Temperature-frequency dependence and mechanism of dielectric properties for γ-$Y_2Si_2O_7$*

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This paper reports that single-phase γ-$Y_2Si_2O_7$ is prepared via a sufficient blending and cold-pressed sintering technique from Y_2O_3 powder and SiO_2 nanopowder. It studies the dielectric properties of γ-$Y_2Si_2O_7$ as a function of the temperature and frequency. The γ-$Y_2Si_2O_7$ exhibits low dielectric loss and non-Debye relaxation behaviour from 25 to 1400 °C in the range of 7.3–18 GHz. The mechanism for polarization relaxation of the as-prepared γ-$Y_2Si_2O_7$ differing from that of SiO_2 is explained. Such particular dielectric properties could potentially make specific attraction for extensive practical applications.

Keywords: γ-$Y_2Si_2O_7$, dielectric properties, structural relaxation polarization, low dielectric loss
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1. Introduction

The rare earth disilicates have attracted wide interest from plenty of groups for their magnetic, electrical, and optical properties. These materials display appropriate behaviours that allow them to be used in thermal and luminescent applications, such as plasma displays, laser materials and high-energy phosphors.[1−4] The $Y_2Si_2O_7$ occurs naturally as yttrialite; it is one of the most refractory silicates with a melting point of 1775 °C and is thus potentially useful as a high-temperature structural ceramic.[5,6] In particular, γ-$Y_2Si_2O_7$ is the one high-temperature phase of six polymorphs (y, α, β, γ, δ, and z),[7] which is considered as a precipitated intergranular phase in the grain boundary of Si_3N_4 when Y_2O_3 is used as a sintering aid. Investigations have shown that such a crystallized intergranular phase with chemical composition of $Y_2Si_2O_7$ enhances the high-temperature mechanical properties of Si_3N_4, and $Y_2Si_2O_7$ can dominate the mechanical and dielectric properties of Si_3N_4.[8−11] Meanwhile, regarded as a specific silicate ceramic for damage tolerance and good machinability, γ-$Y_2Si_2O_7$ can be used in severe environments with corrosive media or fast cooling–heating owning to its good erosion resistance, low thermal expansion coefficient and low thermal conductivity, which extends its applications.[12−14] Recently, great attention has been paid to the dielectric properties of materials,[15−23] and the exploration of high-temperature dielectric properties has been extensively developed in Si_3N_4, BN, Cr_2O_3, and MnO_2 nanorods etc.[24−30] Unfortunately, few reports on the high-temperature dielectric properties of γ-$Y_2Si_2O_7$, which might be considered as a potential candidate for antenna window materials due to its extraordinary high-temperature properties, have appeared in the literature to date.

In this paper, investigations were carried out on the preparation, structure and dielectric properties of γ-$Y_2Si_2O_7$. Focusing mainly on the temperature and frequency dependence of the dielectric response in the range of 7.3–18 GHz at temperatures from 25 to 1400 °C, we have analysed the mechanism of dielectric relaxation observed in this crystal.

2. Experiment

The samples of $Y_2Si_2O_7$ were synthesized from a mixture of Y_2O_3 powder and SiO_2 xerogel nanopow-

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der by the conventional solid-state ceramic route without sintering additives. The SiO_2 xerogel nanopowder was produced by the sol-gel method. In brief, according to the nominal composition of $Y_2Si_2O_7$, both raw materials were mixed in an ethanol solution in a planetary ball mill with a rotation speed of 400 rpm. Polyvinyl butyral (PVB) was added (2 wt%) as a milling agent to prevent severe agglomeration. After ball milling for 12 h, the slurry was dried, and the dried powder was crushed and sieved (150 μm). The fine powder was then compacted into discs 65 mm in diameter and 4 mm in thickness under a pressure of 250 MPa. The green compacts were heated at a heating rate of 7 °C min^{-1} up to the sintering temperature. An intermediate soaking at 500 °C for 2 h was used to expel the PVB. The sintering temperature of the samples was in the range of 1300–1400 °C for 6 h.

