RESEARCH ON THE PREPARATION AND THE DIELECTRIC PROPERTIES OF SiBON WAVE TRANSPARENT CERAMIC BY THE SOLID-STATE REACTION

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The SiO_2 powder and BN powder were uniformly mixed, and then was squashed to make SiBON block, which was sintered in certain N_2 atmosphere to make the SiBON wave transparent ceramic. SEM, XRD and FT-IR were applied to study the surface microstructure, main components and chemical bond of ceramic.The experimental results showed the properties of the wave transparent ceramic were good, when SiO_2 and BN were mixed at the wt% ratio of 40:60 and the sintered temperature was 1600℃. The main components of the sintered ceramic in 1600 ℃ were SiO_2 and BN. The precipitation of SiO_2 crystals and BN crystals was thin granular sheet. In the sintering process, the solid-state reaction had taken place between SiO_2 and BN because of the formation of Si-O-B and B-N-Si structure. The dielectric constant of the ceramic is in the range of 2.67-3.75, which can meet the demand of application in projects.

Keywords: SiBON, wave transparent ceramic, the dielectric constant, the solid-state reaction

1. Introduction

The wave transparent material is a multifunctional material with wave transparent, loading and anticorrosion, which has the transmittance of more than 70% in the wavelength range of 1-1000mm and 0.3-300GHz in frequency range. It is widely used in aerospace aircraft, spaceships, missiles and return satellites [1-3].

With the continuous increasing of the flight Maher number, the missile radome is becoming more and more demanding for the dielectric properties, mechanical properties, technological properties and weight of the wave transparent materials [4-6]. The types of wave transparent materials are gradually developed from polymer materials and single ceramic materials to ceramic matrix composites [2,7]. Compared with aluminum oxide, silicon oxide, microcrystalline glass ceramic materials, silicon dioxide (SiO_2) has excellent thermal shock

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resistance and dielectric permeability, especially with the low dielectric constant and dielectric loss; furthermore, its dielectric constant is very stable with temperature and frequency variation, therefore, SiO_2 is one of the best antenna window materials with the dielectric-thermal function[8-9]; Boron nitride (BN) is one of the few compounds as the decomposition temperature can reach 3000℃, and it has stable thermal performance and electrical performance in a wide temperature range, and the dielectric constant and dielectric loss is low, but the low mechanical strength and the lack of resistance of rain erosion are the shortcomings[10-11]. The preparation of SiBON ceramic materials with SiO_2 and BN can combine the advantages of SiO_2 and BN materials. It does not only meet the mechanical performance requirements of radome, but also meets the dielectric performance requirements of radome [12-13].

2. Experiments

2.1 Main experimental raw materials

The main raw materials used in the experiments were shown in Table 1.

Table 1

The main raw materials in the experiment

Raw material	Source	Specification
Silica sol	Zhejiang Yuda Chemical Co. Ltd.	HS-25
BN powder	Zibo Fuxinkang special material Co., Ltd.	Mass fraction is greater than 99.16%
Anhydrous ethanol	Tianjin Fuyu Fine Chemical Co., Ltd.	analysis of more than 99.7%
Polyvinyl alcohol	Suzhou Zhongyuan Chemical Co., Ltd.	1788

The main use of raw materials: The silicon sol was used to prepare SiO_2 powder raw material; BN powder was used to prepare wave transparent ceramic powder; the anhydrous ethanol was for SiO_2 powder and BN powder wet ball milling; and the polyvinyl alcohol, as the binder, when SiO_2 and BN powder were mixed for granulation.

2.2 The Ratio of raw materials

The mixed powder used in the experiment consisted of different proportions (*wt%*) of SiO_2 powder and BN powder. The *wt%* ratio of raw materials is shown in Table 2.

Table 2

The mixing ratio of SiO_2 powder and BN powder

Raw material number	SiO_2 powder /*wt%*	BN powder /*wt%*
1#	70	30
2#	60	40

3#	50	50
4#	40	60
5#	30	70

2.3 The main equipment and testing instruments

The experimental equipments were the Nitrogen atmosphere sintering furnace(KJ-A1700-8LZ), the X-ray Diffractometer (XRD) (D8 ADVANCE; BRUKER AXS, Inc., Karlsruhe, Germany), the Scanning Electron Microscope (SEM) (S-2500, Hitachi, Tokyo, Japan), A Fourier Transform Infrared Spectroscopy(FT-IR) (Nicolet 380, Thermo Electron Corporation, Waltham, MA, USA), the Vector Network Analyzer (Agilent N5234A, 10 GHz).

