Permittivity and its temperature dependence in hexagonal structure BN dominated by the local electric field*

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This paper presents an analysis of the local electric field in hexagonal boron nitride (h-BN) by introducing a modified parameter. Based on the determination of the modified parameter of h-BN, the revised Lorenz equation is developed. Then the permittivity at high temperature and in the microwave frequency is investigated. In addition, this equation is derived for evaluating the temperature coefficient of the permittivity of h-BN. The analyses show that the permittivity increases with increasing temperature, which is mainly attributed to the positive temperature coefficient of the ionic polarizability.

Keywords: hexagonal boron nitride, permittivity, temperature dependence, microwave frequency

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1. Introduction

Boron nitride (BN) has motivated numerous theoretical and experimental studies for a long time[1−3] due to its outstanding physical and chemical properties. It is known that there are three polytypes of BN, cubic zincblende structure (c-BN), wurtzite structure (w-BN), and hexagonal structure (h-BN). Among these polytypes of BN, h-BN is the most important material for applications in aerospace technologies because it has low permittivity and loss tangent at room temperature, a very high sublimation temperature, and good machinability.[4−6]

It is important to study the dielectric properties of h-BN in a wide range of frequencies and at high temperature for its applications in microwave electronic circuits and electromagnetic shielding devices. Recently, a great deal of effort has been made to study its ionic conductivity and dielectric loss.[7,8] In our previous study,[9] the dielectric loss of h-BN at high temperature was investigated. However, little work has been carried out on the theoretical study of the microwave permittivity of h-BN. The Clausius–Mosotti formula is important for dielectric materials as it provides a physical description of the interaction of the electromagnetic field with the materials.[10] And the equation is extended to predict the permittivity of non cubic materials, i.e., Si_2N_2O.[11] Similarly, we consider if this formula can be used to calculate the permittivity of h-BN.

Consequently, the aim of this paper is to study the permittivity of h-BN by experimental and theoretical analyses in temperature ranging from 300 K to 1600 K and at microwave frequencies. Through consideration of the overlap and the permeation of electron clouds, the local electric field of h-BN is analyzed by introducing a modified parameter, since the Lorenz approximation is invalid therein. Then the permittivity of h-BN is calculated according to the revised Lorenz local electric field.

It is also necessary to derive a modified Lorenz equation to discuss the temperature variation of the permittivity of h-BN. Starting with the Clausius–Mosotti equation, Bosman and Havinga

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showed that three effects contribute to the temperature dependence of the dielectric constant at low temperature.[12,13] Many authors used this model to analyze $\mathrm{d}\varepsilon/\mathrm{d}T$ of cubic symmetry crystals.[14–16] In the present work, the method proposed by Havinga is extended to h-BN for discussing its $\mathrm{d}\varepsilon/\mathrm{d}T$. In addition, a comparison between the calculated permittivity of h-BN samples and the experimental data is performed to validate our calculation method.

2. Local electric field in h-BN

An h-BN sample of density 1.94 g/cm^{-3} is selected to measure its permittivity in the microwave frequency range (10 GHz) by using the cavity perturbation technique at high temperatures ranging from 300 K to 1573 K, with the measurements made every 100 K. Table 1 shows the impurity contents of the boron nitride sample. The details of this technique have been reported in Ref. [17]. Figure 1 gives the data obtained using the circular cavity method. As indicated in Fig. 1, the microwave permittivity increases with the increasing temperature. In order to reveal the underlying mechanism, the following discussion focuses on the theoretical investigation of the permittivity of h-BN.

Table 1. The components of the h-BN sample (in ppm).

Na	K	Ca	Li	Al	Mg
24	8	510	< 1	88	94

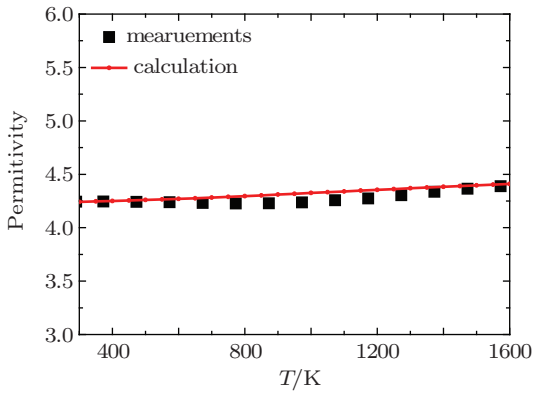


Fig. 1. (colour online) Comparison between the results from our calculations and the measurements.