The phase purity of the samples was investigated by powder x-ray diffraction (XRD) using a PHILIPS X' Pert PRO x-ray diffractometer (Cu Kα). Microstructural observation was carried out by using a JSM-6301F scanning electron microscope (SEM). The dielectric properties of the cylindrical compacts were measured from room temperature to 1400 °C by a vector network analyser (Anritsu 37269D) according to the post resonator method.[31]

3. Results and discussion

Figure 1 shows the XRD patterns of the sintered samples at temperatures between 1300 °C and 1400 °C for 1 h. After sintering at 1300 °C for 1 h, the monoclinic β-$Y_2Si_2O_7$ phase is confirmed. When the sintering temperature is increased to 1350 °C, the monoclinic γ-$Y_2Si_2O_7$ phase appears in the synthesized product, as represented by the strong γ-$Y_2Si_2O_7$(12-1) peak. With a further increase in sintering temperature, it is seen that the γ-$Y_2Si_2O_7$ peak width decreases, which indicates that grains grow due to the sintering at a higher temperature. Moreover, all the diffraction peaks of the sample (sintered at 1400 °C) can be exclusively indexed to a pure monoclinic phase of γ-$Y_2Si_2O_7$ (JCPDS Card, No. 42-0167). No peaks for other phases are observed, which exhibits its high purity and crystallization. The SEM observations on the fracture surfaces confirm that the grain growth is the result of the increase in sintering temperature. Figures 1(a)–1(c) show the SEM images of fractured surfaces of the samples sintered at 1300, 1350 and 1400 °C, respectively. When the sample is sintered at 1300 °C, the average grain size is about 0.4 μm, as shown in Fig. 1(a). After the sample is sintered at 1350 °C, the typical grain size is about 0.6 μm, as shown in Fig. 1(b). The typical grain is about 1–2 μm when the sample is sintered at 1400 °C (Fig. 1(c)). These samples contain many pores residing in the grains or at grain boundaries due to grain growth, which indicates that full density was not achieved.

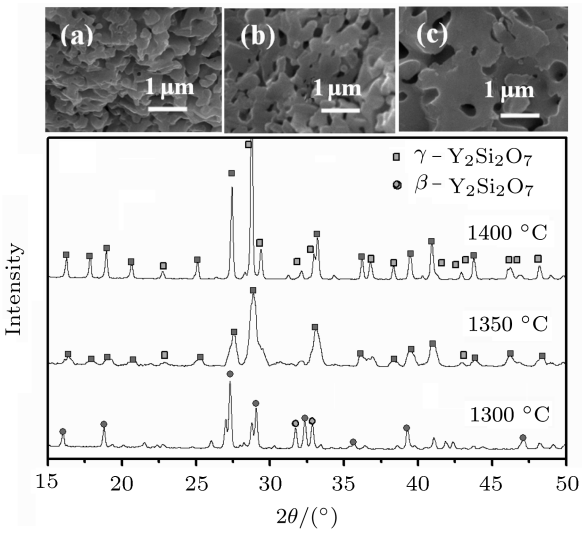

Fig. 1. SEM images of the fracture surface of $Y_2Si_2O_7$ samples sintered at various temperatures: (a) 1300 °C; (b) 1350 °C; (c) 1400 °C. (d) Corresponding XRD patterns.

Figure 2 illustrates the complex permittivity of γ-$Y_2Si_2O_7$ vs. temperature at various frequencies. From Fig. 3(a), the real permittivity (ε') shows the quasi-linear dependence on temperature at all measured frequencies. The real permittivity is found to increase by 17.5 percent at 1400 °C, in comparison with that at room temperature. The increase implies that the complex permittivity presents an enhanced response to increasing temperature. However, γ-$Y_2Si_2O_7$ exhibits a complicated dielectric loss behaviour with increasing temperature, as shown in Fig. 2(b). The imaginary permittivity (ε'') presents a peculiar dielectric relaxation peak at about 800 °C for all measured frequencies, while the change in imaginary permittivity is weak in both the low temperature region (25–400 °C) and the high temperature region (1100–1400 °C). All the values of dielectric loss are less than 0.05 and the dielectric relaxation peaks at three frequencies (7.3, 8.0 and 9.1 GHz) are almost the same, as shown in the inset of Fig. 2(b), which implies that there is not a single relaxation time. However, the peculiar relaxation behaviour observed in γ-$Y_2Si_2O_7$ cannot be found in

SiO_2.[24,25] This indicates that the dielectric relaxation mechanism of γ-$Y_2Si_2O_7$ could be more complicated than any raw material. The dielectric response of γ-$Y_2Si_2O_7$ is a non-Debye relaxation.[32] The polarization relaxation time, which is the inverse of the frequency of maximum dielectric loss, is of the order of magnitude of 10^{-11} s at about 800 °C.