3. Results analysis

3.1 The effect of BN content on the density of SiBON ceramic

The influence of BN content on ceramic density is shown in Fig.1. It can be seen that with the increase of BN *wt%* content, the density of ceramic gradually decreases, which shows an obvious trend of decline.

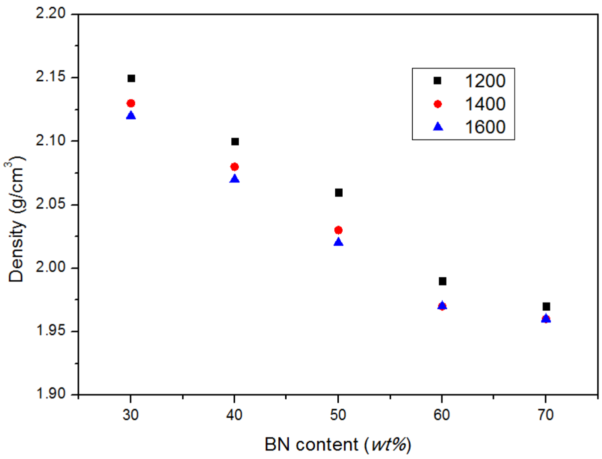

Fig. 1 The relationship between the *wt%* content of BN and the density of composite.

Take the example of ceramic material sintered at 1200°C, the density of ceramic materials decreased from 2.15g/cm^3 to 1.97g/cm^3 when the *wt%* content of BN increased from 30% to 70%. It indicates that the addition of BN has an adverse effect on the density of the ceramic.

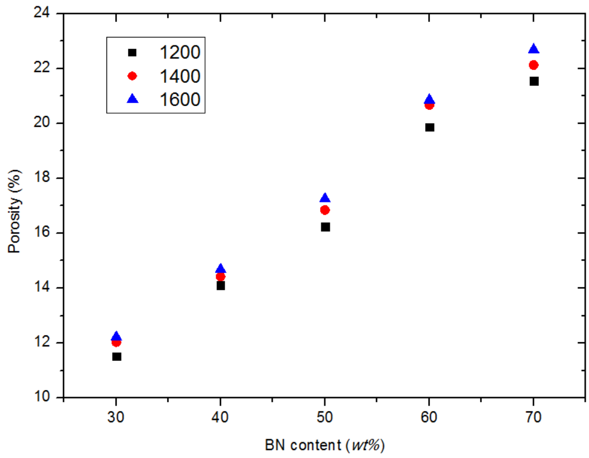

Fig.2 The relationship between the *wt%* content of BN and the porosity of composite

3.2 The effect of BN content on the porosity of SiBON ceramic

The effect of BN content on the porosity of ceramic is shown in Fig.2. The porosity of ceramic rised from 12.22% to 22.69% when the *wt%* content of BN was increased from 30% to 70%, with the ceramic sintered at 1600℃. The trend of increasing is very obvious. Consequently, it can be concluded that the porosity of ceramic rises with the increase of BN content, which is also consistent with the influence of BN on ceramic density.

3.3 The effect of porosity on the properties of SiBON ceramic

The high porosity is an important characteristic of the wave transparent ceramic system, which is beneficial to improve the transmission rate of the ceramic. However, it can damage the mechanical properties of the material and is not conducive to the engineering application. Table 3 shows the influence of BN content on the flexural strength of ceramic.

Table 3

The relationship between the BN content and flexural strength

BN powder /*wt%*	30	40	50	60	70
The flexural strength(MPa)	182.6	165.7	151.3	132.6	92.7

It shows that with the increase of BN content as sintering temperature at 1600℃, the flexural strength of SiBON ceramic gradually decreas. When the BN content reaches to 60%, the flexural strength of SiBON ceramic decreases from 182.6MPa to 132.6MPa. The decreasing flexural strength is due to the high porosity in composite after the introduction of a certain amount of BN content.

The micropore in the material includes open pores and closed pores. The two kinds of pores are actually occupied by air in dry condition, and the air dielectric constant is generally close to 1, therefore, the porosity increases, which accounted for the larger volume, on the whole wave transparent ceramic, dielectric constant will be reduced. In the process of wave transparent, the reflection and heat consumption are reduced, and the permeability is increased.