It is typically assumed that the number density of molecules in the classical Lorentz–Lorenz formula is sufficiently small so that the formula can be simplified to a simple linear relationship between the mean molecular polarizability α_i and the permittivity ε.[18] The Lorentz–Lorenz formula leads to the well-known Clausius–Mosotti equation, which is expressed as

$$\frac{\varepsilon-1}{\varepsilon+2}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i, \tag{1}$$

where N_i is the number of polarized particles.

In our previous study,[11] for the non-cubic solids, the above equation is replaced by

$$\frac{\varepsilon_1}{\gamma(\varepsilon-1)+3}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i, \tag{2}$$

where γ is the modified parameter for the local electric field, $0\le\gamma\le 1$.[19]

The optical permittivity is given by

$$\frac{\varepsilon_\infty-1}{\gamma(\varepsilon_\infty-1)+3}=\frac{1}{3\varepsilon_0}N_\mathrm{e}\alpha_\mathrm{e}, \tag{3}$$

where N_e and α_e are the number and the electronic polarizability of the particles, respectively. In Eq. (3), we note that the optical permittivity ε_∞ is determined by γ. In order to obtain the value of ε_∞, the electronic polarization of h-BN should be known. The value of electronic polarizability α_e of h-BN is found to be 5.5944×10^{-40} F·m^2,[20] and the number of h-BN N_e can be deduced as

$$N_\mathrm{e}=\frac{N_\mathrm{A}}{M_\mathrm{BN}}\rho_\mathrm{BN}=5.68\times10^{28}\ (\mathrm{ind/m^3}), \tag{4}$$

where N_A and M_BN are the Avogadro's constant and the molecular weight, respectively. Furthermore, we can obtain the value of ε_∞ by combining Eqs. (3) and (4) with different values of γ, as shown in Table 2. On the other hand, to determine an appropriate factor γ, ε_∞ of h-BN should be obtained in advance. Fortunately, it can be calculated using a plane-wave pseudopotential method in the following section.

Table 2. Values of ε_∞ for different γ.

γ	0	0.2	0.5	0.8	0.9	1.0
ε_∞	4.59	5.72	9.94	85.69	–47.46	–19.23

3. Computational details

We have performed a first-principles calculation of two BN polytypes based on the density-functional theory through the Cambridge Sequential Total Energy Package (CASTEP) with the local-density approximation and the ultrasoft pseudopotential technique. This

method is a great success in describing and predicting the properties of materials.[21−25] The exchange–correlation interactions are described in the Perdew–Wang form. The kinetic energy cutoff for the plane waves is 550 eV, and a 12×12×4 k-point mesh set is used for the Brillouin-zone sampling, which makes the separation in the reciprocal space less than 0.03 Å^{-1}.

4. Results and discussion

4.1. Optical permittivity

As we know, crystal symmetry makes the dielectric tensors be composed of only a few independent components. For w-BN and h-BN, the dielectric tensors are diagonal and have two independent components, $\varepsilon_{\infty}^{\perp c}$ and $\varepsilon_{\infty}^{\parallel c}$, which are along and perpendicular to the c axis, respectively. Our results for the optical dielectric properties of two polytypes of BN are presented in Table 3. And for comparison, the reference data[26−29] are also listed in Table 3. For w-BN, an agreement between our calculations and the former studies[26,28,29] is obtained. In the case of h-BN, there is a relatively large deviation concerning the perpendicular component. Our calculated value is 3.03 for the optical permittivity, whereas the corresponding measured value is 4.1,[27] except that our value is closer to the experimental data than the former calculation results.[28,29]

Table 3. The optical permittivity of two polytypes of BN.