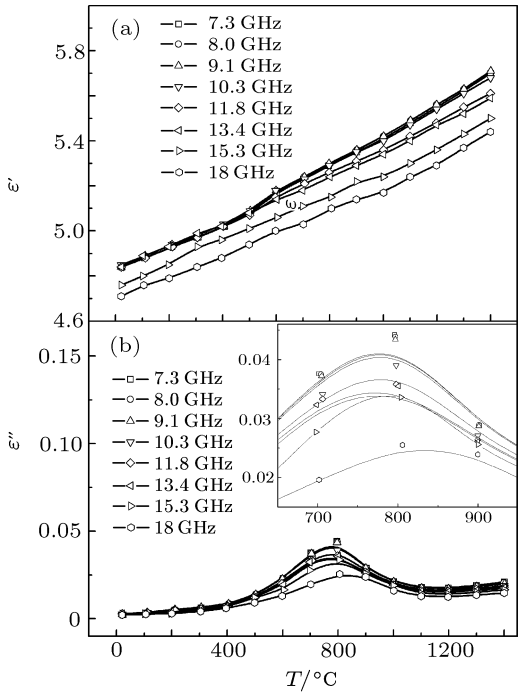

Fig. 2. Temperature dependence of real permittivity (a) and imaginary permittivity (b). The inset is ε''–T at temperature range from 650°C to 950 °C.

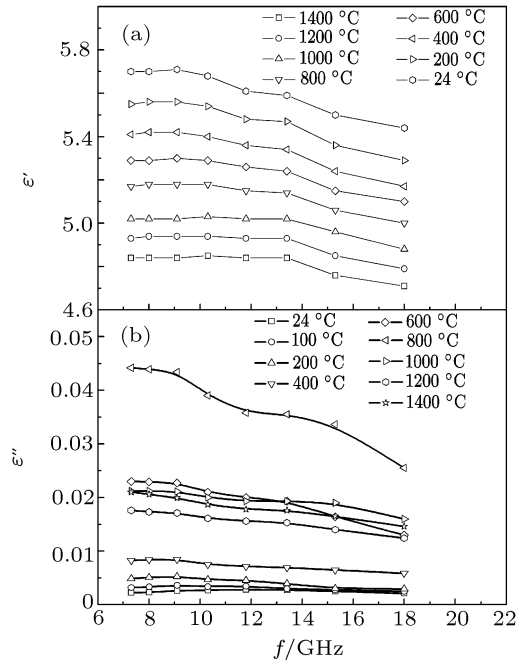

Fig. 3. Frequency dependence of real permittivity (a) and imaginary permittivity (b).

Figure 3 shows the complex permittivity of γ-$Y_2Si_2O_7$ vs. frequency at different temperatures. With increasing frequency, the weak changes of both ε' and ε'' appear in the low temperature region (25–400 °C), while they decrease apparently above 500 °C, as shown in Figs. 3(a) and 3(b), respectively. These decreases imply that the main polarization mechanism at high temperature is different from that at room temperature.

The dielectric loss tangent, a ratio of the imaginary permittivity to real permittivity, is plotted in Fig. 4. It is clear that the loss tangent decreases obviously with increasing frequency. An apparent dielectric loss peak can also be observed at about 800 °C in the investigated frequency range. The loss tangent maximum is 8.3×10^{-3} (less than 10^{-2}) in the temperature range from room temperature to 1400 °C. Consequently, the low dielectric loss of γ-$Y_2Si_2O_7$ may draw much attention for potential applications at high temperature. Based on the above experimental phenomenon, we proposed the temperature-response dielectric relaxation mechanism of γ-$Y_2Si_2O_7$.

