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Complex permittivity and microwave absorbing properties of SiC fiber woven fabrics

Donghai Ding · Wancheng Zhou · Biao Zhang · Fa Luo · Dongmei Zhu

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Abstract A comparative investigation of electric conductivity, complex permittivity, and microwave absorbing properties of KD-1 and Nicalon-202 fibers in the form of fabrics within the range of 8.2–12.4 GHz (X band) has been carried out. The electric conductivity value of KD-1 filaments is two orders larger than Nicalon-202. Both the values of real part (ε') and imaginary part (ε'') of KD-1 fabrics are larger than their counterparts of Nicalon-202 especially the imaginary part, which is in agreement with larger DC conductivity (σ_d). The surface morphology and chemical component were characterized by SEM, EDS, Raman spectroscopy and XRD, which shows that both the KD-1 and Nicalon-202 SiC fibers are rich in carbon, while there is rich carbon layer on the surface of the former and the degree of order in the free carbon phase is higher compared with the latter. In addition, the amount of amorphous Si–C–O phase of KD-1 fibers is higher while the SiC crystal is smaller than Nicalon-202. The free carbon on the surface of KD-1 fibers can establish electric conductivity network. The larger ε'' and ε' of KD-1 fabrics are believed to be mainly caused by conductive network established by rich carbon outer layer and relaxation polarization enhanced by more Si–C–O phase. The reflection loss of KD-1 and Nicalon-202 fabrics is −3.5 to 0.7 and −5.1 to −4.3 dB, calculated according to tested complex permittivity.

D. Ding (✉) · W. Zhou · B. Zhang · F. Luo · D. Zhu
State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, China
e-mail: 290610692@qq.com

Introduction

Microwave absorbing materials, which can absorb and dissipate electromagnetic wave, have attracted considerable attention because of its widespread applications in the stealth technology of aircrafts, television image interference of high-rise buildings, and microwave dark room during the past few decades. Ferrite [1], carbon nanotube [2], and cobalt [3] have been successfully used as absorbers dispersed in polymer, but lose their absorbing performance at high temperature or in high frequency. At the same time, silicon carbide materials in the form of particle have been deeply studied as the purpose of absorbing GHz frequency microwave at high temperature and high frequency. Microwave absorbing properties of nano SiC particles can be improved via doping by nitrogen [4] or aluminum [5] because of the relaxation polarization and loss of bond holes from Al_{Si} or N_C.

SiC fibers have been used as reinforcement in high temperature ceramic matrix composites due to its excellent properties of thermal resistance, chemical stabilization, high tension strength, and low density [6–9]. And researchers have studied the microwave absorbing properties of SiC fiber reinforced ceramic matrix composites. For examples, Mouchon et al. researched radio frequency permittivity of SiC/Nasicon [10]. The research of Yu et al. shown that matrix fabrication atmosphere played important role in complex permittivity of SiC/SiC composites [11]. Liu et al. reported that the permittivity of the SiC_f/SiC composites with the CVD SiC interphases was remarkable at X band due to the existence of the carbon-rich layers in CVD SiC [12]. The attentions were also focused on chopped SiC fibers as absorbent in LAS glass matrix by Zhai et al. [13].

Besides, the dielectric properties of SiC fibers have also received the attention of researchers. Chu et al. [14]

researched the anisotropic microwave absorbing properties of oriented SiC short fiber sheets, and it was found that axial permittivity of SiC fibers were several times larger than their radial permittivity. Also, some researchers have paid attentions to the adjusting permittivity of SiC fibers through changing the cross-section and coating the fiber surface. Articles concerning the non-circular SiC fibers, suggested that cross-shaped SiC fibers have good microwave absorbing property due to dipoles hysteresis loss which is absent in circular ones [15]. Researchers have found that turbostratic carbon outer layer with thorn-like morphology and excess carbon layer play a key role in higher permittivity of SiC nanofibers [16] and lower electrical resistivity of SiC fibers [17], respectively.