	Present		Cal.[26]	Exp.[27]	Cal.[28]		Cal.[29]	
	$\varepsilon_{\infty}^{\perp c}$	$\varepsilon_{\infty}^{\parallel c}$	$\varepsilon_{\infty}^{\perp c}$	$\varepsilon_{\infty}^{\parallel c}$	$\varepsilon_{\infty}^{\perp c}$	$\varepsilon_{\infty}^{\parallel c}$	$\varepsilon_{\infty}^{\perp c}$	$\varepsilon_{\infty}^{\parallel c}$
w-BN	4.4	4.45	4.16	4.18	4.5	4.64	4.5	4.67
h-BN	4.94	3.03	4.95	4.1	4.85	2.84	4.32	2.21

4.2. Microwave permittivity of h-BN

From the above discussion, the average value of ε_{∞} is 4.53, so the value of γ is close to zero, approximately γ=0. If $\gamma = 0$, expression (3) has the following form:[19]

$$\varepsilon_{\infty} - 1 = \frac{1}{\varepsilon_0} N_{\rm e}\alpha_{\rm e}. \tag{5}$$

Similarly, the permittivity of h-BN can be given by

$$\varepsilon - 1 = \frac{1}{\varepsilon_0}(N_{\rm e}\alpha_{\rm e} + N_{\rm a}\alpha_{\rm a} + N_{\rm d}\alpha_{\rm d} + N_{\rm s}\alpha_{\rm s}), \tag{6}$$

where the four terms are electronic polarizability $\alpha_{\rm e}$, atomic (ionic) polarizability $\alpha_{\rm a}$, dipole orientation polarizability $\alpha_{\rm d}$, and interfacial or space charge polarizability $\alpha_{\rm s}$. However, when we consider the microwave region, the interfacial polarization should not be included, because it only occurs at the zero frequency. Correspondingly, we note from Eq. (5) that the value of $N_{\rm e}\alpha_{\rm e}$ can be determined by ε_{∞}.

The atomic polarizability arises due to the displacements of the positive ions with respect to the negative ions. The atomic (ionic) polarizability can be given by

$$\alpha_{\rm a} = \frac{e^2}{\left(\dfrac{\partial^2 \psi_{\rm E}}{\partial R^2}\right)\Big|_{R=0}}, \tag{7}$$

where $\psi_{\rm E}$ is the potential energy. For h-BN, the potential energy is commonly given by[19]

$$\psi_{\rm E} = -\frac{Ae^2}{4\pi\varepsilon_0 R} + bR^{-n}, \tag{8}$$

where R is the interionic distance and approximately equal to the length of the B–N bond, A is the Madelung parameter, i.e., 1.3,[30] n is a constant occurring in the repulsion term of the potential function for the crystal, and b is the pre exponential factor and can be expressed as

$$b = \frac{AR^{n-1}e^2}{6n}. \tag{9}$$

So, the atomic (ionic) polarizability may be simplified to[19]

$$\alpha_{\rm a} = \frac{4\pi\varepsilon_0 R^3}{A(n-1)}, \tag{10}$$

with n being given by

$$n = 1 + \frac{72\pi\varepsilon_0 R^4}{Ae^2} M', \tag{11}$$

where M' is the bulk modulus, ie., 36.5 GPa. From Eq. (11), the value of n is determined to be 8.68. However, it is known that covalent and ionic bonds coexist in h-BN. So we should consider the proportion of ionic part $f_{\rm i}$. Accordingly, equation (7) may be written as

$$\alpha_{\rm a} = \frac{4\pi\varepsilon_0 R^3}{A(n-1)} \times f_{\rm i} = \frac{\pi\varepsilon_0 R^3}{A(n-1)}. \tag{12}$$

In fact, the bond length R may change with temperature, i.e.,

$$R^3 = R_0^3[1 + 3\beta_1(T - T_0)], \tag{13}$$

where R_0 is the bond length at 300 K, and β_1 is the temperature coefficient of the bond length.