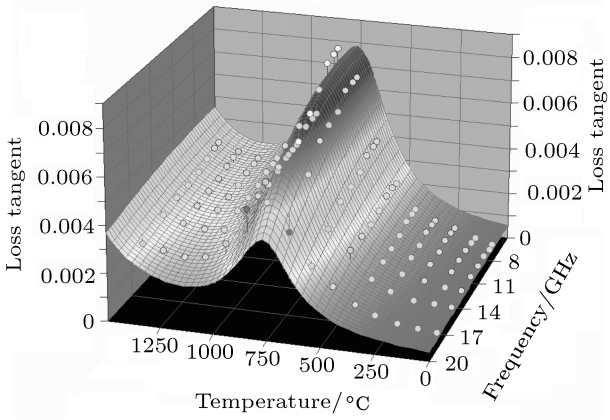

Fig. 4. The 3D curve of the frequency and temperature dependence in the loss tangent.

The crystal structure of γ-$Y_2Si_2O_7$ is a monoclinic lattice with the $P2_1/c$ space group. In γ-$Y_2Si_2O_7$, there are only one Y site, one Si site and four O sites. The Y has six nearest neighbour O ions with bond lengths ranging from 2.250 Å (1 Å=0.1 nm) to 2.328 Å, which forms the YO_6 octahedron, and Si is tetrahedrally bonded to four O atoms with bond lengths ranging from 1.616 to 1.637 Å.[12] Two adjacent SiO_4 tetrahedrons share one O at the corner, which forms the Si_2O_7 pyrosilicate structure with a linear Si–O–Si bridge. The γ-$Y_2Si_2O_7$ can be conveniently described as a framework of YO_6 octahedron and Si_2O_7 pyrosilicate alternately stacked in three

dimensions. The γ-$Y_2Si_2O_7$ contains two types of interatomic bonds: Si–O bonds in the SiO_4 tetrahedron and Y–O bonds in the YO_6 octahedron. Wang *et al.*[33] found that Si–O bonds in Si_2O_7 tetrahedra are much stronger than the Y–O bonds in YO_6 polyhedra, which leads to low shear deformation resistance and good machinability of γ-$Y_2Si_2O_7$. Since the Y–O bonds are much weaker than the Si–O bonds, they are easy to stretch and shrink, and the Y–O bonds become weaker with the increase of temperature, which results in the elongation or break of certain Y–O bonds. Hence, the rigid Si_2O_7 pyrosilicates and Y ions can rotate or move more easily at high temperature. When an electromagnetic wave is incident on the bulk γ-$Y_2Si_2O_7$, the local motion of the thermal-activation atomic groups (rigid Si_2O_7 pyrosilicates and Y ions) could bring structural relaxation polarization. The structural relaxation polarization usually occurs in the weak interfaces. Previous investigations[14] showed that the (100) and (010) planes are weakly bonded atomic planes. These atomic planes are crossed only by weak Y–O bonds and only weak correlations exist between the atoms at each side of these planes, which suggests

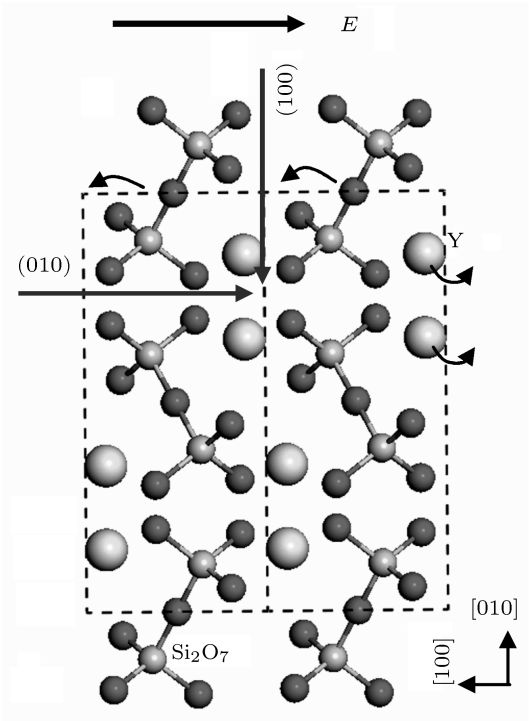

Fig. 5. Schematic illustration of the motions of the atomic group in electric field.

that these are low-energy boundary planes cleavaging, slipping, or twinning easily. When either of both atomic planes is perpendicular to the electric field, the thermal-activation atomic groups might move or rotate easily along with the direction of electric field, as illustrated in Fig. 5. Therefore, the peculiar relaxation loss peak and the strong temperature-dependent permittivity could be attributed to the structural relaxation polarization caused by the local motion of the thermal-activation atomic groups. Simultaneously, it also indicates that no ionic conductance exists in this material. As a consequence, γ-$Y_2Si_2O_7$ may still present low dielectric loss even at higher temperature.