Although the SiC fibers used mainly in the form of continuous fiber woven fabrics, the complex permittivity and microwave absorbing properties of SiC fiber usually is characterized in the form of short chopped fiber. So far, data regarding the permittivity and microwave absorbing properties of SiC fiber woven fabrics is rarely. In this article, the complex permittivity of KD-1 and Nicalon-202 SiC fiber woven fabrics (fabric K and fabric N) was studied in X band at room temperature. The surface morphology and chemical component were characterized by SEM, EDS, Raman spectroscopy, and XRD in order to gain a better understanding on the mechanism in the complex permittivity and microwave absorbing properties of these two kinds of fabrics.

Experimental

Materials and preparation of fabric

The KD-1 and Nicalon-202 SiC fibers were provided by National University of Defense Technology (China) and Nippon Carbon Co. (Japan), respectively. Table 1 shows the parameters of these two kinds of SiC fibers. The fabrics were braided by Nanjing Glass Fiber Institute (China). Both fabrics K and N were 2.5D bending joint structure shown by Fig. 1. The fiber volume fraction of fabrics is 40%.

Complex permittivity and permeability measurement

The ε' and ε'' of complex permittivity are macroscopical parameters that correlate polarization and dielectric loss, respectively; the real part (μ') of complex permeability

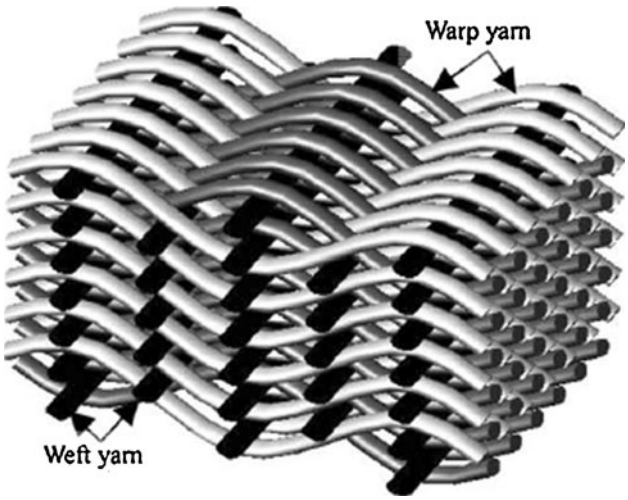

Fig. 1 Schematic showing of fabrics structure

represents the mount of energy stored in the material from ac magnetic field, while the imaginary part (μ'') is the energy loss to the magnetic field. The complex permittivity and permeability of fabrics were measured by the method of waveguide using vector network analyzer (E8362B). Because of the low melting point of paraffin wax, melted paraffin was cast into the fabrics to obtain fabric/wax composites (samples K and N) so that the fiber bundles in fabric were fixed to facilitate the measurement of permittivity. The sizes of measured samples were cut into 22.86 mm × 10.16 mm × 2.0 mm. The wax is insulator, whose ε' and ε'' are 2.26 and 0 at X band frequency. So the complex permittivity of the fabric/wax composites was determinated mostly by the fabrics. Given the convenience of discussions later, the influence of wax on the complex permittivity was ignored. Based on the measured complex permittivity and permeability, we evaluated the microwave absorbing properties by the following equations with MATLAB [19]:

$$\mathrm{RL} = 20\log\left|\frac{Z_{\mathrm{in}} - Z_0}{Z_{\mathrm{in}} + Z_0}\right| \tag{1}$$

where RL denotes the reflection loss in dB unit. Z_0 is the characteristic impedance of free space. Z_{in} is the input characteristic impedance at the absorber/free space interface, which can be expressed as:

$$Z_{\mathrm{in}} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\left(\frac{2\pi ft}{c}\right)\sqrt{\mu_r\varepsilon_r}\right) \tag{2}$$

Table 1 Parameters of KD-1 and Nicalon-202 SiC fibers [6, 18]

Fiber type	Diameter (μm)	Density (g/cm^3)	Tension strength (MPa)	Young's modulus (Gpa)
KD-1	14–16	2.54	1,800–2,200	–
Nicalon-202	14	2.55	3,000	200

where c is the velocity of light, t is the thickness of an absorber. In this article, t values are in mm unit. The ε_r and μ_r are the measured relative complex permittivity and permeability, respectively.