Moreover, the number of ion pairs may be written as

$$N_{\rm a} = \frac{N_{\rm A}\rho_0}{M}[1 - 3\beta_2(T - T_0)], \tag{14}$$

where ρ_0 is the density of h-BN at room temperature, ie., 2.34 g/cm^3, and β_2 is the average thermal expansion coefficient of h-BN. The orientational polarization should be expressed as a function of the impurity ions and defects, i.e.,

$$N_{\rm d}\alpha_{\rm d} = N_{\rm dim}\alpha_{\rm dim}. \tag{15}$$

The polarizability and the number of impurities or defects can be expressed as

$$\alpha_{\rm dim} = \sum (q\delta)^2/12kT, \tag{16}$$

$$N_{\rm dim} = \sum p_{\rm im}\rho_0 N_{\rm A}/m_{\rm im}, \tag{17}$$

where q is the charge of impurity ions or defects, δ is the typical jumping distance, which has the same order as the lattice constants, $m_{\rm im}$ is the molar mass, and $p_{\rm im}$ is the concentration.

Using Eqs. (6)–(17), we have

$$\begin{aligned}\varepsilon - 1 &= \frac{1}{\varepsilon_0}(N_{\rm e}\alpha_{\rm e} + N_{\rm a}\alpha_{\rm a} + N_{\rm d}\alpha_{\rm d}) \\ &= \varepsilon_\infty[1 - 3\beta_2(T - T_0)] + \frac{\pi\varepsilon_0 R_0^3\rho_0 N_{\rm A}}{\varepsilon_0 MA(n-1)} \\ &\quad \times [1 + 3\beta_1(T - T_0)][1 - 3\beta_2(T - T_0)] \\ &\quad + \frac{p_{\rm im}\rho_0 N_{\rm A}(q\delta)^2}{12k\varepsilon_0 T m_{\rm im}}.\end{aligned} \tag{18}$$

Cole and Cole[31] have proposed an empirical function for complex permittivity ε'

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 + ({\rm i}\omega\tau)^\beta}, \tag{19}$$

where ω is the angular frequency of the oscillation of the electric field; β is the parameter that describes the symmetric and asymmetric broadening of the relaxation time distribution, $0 < \beta < 1$; and τ is the average relaxation time, which can be obtained from the dielectric spectrum of h-BN.[7]

Consequently, the microwave permittivity (at 10 GHz) of h-BN at 300–1600 K can be calculated using Eqs. (6)–(19). In order to validate our calculation results, a comparison between the theoretical results and the experimental data should be made.

Actually, the boron nitride sample must contain some pores, because its density is lower than that of the dense sample, i.e., 2.34 g/cm^{-3}. So, the permittivity of the porous boron nitride sample ($\varepsilon'_{\rm p}$) is calculated from the following expression:

$$\varepsilon'_{\rm p} = \varepsilon'_{\rm d}(1 - s), \tag{20}$$

where $\varepsilon'_{\rm d}$ is the permittivity of the dense sample, which can be calculated from Eqs. (18) and (19), and s is the porosity given by

$$s = 1 - \frac{\rho({\rm porous})}{\rho({\rm dense})}. \tag{21}$$

Figure 1 shows the comparison between the results from our calculations and those from the measurements using the circular cavity method. The consistence reveals that our calculation method is reliable for obtaining the microwave permittivity of h-BN, which is very useful for high-temperature applications of h-BN as high-temperature semiconductors and temperature sensors.

4.3. Temperature dependence of the permittivity of h-BN

In order to calculate the temperature variation of the permittivity ($\mathrm{d}\varepsilon/\mathrm{d}T$), three factors relating to the expansion and polarizability of the material have been studied by Bosman,[12] who considered them in light of the Clausius–Mosotti equation and expressed the temperature dependence at a constant pressure p in the form

$$\begin{aligned}&\frac{1}{(\varepsilon-1)(\varepsilon+2)}\left(\frac{\partial\varepsilon}{\partial T}\right)_P \\ &= -\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P + \frac{V}{\alpha_{\rm m}}\left(\frac{\partial\alpha_{\rm m}}{\partial V}\right)_T\left(\frac{1}{3V}\right)\left(\frac{\partial V}{\partial T}\right)_P \\ &\quad + \frac{1}{3\alpha_{\rm m}}\left(\frac{\partial\alpha_{\rm m}}{\partial T}\right)_V \\ &= A + B + C.\end{aligned} \tag{22}$$