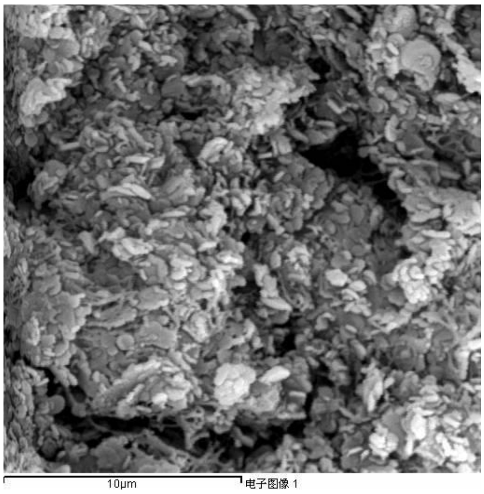

Fig. 3 The SEM of 4# sintered composite

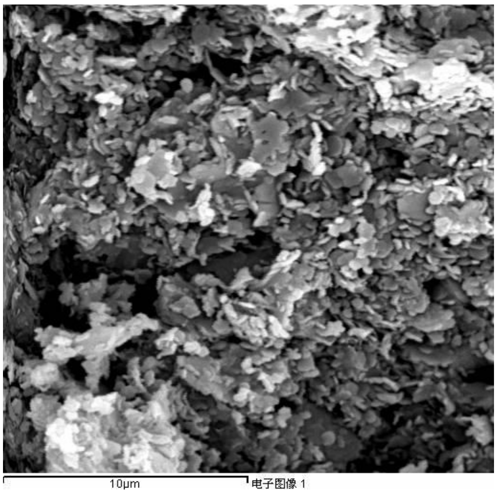

Fig. 4 The SEM of 5# sintered composite

Fig.3 and Fig.4 are scanning electron microscope images of sample 4# and 5# sintered at 1600℃. It can be seen that the existence of porosity makes the original continuous phase cut off and the effective bearing area of ceramic materials reduced. Therefore, the mechanical properties will decrease. The control of the porosity of the material can be determined according to the need. If the requirement for dielectric properties is not very high, the proper reduction of BN in the ceramic can reduce the porosity of the material.

The influence of BN content on the density and porosity of ceramic can be analyzed as follows:

(1) In Fig.1, when the *wt%* content of BN is 60% and 70%, the density of the ceramic is small, which helps to reduce the weight of the material.

(2) In Fig.2, the porosity of the corresponding wave transparent ceramic is higher with lower density, which makes the mechanical properties of the material lower, and is not conducive to the processing and application of ceramic.

(3) The SiBON ceramic requires low density and high porosity. Sintered ceramic with BN *wt%* content of 60% can meet these requirements better than that with BN *wt%* content of 70%, because the flexural strength(132.6MPa) of the former is higher than that(92.74MPa) of the later. Therefore, it can be determined that the *wt%* content of BN is 60%, which is the best mixing ratio of SiO_2 powder and BN powder.

3.4 The relative dielectric constant

The test sample was processed to make the thickness of all the samples about 3.0mm. The capacitance of all the samples was measured and the relative dielectric constant was calculated. The effective surface of the measured sample was a circle with a radius of 10.0 mm. The relative dielectric constant curves changing with the test frequency of the wave transparent ceramics composite with BN *wt%* content of 60% at 1200℃, 1400℃ and 1600℃ are shown in Fig. 5.

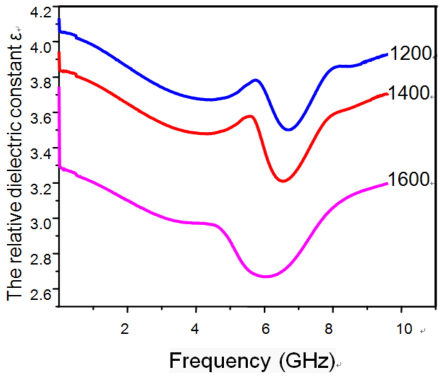

Fig.5 The dielectric constant changing with frequency

It can be seen from Fig. 5, the relative dielectric constant of wave transparent ceramic with BN *wt%* content of 60% and sintered at 1600℃ is lower than that sintered at 1200℃ and 1400℃. The best relative dielectric constant of SiBON ceramic can be obtained at 1600℃. That is to say, the best sintering temperature is 1600℃.