Electric conductivity measurement

Conductivity is important for many dielectric materials, and the relation between σ_a (AC conductivity) and ε'' can be expressed as:

$$\sigma_a = \omega\varepsilon'' \tag{3}$$

where ω is the angular frequency.

The DC special conductivity (σ_d) of SiC filaments can be calculated as the equation:

$$\sigma_d = 1/\rho = \frac{L}{RS} \tag{4}$$

where σ_d is special conductivity, R is the resistance, S is the cross-section area of filament, and L is the length of filament. The electrical resistance of SiC filaments at room temperature was measured by two probes direct current method. The filaments were tin–lead bonded on alumina substrate. The length of filaments was 1 cm. The diameter of KD-1 and Nicalon filaments were both tested by SEM.

Results and discussions

Microstructure and chemical composition characterization

Various studies have shown that Nicalon SiC fibers comprise SiC and C nanocrystals, embedded in an amorphous Si–C–O phase [6]. SEM photographs of KD-1 and Nicalon-202 SiC fibers are shown in Fig. 2. Table 2 displays the chemical composition of KD-1 and Nicalon-202 SiC fibers which was characterized by EDS. There is no obvious difference of surface morphology between the two kinds of fibers. The C/Si ratio of KD-1 fiber is a little higher than that of Nicalon-202, while the amount of oxygen of KD-1 fibers is obviously larger than that of Nicalon-202 fiber. Figure 3 shows the chemical element intensity profile along KD-1 and Nicalon-202 SiC fibers diameter characterized by EDS. It can be observed that there is an excess carbon outer layer on KD-1 SiC fibers while the carbon element density along the Nicalon-202 SiC fiber diameter is approximately uniform, which is agreed to the previous investigation showed that the surface of Nicalon-202 SiC fiber is coated with an excess oxygen layer in the form of SiO_2 and amorphous Si–C–O phase [20].

XRD is one of the important technologies for studying crystal phase in materials science. Figure 4 shows the XRD patterns of KD-1 and Nicalon-202 SiC fibers, which are similar to the data of Takeda [21] and Liu [12], respectively. It can be observed that there is obvious difference between the XRD patterns of these two kinds of SiC fibers. The diffraction peaks of KD-1 SiC fiber are obviously broader than that of Nicalon-202. And, there is no sharp peak in pattern of KD-1. It can be deduced that the grain size of SiC crystal of KD-1 SiC fiber is much smaller than Nicalon-202 SiC fiber while the amorphous Si–C–O phase or free carbon may be more than Nicalon-202. The higher amount of oxygen indicated by EDS is agreed partly to the XRD patterns.