It has been shown in the above section that formula (6) can be applied to describe the permittivity of h-BN. So the temperature dependence of the permittivity can be obtained by the differentiation of formula (6) with respect to temperature at a constant pressure

$$\begin{aligned}\varepsilon_0\left(\frac{\partial\varepsilon}{\partial T}\right)_P &= \left(\frac{\partial N}{\partial T}\right)_P\alpha_{\rm m} + N\left(\frac{\partial\alpha_{\rm m}}{\partial N}\right)_T \\ &\quad \times \left(\frac{\partial N}{\partial T}\right)_P + \left(\frac{\partial\alpha_{\rm m}}{\partial T}\right)_V N,\end{aligned} \tag{23}$$

where $\alpha_{\rm m} = \alpha_{\rm e} + \alpha_{\rm a} + \alpha_{\rm d}$. In terms of individual components, the temperature derivative of the static permittivity is expressed as

$$\varepsilon_0\left(\frac{\partial\varepsilon}{\partial T}\right)_P = \left(\frac{\partial N_\mathrm{e}}{\partial T}\right)_P\alpha_\mathrm{e} + N_\mathrm{e}\left(\frac{\partial\alpha_\mathrm{e}}{\partial N}\right)_T\left(\frac{\partial N_\mathrm{e}}{\partial T}\right)_P + \left(\frac{\partial\alpha_\mathrm{e}}{\partial T}\right)_V N_\mathrm{e} + \left(\frac{\partial N_\mathrm{a}}{\partial T}\right)_P\alpha_\mathrm{a} + N_\mathrm{a}\left(\frac{\partial\alpha_\mathrm{a}}{\partial N}\right)_T\left(\frac{\partial N_\mathrm{a}}{\partial T}\right)_P + \left(\frac{\partial\alpha_\mathrm{a}}{\partial T}\right)_V N_\mathrm{a} + \left(\frac{\partial N_\mathrm{d}}{\partial T}\right)_P\alpha_\mathrm{d} + N_\mathrm{d}\left(\frac{\partial\alpha_\mathrm{d}}{\partial N}\right)_T \times\left(\frac{\partial N_\mathrm{d}}{\partial T}\right)_P + \left(\frac{\partial\alpha_\mathrm{d}}{\partial T}\right)_V N_\mathrm{d}. \quad (24)$$

Considering that

$$\left(\frac{\partial N_\mathrm{e}}{\partial T}\right)_P = \left(\frac{\partial N_\mathrm{a}}{\partial T}\right)_P = -N_0\beta_2,$$
$$\left(\frac{\partial N_\mathrm{d}}{\partial T}\right)_P = -\sum\frac{N_0 M p_\mathrm{im}}{m_\mathrm{im}}\beta_2,$$

where β_2 is the thermal expansion, we can write Eq. (24) as

$$\left(\frac{\partial\varepsilon}{\partial T}\right)_P = -\frac{N_0\beta_2}{\varepsilon_0}\left(\alpha_\mathrm{e}+\alpha_\mathrm{a}+\sum\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\alpha_\mathrm{d}\right) - \frac{NN_0\beta_2}{\varepsilon_0}\left[\left(\frac{\partial\alpha_\mathrm{e}}{\partial N}\right)_T + \left(\frac{\partial\alpha_\mathrm{a}}{\partial N}\right)_T + \sum\left(\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\right)^2\left(\frac{\partial\alpha_\mathrm{d}}{\partial N_\mathrm{d}}\right)_T\right] + \frac{N}{\varepsilon_0}\left[\left(\frac{\partial\alpha_\mathrm{e}}{\partial T}\right)_V + \left(\frac{\partial\alpha_\mathrm{a}}{\partial T}\right)_V + \sum\left(\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\right)^2\left(\frac{\partial\alpha_\mathrm{d}}{\partial N_\mathrm{d}}\right)_P\right]. \quad (25)$$