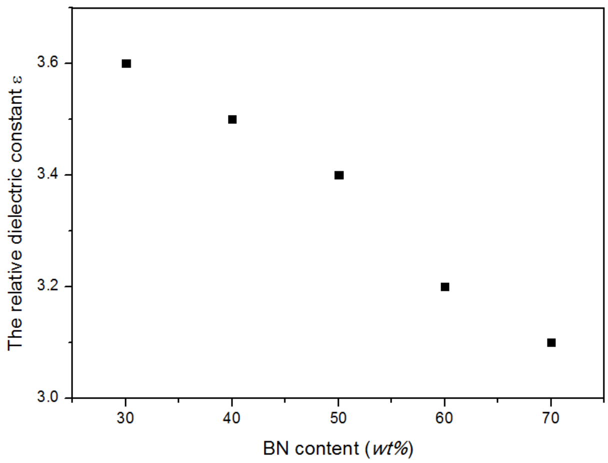

Fig.6 The relationship between the BN *wt%* content and the relative dielectric constant

Fig. 6 shows the relationship between BN *wt%* content and the relative dielectric constant ε_r of the wave transparent ceramic sintered at 1600℃ at the frequency of 10GHz. It can be seen from the diagram that the addition of BN powder effectively reduces the dielectric constant of the ceramic. On the one hand, the addition of BN has a certain impact on the densification of ceramic, then porosity increased, and the dielectric constant of occupied air is relatively low (close to 1), therefore, the dielectric constant of the ceramic reduced; on the other hand, the dielectric properties of the BN is better than that of SiO_2.

3.5 The microstructure and phase analysis

3.5.1 The SEM analysis of the surface and fracture

Fig.7 is the fracture morphology of sample 1# sintered at 1600℃. From Fig.7, it can be seen that there are spherical particle in the fracture, which is due to the high *wt%* content of SiO_2 and the presence of the excess SiO_2 in the form of glass after sintering. There are a lot of fine particles on the fracture, and the porosity is not obvious.

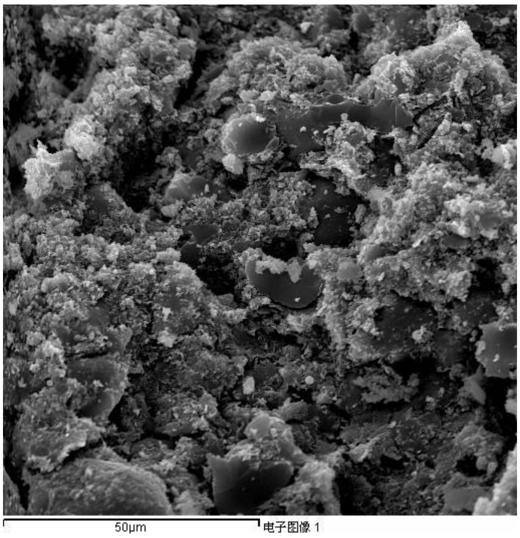

Fig. 7 The SEM of sample 1# sintered composite

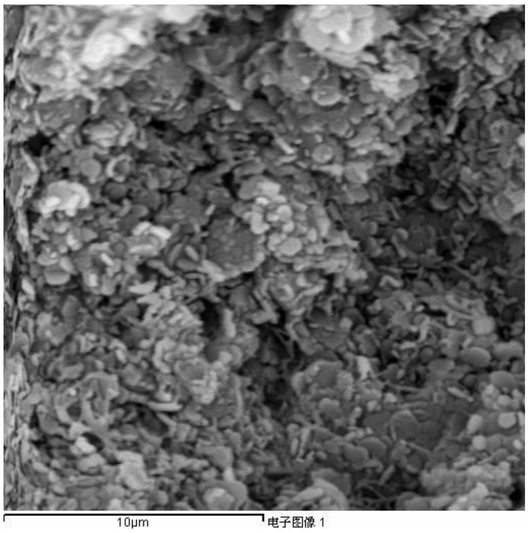

Fig.8 The SEM of sample 4# sintered composite

Fig. 8 is the fracture morphology of sample 4# sintered at 1600 C. As can be seen that the fracture of the ceramic is mostly sheet material, and it has more distribution and close connection. Since SiO_2 is mostly grainy after sintering, the sheet material is BN grain, which increases with the addition of BN *wt%* content, and the BN grain sheet structure is distributed evenly on the surface of the material, but not closely.

Compared with Fig.7 and Fig.8, it can be concluded that with the increase of BN *wt%* content, the fracture morphology of sintered ceramic changed from granular into thin sheet, which also reduced the densification degree of ceramic and increased the porosity inside the sintered materials. This may be the main reason for the decrease of material density and the increase of porosity.

3.5.2 The X-ray analysis

Fig.9 is the X-ray electron diffraction (XRD) of wave transparent ceramic (sample 4# and sample 5#) sintered at 1600°C. The X-ray analysis results showed that the sintered ceramic contained SiO_2 and BN crystals, and the diffraction peak intensity is very strong, which indicated that large degree crystallization occurred in the process of sintering ceramic, furthermore, the crystal is more.