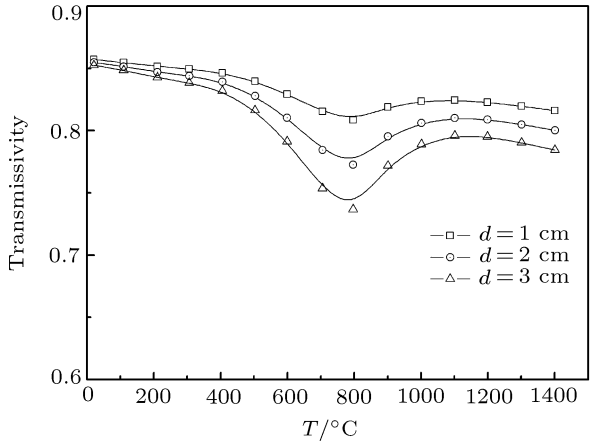

Fig. 6. Transmissivity at different thicknesses (9.1 GHz).

This structural relaxation polarization is different from ionic displacement polarization: the relaxation time of the former is longer than that of the latter since the polarized ion is still restrained nearby the equilibrium site for ionic displacement polarization which is elastic rapid polarization. However, the polarized charge carriers can move over a long distance for structural relaxation polarization. The structural relaxation of γ-$Y_2Si_2O_7$ is mainly attributed to the orientation polarization since it is difficult to break up all Y–O bonds. In this case, the relaxation time can be obtained in the following way:[34]

$$\tau_0 = \frac{4\pi\eta a^3}{kT} \tag{1}$$

where a is the radius of the thermal-activation atomic group, η is the coefficient of viscosity, k is Boltzmann's constant and T is the Kelvin temperature. According to Eq. (1), τ_0 decreases with increasing temperature which produces maximum dielectric loss when the inverse of τ_0 is close to the measured frequency at high temperature. As a result, we can clearly observe a dielectric loss peak at about 800 °C in Fig. 4. On the other hand, there are a lot of thermal-activation atomic groups with different radii (a) owing to the nonuniform defect in γ-$Y_2Si_2O_7$. Hence, τ_0 is not a

single relaxation time according to Eq. (1), which indicates that the dielectric response of γ-$Y_2Si_2O_7$ is a non-Debye relaxation. Consequently, the low relaxation loss peak is attributed to multi-relaxation time in γ-$Y_2Si_2O_7$. According to the complex permittivity of γ-$Y_2Si_2O_7$, the transmissivities at 9.1 GHz with different thicknesses are calculated by electromagnetic field theory,[35] as shown in Fig. 6. Obviously, γ-$Y_2Si_2O_7$ is a low-loss dielectric material and its transmissivities at all investigated temperatures are higher than 80% and 73% when its thicknesses are 1 cm and 3 cm, respectively.

4. Conclusions

In summary, γ-$Y_2Si_2O_7$ with a single phase is obtained from a mixture of Y_2O_3 powder and SiO_2 nanopowder without sintering additives at a relative low sintering temperature 1400 °C. High-temperature dielectric investigations show that the real permittivity and loss tangent increase with increasing temperature. Moreover, an obvious dielectric loss peak is observed at about 800 °C in the investigated frequency range. The peculiar relaxation behaviour which differs from SiO_2 is a non-Debye relaxation process. The relaxation peak is attributed to the structural relaxation polarization caused by the local motion of the thermal-activation atomic groups, which implies that no ionic conductance exists in this material. In particular, the real permittivity maximum and the loss tangent maximum is 5.71 and 8.3×10^{-3} in the temperature range from room temperature to 1400 °C, respectively. The low dielectric loss of γ-$Y_2Si_2O_7$ may draw much attention for potential applications at high temperature.