It's assumed that the sum of the electronic polarization and the ionic polarization is equal to the high-frequency permittivity ε_h, as the orientation polarization is negligible at the high frequency, i.e., $\varepsilon_\mathrm{h} = N(\alpha_\mathrm{e}+\alpha_\mathrm{a})/\varepsilon_0+1$, so the above equation can be simplified to

$$\left(\frac{\partial\varepsilon}{\partial T}\right)_P = -\left[\beta_2(\varepsilon_{\mathrm{h}0}-1)+\sum\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\alpha_\mathrm{d}\right] - \frac{NN_0\beta_2}{\varepsilon_0}\left[\left(\frac{\partial\alpha_\mathrm{e}}{\partial N}\right)_T + \left(\frac{\partial\alpha_\mathrm{a}}{\partial N}\right)_T + \sum\left(\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\right)^2\left(\frac{\partial\alpha_\mathrm{d}}{\partial N_\mathrm{d}}\right)_T\right] + \frac{N}{\varepsilon_0}\left[\left(\frac{\partial\alpha_\mathrm{e}}{\partial T}\right)_V + \left(\frac{\partial\alpha_\mathrm{a}}{\partial T}\right)_V + \sum\left(\frac{Mp_\mathrm{im}}{m_\mathrm{im}}\right)^2\left(\frac{\partial\alpha_\mathrm{d}}{\partial T}\right)_V\right] = A+B+C, \quad (26)$$

where $A = A_\mathrm{e}+A_\mathrm{a}+A_\mathrm{d}$, $B = B_\mathrm{e}+B_\mathrm{a}+B_\mathrm{d}$, $C = C_\mathrm{e}+C_\mathrm{a}+C_\mathrm{d}$, A and B are the volume-dependent contributions, and C describes the direct-temperature effect.

4.3.1. Volume-dependent terms

The volume derivatives of electronic polarizability and ionic polarizability at a constant temperature are given by[13,15]

$$\left(\frac{\partial\alpha_\mathrm{e}}{\partial V}\right)_T = \frac{\alpha_\mathrm{e}}{3\alpha V}\left[n-\frac{2}{n-1}+1\right] \times(2\alpha_{\mathrm{f}-}-\alpha_{\mathrm{f}+})\left(1-\frac{e^*}{e}\right), \quad (27)$$

$$\left(\frac{\partial\alpha_\mathrm{a}}{\partial V}\right)_T = \frac{\alpha_\mathrm{a}}{V}\left[\frac{(n+1)^2-2(n+1)+2}{3(n-1)}\right], \quad (28)$$

where $e^*/e = q^*$ is the effective ionic charge, and $\alpha_{\mathrm{f}-}$, $\alpha_{\mathrm{f}+}$ are the free ion polarizabilities of the cation and anion, respectively.

Based on the relation $N = 4\pi\varepsilon_0/V$, the volume derivative of the polarizability at a constant temperature becomes

$$\left(\frac{\partial\alpha}{\partial V}\right)_T = -\frac{1}{4\pi\varepsilon_0 N^2}\left(\frac{\partial\alpha}{\partial N}\right)_T. \quad (29)$$

Thus, equations (27) and (28) are expressed as

$$\left(\frac{\partial\alpha_\mathrm{e}}{\partial N}\right)_T = \frac{\alpha_\mathrm{e}}{12\pi\varepsilon_0 N^2\alpha V}\left[\frac{2}{n-1}-(n+1)\right] \times(2\alpha_{\mathrm{f}-}-\alpha_{\mathrm{f}+})\left(1-\frac{e^*}{e}\right), \quad (30)$$

$$\left(\frac{\partial\alpha_\mathrm{a}}{\partial N}\right)_T = \frac{-\alpha_\mathrm{a}}{12\pi\varepsilon_0 N^2 V} \times\left[\frac{(n+1)^2-2(n+1)+2}{(n-1)}\right]. \quad (31)$$