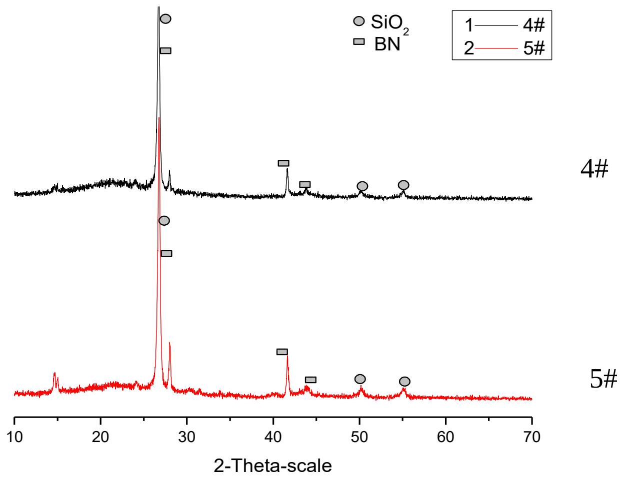

Fig. 9 The XRD of sintered ceramic composite

3.5.3 The FT-IR analysis

Through the infrared spectrum analysis of ceramic, it was obvious that the solid state reaction and crystal transformation in the sintering process can be obtained. The infrared analysis of BN and SiO_2 before and after the sintering has been made. The interpretation and comparison of these atlases can help us to understand more deeply the evolution of the chemical bonds during the sintering process. The 1, 2, and 3 curves in Fig.10 are infrared spectra of ceramic with SiO_2 and 60% BN, pure BN powders and pure SiO_2 powders.

It is clear that the infrared spectra of the SiO_2/BN wave transparent ceramics are basically the superposition of the infrared spectra of pure BN powder and pure SiO_2 powder. In the infrared spectrogram of SiO_2/BN wave transparent ceramic, there are two absorption bands at 670cm^{-1} and 940cm^{-1}, which are not found in the spectrogram of BN and SiO_2 powder. It is caused by the vibration of Si-O-B and B-N-Si [14, 15].

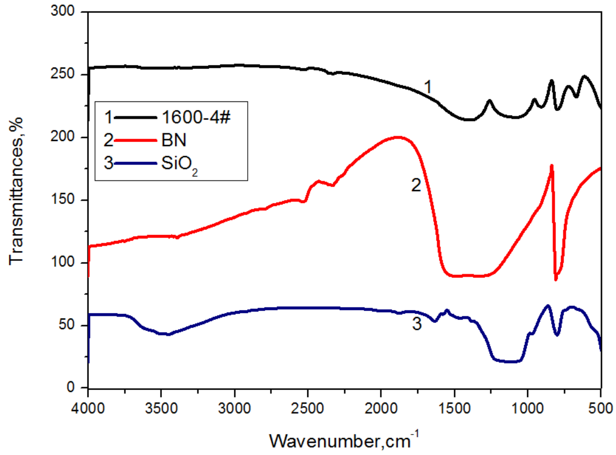

Fig.10 The infrared spectrogram of different materials

Therefore, the appearances of the absorption bands at 670cm^{-1} and 940cm^{-1} indicate that the solid state reaction occurs between the BN powder and the SiO_2 powder[16,17].

4. Conclusions

(1) The optimum *wt%* ratio of SiBON wave transparent ceramic is SiO_2 *wt%* content 40%, BN *wt%* content 60%, and the optimum sintering temperature 1600°C.

(2) Under the optimum ratio and the best sintering temperature, the SiBON wave transparent ceramic has better comprehensive properties, the density is 1.97g/cm^3, the porosity is 20.86%, and the relative dielectric constant is 2.67-3.74, which can meet the dielectric performance requirements of the transparent ceramic.

(3) When the sintering temperature is 1600°C, and the *wt%* content of BN is 60%, during the sintered ceramic materials, the BN grain is thin sheet and more distributed. With the addition of BN powder, the densification degree of the material is obviously reduced, and the inner porosity of the material becomes more and more. This may be the main reason for the decrease of material density and the increase of porosity.

(4) The SiBON ceramics sintered at 1600°C have absorption bands at 670cm^{-1} and 940cm^{-1}, which is caused by the vibration of Si-O-B and B-N-Si bonds. The existence of Si-O-B and B-N-Si shows that solid state reaction occurs between BN and SiO_2.

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