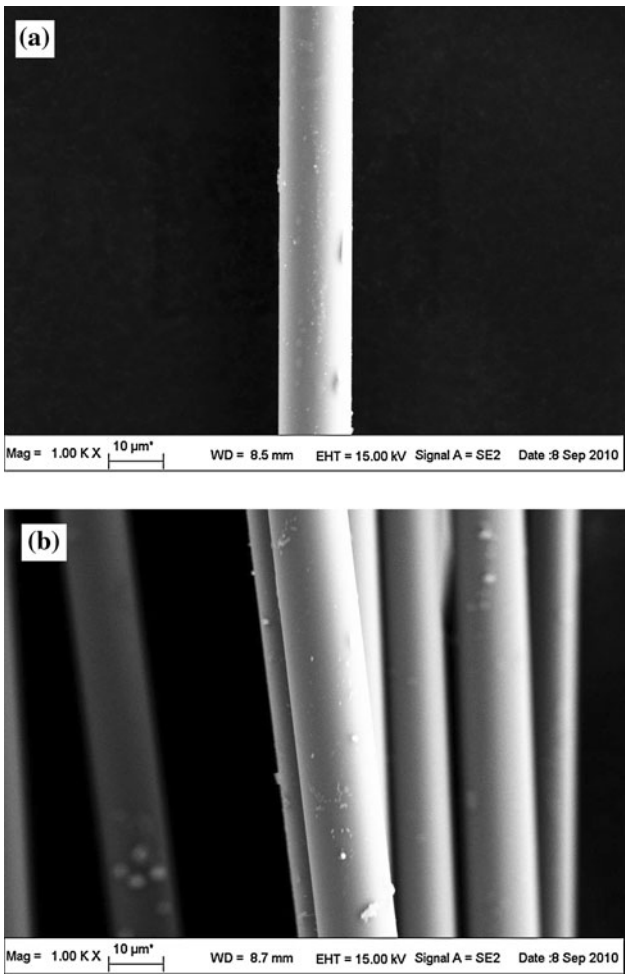

Fig. 2 SEM photographs of SiC fibers. **a** KD-1 SiC fiber. **b** Nicalon-202 fiber

Table 2 Chemical composition of KD-1 and Nicalon-202 SiC fibers

Chemical composition (at.%)	C	Si	O	C/Si
KD-1	39.13	31.59	29.20	1.241
Nicalon-202	44.94	34.80	20.26	1.290

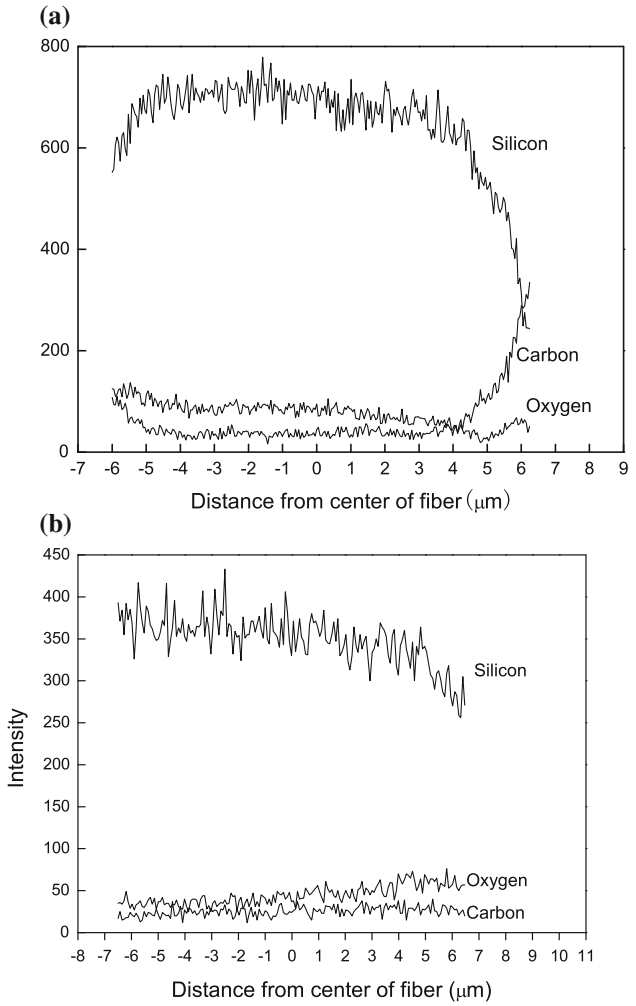

Fig. 3 Chemical element intensity profile along fibers diameter. **a** KD-1. **b** Nicalon-202

