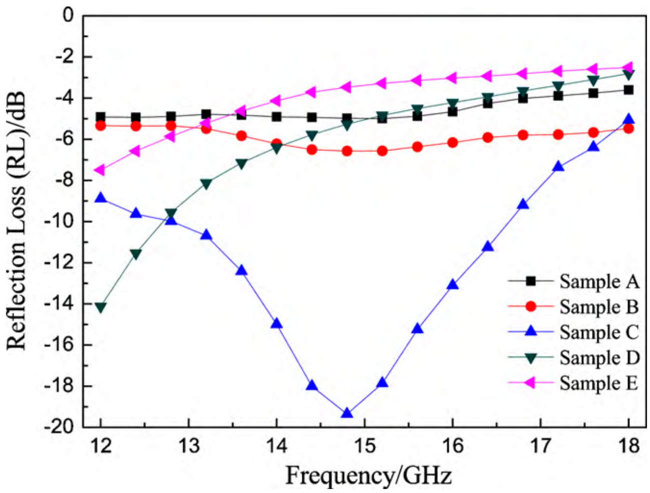

Fig. 6. The microwave absorption curves of samples A–E.

3.4. Microwave absorbing properties

From the above microwave magnetic parameters, samples A and B exhibit high value of μ'' but low value of ε''. In the other hand, samples D and E obtain high value of ε'', but low value of μ''. The dependence could facilitate the control of reflection behavior according to the formula [24]:

$$RL = 20\ \log\left|\frac{1-\sqrt{\mu_r/\varepsilon_r}\tanh(-j2\pi f_0 d\sqrt{\varepsilon_r\mu_r}}{1+\sqrt{\mu_r/\varepsilon_r}\ \tanh(-j2\pi f_0 d\sqrt{\varepsilon_r\mu_r}}\right| \quad (1)$$

where ε_r, μ_r, f_0, and d are the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$), the complex permeability ($\mu_r = \mu' - j\mu''$), frequency and the absorber thickness, respectively. The reflection loss (RL) of absorber is measured by the software of YRCompute. The microwave absorption curves for the single-layer coating of all the samples at thickness d = 1.6 mm are summarized in Fig. 6. It is found that RL of sample A (pure ferrite) and sample E (pure ATO) are rather low within the entire frequency range, and the peak values are −5.0 dB at 15.2 GHz and −7.5 dB at 12 GHz, respectively. However, microwave absorption is evidently improved by compounding 50 wt% ATO and 50 wt% ferrite (sample C). The peak value increases to −19.4 dB at 14.8 GHz, and RL reaches −10 dB in the frequency range of 12.8–16.4 GHz.

It is well known that perfect matching between magnetic loss and dielectric loss brings excellent microwave absorption [25]. For the optimized sample C, the improvement in RL properties originates from the balance of ferromagnetic resonance loss and dielectric loss. Ferromagnetic resonance loss is caused by the combination of electromagnetic wave and spin magnetic moments of ferrite. Dielectric loss is partly due to the orientation polarization of intrinsic electric dipole of ATO. Furthermore, dielectric loss is also contributed by the interfacial polarization absorption.

4. Conclusions

(1) Antimony-doped tin oxide (ATO) and barium ferrite were synthesized successfully via coprecipitation method and polymer adsorbent combustion method, respectively. Besides, the composite microwave absorbers were obtained by uniformly mixing the prepared ATO and barium ferrite with different ratios.
(2) Resistivity of ATO/ferrite composites was modified significantly by tuning the ratios of ATO to ferrite. Electromagnetic wave could scatter and reflect repeatedly between interfaces of ferrite and ATO because of the skin effect.
(3) ATO showed strong dielectric properties and ferrite exhibited excellent magnetic properties. The complex permittivity of ATO/ferrite composites could be improved by increasing the ratio of ATO. Moreover, the complex permeability μ'' could be enhanced by increasing the content of ferrite.
(4) The combination of the dielectric loss and magnetic loss was established when the composite absorber contained 50 wt% ATO and 50 wt% ferrite. The reflection loss (RL) reached −10 dB in the frequency range of 12.8–16.4 GHz and the maximum RL was about −19.4 dB at 14.8 GHz. The ATO/ferrite composites can be attractive for being utilized as a new microwave absorber.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from the National Defense Fundamental Research of China (6134502-1), Mr. Yu and Miss Zhu of Institute 53 of China's Ordnance Industry for providing the software of YRCompute.

References

[1] D.L. Zhao, F. Luo, W.C. Zhou, J. Alloys Compd. 490 (2010) 190.
[2] Y. Yang, C.L. Xu, Y.X. Xia, et al., J. Alloys Compd. 493 (2010) 549.
[3] T.C. Zou, H.P. Li, N.Q. Zhao, et al., J. Alloys Compd. 496 (2010) L22.
[4] F. Tabatabaie, M.H. Fathi, A. Saatchi, et al., J. Alloys Compd. 470 (2009) 332.
[5] L.X. Wang, J. Song, Q.T. Zhang, et al., J. Alloys Compd. 481 (2009) 863.
[6] J. Wang, H. Zhang, S.X. Bai, et al., J. Magn. Magn. Mater. 312 (2007) 310.
[7] J.J. Xu, H.F. Zou, H.Y. Li, et al., J. Alloys Compd. 490 (2010) 552.
[8] A. Ghasemi, X. Liu, A. Morisako, IEEE Trans. Magn. 45 (2009) 4420.
[9] S.B. Ni, X.H. Wang, G. Zhou, et al., J. Alloys Compd. 489 (2010) 252.
[10] C.C. Yang, Y.J. Gung, W.C. Hung, et al., Compos. Sci. Technol. 70 (2010) 466.
[11] L.G. Yan, J.B. Wang, Y.Z. Ye, et al., J. Alloys Compd. 487 (2009) 708.
[12] X.C. Gui, W. Ye, J.Q. Wei, et al., J. Phys. D: Appl. Phys. 42 (2009) 075002.
[13] X. Tang, Y.G. Yang, Appl. Surf. Sci. 255 (2009) 9382.
[14] X.L. Chen, C.Z. Li, W. Shao, et al., J. Appl. Polym. Sci. 105 (2007) 2783.
[15] L.X. Wang, Q.T. Zhang, J. Alloys Compd. 469 (2009) 251.
[16] E.J. Vanzura, J.R. Baker-Jarvis, J.H. Grosvenor, et al., IEEE. Trans. Microw. Theory Tech. 42 (1994) 2063.
[17] M. Wang, Y.P. Duan, S.H. Liu, et al., J. Magn. Magn. Mater. 321 (2009) 3442.
[18] C.H. Peng, H.W. Wang, S.W. Kan, et al., J. Magn. Magn. Mater. 284 (2004) 113.
[19] L.Y. Xing, Stealth Materials, Chemical Industry Press, Beijing, 2004.
[20] S.B. Liao, Ferromagnetism, Scientific Press, Beijing, 1988.
[21] Y.Q. Li, J.L. Wang, S.Y. Fu, et al., Mater. Res. Bull. 45 (2010) 677.
[22] T. Krishnakumar, R. Jayaprakash, N. Pinna, et al., J. Phys. Chem. Solids 70 (2009) 993.
[23] M.C. Dimri, S.C. Kashyap, D.C. Dube, Ceram. Int. 30 (2004) 1623.
[24] G.Z. Shen, M. Xu, Z. Xu, J. Magn. Magn. Mater. 105 (2007) 271.
[25] Y.L. Cheng, J.M. Dai, D.J. Wu, et al., J. Magn. Magn. Mater. 322 (2010) 97.