References

[1] Schmittrink S, Varma C M and Levi A F J 1991 *Phys. Rev. Lett.* **66** 2782
[2] Shin S H, Jeon, D Y and Suh K S 2001 *Jpn. J. Appl. Phys.* Part 1 40 4715
[3] Bottger T, Sun Y, Reinemer G J and Cone R L 2001 *J. Lumin.* **94&95** 565
[4] Zhou P, Yu X , Yang L, Yang S and Gao W 2007 *J. Lumin.* **124** 241
[5] MacLaren I, Trusty P A and Ponton C B 1999 *Acta. Mater.* **47** 779
[6] Kahlenberg V, Kaindl R and Konzett J 2007 *Solid State Sci.* **9** 542
[7] Kumar S and Drummond C H 1992 *J. Mater. Res.* **7** 997
[8] Clarke D R and Thomas G 1978 *J. Am. Ceram. Soc.* **61** 114
[9] Choi H J, Lee J G and Kim Y W 1997 *J. Mater. Sci.* **32** 1937
[10] Hong Z L , Yoshida H, Ikuhara Y, Nishimura T and Mitomo M 2002 *J. Eur. Ceram. Soc.* **22** 527
[11] Chen J, Rulis P, Ouyang L, Misra A and Ching W Y 2005 *Phys. Rev. Lett.* **95** 256103
[12] Ching W Y, Ouyang L Z and Xu Y N 2003 *Phys. Rev.* B **67** 245108
[13] Fukuda K and Matrubara H 2004 *J. Am. Ceram. Soc.* **87** 89
[14] Sun Z Q, Zhou Y C, Wang J Y and Li M S 2007 *J. Am. Ceram. Soc.* **90** 2535
[15] Wang X J, Gong Z Q, Qian Y F, Zhu J and Chen X B 2007 *Chin. Phys.* **16** 2131
[16] Sharma M, Resta R, Car R 2007 *Phys. Rev. Lett.* **98** 247401
[17] Kang Y Q, Cao M S, Yuan J and Shi X L 2009 *Mater. Lett.* **63** 1344
[18] Cao M S, Shi X L, Fang X Y, Jin H B, Hou Z L and Zhou W 2007 *Appl. Phys. Lett.* **91** 203110
[19] Wang G S, Deng Y, Xiang Y and Guo L 2008 *Adv. Funct. Mater.* **18** 2584
[20] Guo J Y, Chen H, Li H Q and Zhang Y W 2008 *Chin. Phys.* B **17** 2544
[21] Cao M S, Jin H B, Li J G, Zhang L, Xu Q, Li X and Xiong L T 2007 *Key Engin. Mater.* **336-338** 1239
[22] Gao S J and Ouyang S X 2003 *Acta Phys. Sin.* **52** 1292 (in Chinese)
[23] Chang F G, Fang K, Song G L and Wang Z K 2007 *Acta Phys. Sin.* **56** 6068 (in Chinese)
[24] Zhang L, Jin H B and Cao M S 2007 *Rare. Metal. Mat. Eng.* **36** 515 (in Chinese)
[25] Hou Z L, Zhang L, Yuan J, Song W L and Cao M S 2008 *Chin. Phys. Lett.* **25** 2249
[26] Chen X L, Cheng Y H, Wu K and Xie X J 2007 *J. Phys.* D: *Appl. Phys.* **40** 6034
[27] Chen X L, Cheng Y H, Xie X J, Feng W and Wu K 2007 *J. Phys.* D: *Appl. Phys.* **40** 846
[28] Hou Z L, Cao M S, Yuan J, Fang X Y and Shi X L 2009 *J. Appl. Phys.* **105** 076103
[29] Dube D C, Agrawal D, Agrawal S and Roy R 2007 *Appl. Phys. Lett.* **90** 124105
[30] Shi X L, Cao M S, Fang X Y, Yuan J, Kang Y Q and Song W L 2008 *Appl. Phys. Lett.* **93** 223112
[31] Cao M S, Hou Z L, Shi X L and Wang F C 2007 *High. Technol. Lett.* **13** 279
[32] Cao M S, Hou Z L, Yuan J, Xiong L T and Shi X L 2009 *J. Appl. Phys.* **105** 106102
[33] Wang J Y, Zhou Y C and Lin Z J 2007 *Acta Mater.* **55** 6019
[34] Daniel V V 1967 *Dielectric Relaxation* (New York: Academic Press)
[35] Liu S H, Liu J M and Deng X L 2007 *Electromagnetic Shielding and Absorbing Materials* (Beijing: Chemical Industry Press) p132 (in Chinese)