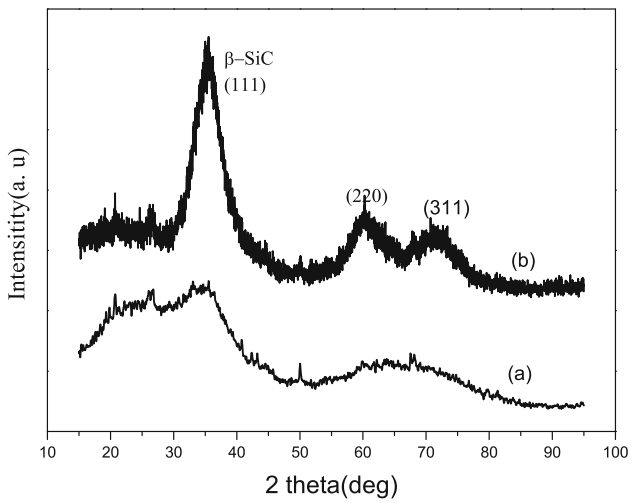

Fig. 4 XRD patterns of SiC fibers. (*a*) KD-1. (*b*) Nicalon-202

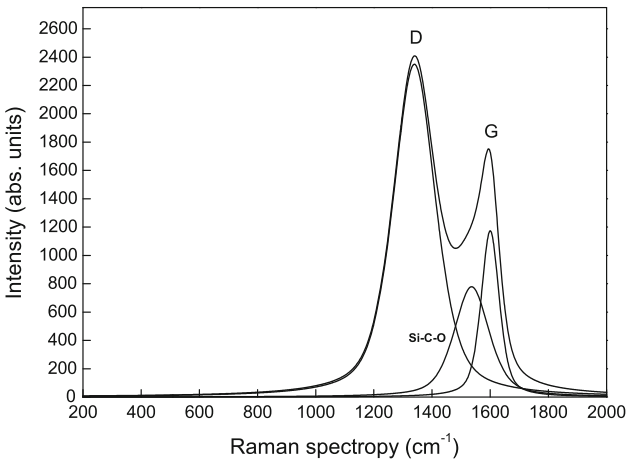

Fig. 5 Raman spectroscopy of KD-1 SiC fiber

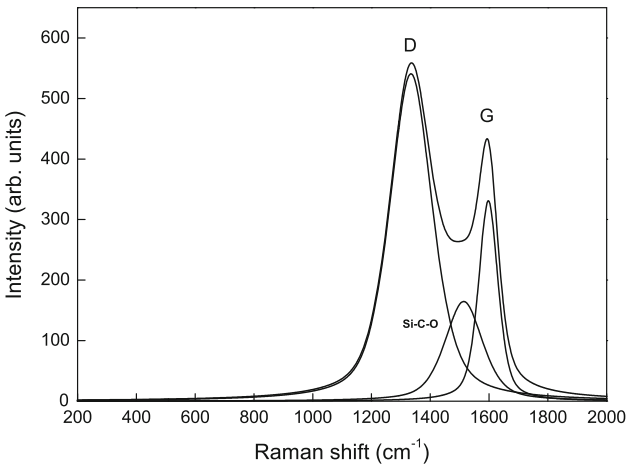

Fig. 6 Raman spectroscopy of Nicalon-202 SiC fiber

Raman spectroscopy has been shown to be very useful for the study of a wide range of structural characteristics of materials. Raman spectroscopy was used successfully to identify the presence of excess carbon and silicon in SiC fibers in previous studies [22–24]. As previous studied, the *D* (disordered) and *G* (graphitic) peaks at about 1,600 and 1,330 cm^{-1} assigned to sp^3 and sp^2 bonded carbons. Generally, the band area ratio (I_D/I_G) was used to obtain information about the degree of disorder in the free carbon of SiC fibers. Raman spectra of KD-1 and Nicalon-202 SiC fibers are presented in Figs. 5 and 6. In present Raman spectroscopy, the peaks of SiC can not be observed due to its insensitivity to Raman scattering while the peaks of carbon can be identified obviously. The values of I_D/I_G of KD-1 and Nicalon-202 fibers are 4.6 and 3.5, respectively, which indicate the degree of order in the free carbon phase. The higher value of I_D/I_G of KD-1 SiC fiber which may be contributed by the rich carbon outer layer.

Electric conductivity

The tested value of σ_d of KD-1 (2–3 S/cm) is two orders larger than Nicalon-202 (0.04–0.05 S/cm). Among the phases occurring in the SiC fibers, Si–O–C phase is insulator ($\sigma = 10^{-14}$–10^{-12} S/cm), whereas SiC and amorphous carbon are semiconductors ($\sigma = 10^{-4}$–10^{-2} S/cm). Turbostratic carbon and graphite have a significantly higher conductivity ($\sigma = 10^{0}$–10^{5} S/cm) [25]. The excess carbon in SiC fibers plays an important role in its electric properties [26–28]. In SiC fibers, the free carbon may consist of excess carbon layer on the surface of fibers [26] and nano-crystals graphite dispersed around SiC crystals or in amorphous Si–C–O phase [6]. The influence of carbon layer on the electrical conductivity of the SiC fibers is obvious [29, 30], while the influence of isolated carbon phase in fiber may be weak according to the percolation effect. In present study, microstructure and chemical composition characterization indicated that both the KD-1 and Nicalon-202 fibers are rich in carbon, which is agreed to previous studies. However, the KD-1 fibers have an excess carbon outer layer while Nicalon-202 fibers do not have. The excess carbon in Nicalon-202 fibers is only in the form of nano-crystals graphite dispersed around SiC crystals or in amorphous Si–C–O phase, which may also exists in KD-1 SiC fibers. The effect of excess carbon on electric conductivity of SiC fibers should mainly depend on the formation of conductive network. The sizes of nano-crystals graphites divided by SiC or Si–C–O phase are very small (several nm), so the continuous conductive network can not form well. However, the free carbon out layer on KD-1 fiber can form the conductive network. So the electric conductivity of KD-1 fibers fibers is much higher than that of Nicalon-202.

Figures 7 and 8 show the complex permittivity and permeability of fabrics K and N as a function of frequency at X band. The values of ε' and ε' of fabric K, which are 7.93–5.33 and 20.10–12.73, respectively, are both higher than fabric N 4.15–3.81 and 1.05–0.37, respectively. The μ' and μ'' of sample K are 1.26 to 0.99 and −0.02 to 0.25, respectively, and the permeability of fabric N is similar to that of fabric K. Both fabrics K and D are kinds of dielectric loss materials.

Possible mechanisms for the polarization in a dielectric material are: electronic polarization, atomic polarization, relaxation polarization, reorientation polarization, and space charge polarization. When the frequency is in GHz, the space charge polarization should lose its effect because it demands too long time (at least several seconds) to establish polarization. Although the permittivity data of Si–C–O phase is not available at the present time, the dangling bonds and vacancies may contribute to the increasing of ε'. So, the increasing of ε' could be attributed to relaxation

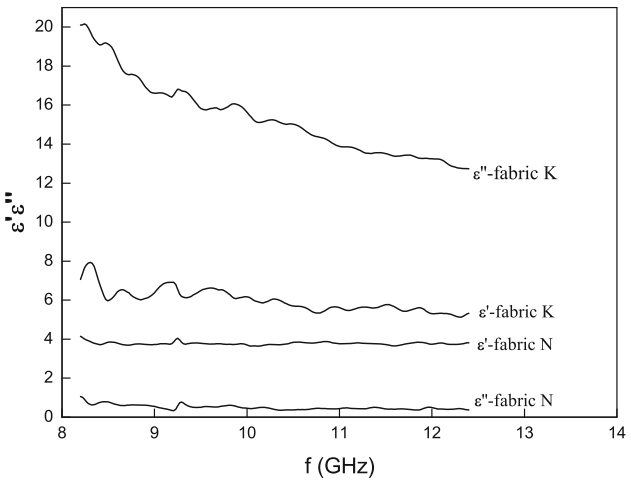

Fig. 7 Frequency dependence of ε' and ε'' of fabrics K and N

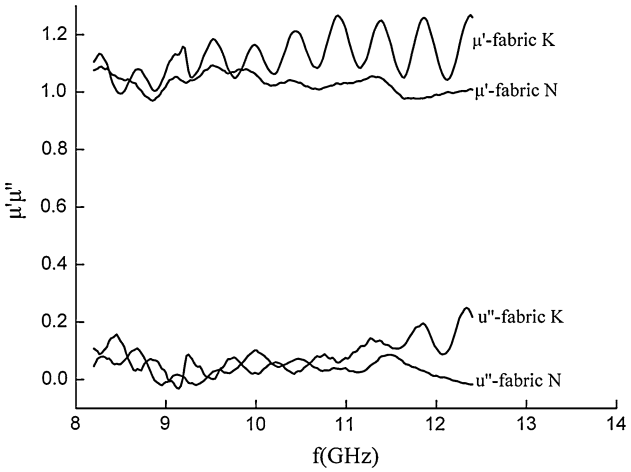

Fig. 8 Frequency dependance of μ' and μ'' of fabrics K and N

polarization enhanced by more Si–C–O phase. On the other hand, the larger ε'', which suggests better capacity of dielectric loss in the microwave frequency, is associated to increased electric conductivity induced by excess carbon layer on the surface of fibers. In addition, the ε'' of fabric K shows better frequency response behavior, which is available on broadening the frequency response behavior.

The reflection loss of fabrics K and N calculated are shown in Fig. 9. Both the microwave absorbing potential of fabrics K and N are not good. The main reason is that the ε'' of fabric K is too larger to impedance match while the ε' and ε'' of fabric N are both too small to effectively store and dissipate microwave. In order to improve the microwave absorbing properties of the fabrics K, thermal oxidation at proper temperature could be considered. And, the coatings such as pyrolysis carbon or CVD SiC may improve the complex permittivity of Nicalon-202 fabric.

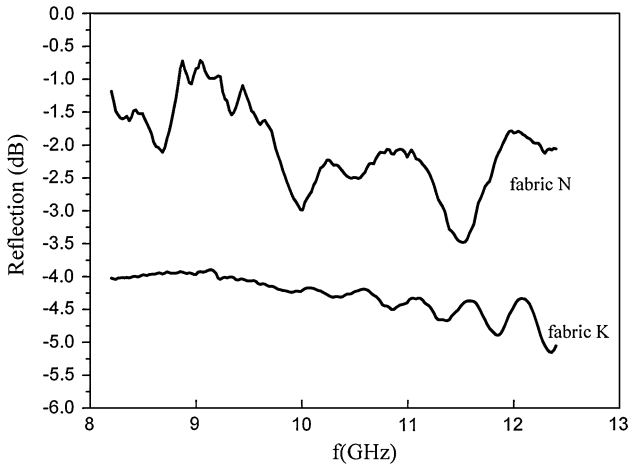

Fig. 9 Reflection loss of fabrics K and N with fiber volume fraction of 40%

Conclusions

The complex permittivity of KD-1 and Nicalon-202 SiC fibers in the form of fabric within the range of 8.2–12.4 GHz were investigated. Both the values of ε' and ε'' of KD-1 fabrics are larger than Nicalon-202 fabrics especially the ε''. And, the electric conductivity values of KD-1 filaments are of two orders larger than Nicalon-202, which is agreed to larger ε''. Although both the KD-1 and Nicalon-202 SiC fibers are rich in carbon, there is rich carbon layer on the surface of KD-1 SiC fibers and the degree of order in the free carbon phase of KD-1 fiber is higher. In addition, the amount of amorphous Si–C–O phase of KD-1 fibers is higher but the SiC crystal is smaller than Nicalon-202. The free carbon on the surface of KD-1 fibers can establish electric conductivity network. The larger ε'' and ε' of KD-1 fabrics are believed to be mainly be caused by conductive network established by rich carbon outer layer and relaxation polarization enhanced by more Si–C–O phase.

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