In the case of perfect crystals, the polarizability α_m of a macroscopic sphere can be separated into two parts, i.e., electronic polarization and ionic polarization. However, the crystals have some impurities and defects, which are involved due to the preparation process. So the derivative of α_d needs to be obtained. From Eq. (16), we have

$$\left(\frac{\partial\alpha_\mathrm{d}}{\partial N}\right)_T = \frac{q^2\delta}{6kT}\left(\frac{\partial\delta}{\partial N}\right)_T, \quad (32)$$

where

$$\left(\frac{\partial\delta}{\partial N}\right)_T = -\frac{1}{3}N^{-4/3}. \quad (33)$$

4.3.2. Direct temperature effect

By using the model proposed by Havinga, the temperature effects of electronic polarizability and ionic polarizability at a constant volume can be expressed as

$$C_{\rm e} = \left(\frac{\partial \alpha_{\rm e}}{\partial T}\right)_V = Rk\left(\frac{\partial \alpha_{\rm e}}{\partial V}\right)_T \left[\left(\frac{V}{\alpha_{\rm e}}\left(\frac{\partial \alpha_{\rm e}}{\partial V}\right)_T - 1\right)\right], \quad (34)$$

$$C_{\rm a} = \left(\frac{\partial \alpha_{\rm a}}{\partial T}\right)_V = \frac{4\pi\varepsilon_0 k R_0}{Ae^2}\left(\frac{3.15}{z-1}P - Q\right), \quad (35)$$

where k is the isothermal compressibility, and P and Q are functions of the derivatives of the short-range repulsive potential. It can be seen from Eq. (8) that the repulsive term of h-BN is $\psi = bR^{-n}$. Then we have

$$P = \frac{(n^2+2n+7)(n+2)^2}{(n-1)^3}, \quad (36)$$

$$Q = \frac{(n+1)(n+2)}{n-1}. \quad (37)$$

The temperature derivative of orientational polarizability is

$$C_{\rm d} = \left(\frac{\partial \alpha_{\rm d}}{\partial T}\right)_V = -\frac{q^2\delta^2}{12kT^2}. \quad (38)$$

The results of the theoretical values of A, B, and C for h-BN are presented in Table 4. Obviously, similar to the NaCl structure, it has a positive temperature dependence of the permittivity, i.e., $\mathrm{d}\varepsilon/\mathrm{d}T = 1.995 \times 10^{-5}$ K^{-1}, which agrees with the average measured value of $\mathrm{d}\varepsilon/\mathrm{d}T = 2.43 \times 10^{-5}$ K^{-1}.

Table 4. Temperature dependences of permittivity and parameters A, B, C, n, and z for three compounds.

	$A/10^{-5}$ K^{-1}	$B/10^{-5}$ K^{-1}	$C/10^{-5}$ K^{-1}	$(\mathrm{d}\varepsilon/\mathrm{d}T)/10^{-5}$ K^{-1}	n	z
h-BN	–5.53	0.255	7.27	1.995	8.68	3
NaCl	–3.8	7.2	1.8	0.037	8	6
CsCl	–4.1	7.7	–1.5	0.02	7.8	8

As shown in the above discussion, the microwave permittivity increases at high temperature. Actually, when the temperature dependence is considered in Eq. (18), we can find that the first (electric polarization contribution), the second (ionic polarization contribution), and the third (orientational polarization contribution) terms are functions of temperature. The contributions of electronic, ionic, and orientation polarizations according to Eq. (18) are shown in the inset of Fig. 2, respectively. It is worth noting that the sum of the three polarization contributions plus one should be the value of the permittivity. The measured data are also given in Fig. 2 for comparison. It can be seen that the value of the permittivity of h-BN mainly comes from the contribution of the electronic polarization. This should be ascribed to the high deformation of the electron cloud under the external field. With the increasing temperature, the contribution of the electronic polarization decreases due to the fall in density. However, the ionic polarizablity is enhanced due to the greater displacements in the ions, while the orientational polarization drops. Hence, if the influence from the increased ionic polarization is larger than that from the decreased density and the orientational polarization, we may obtain a positive temperature coefficient of the permittivity, i.e., $\mathrm{d}\varepsilon/\mathrm{d}T > 0$.

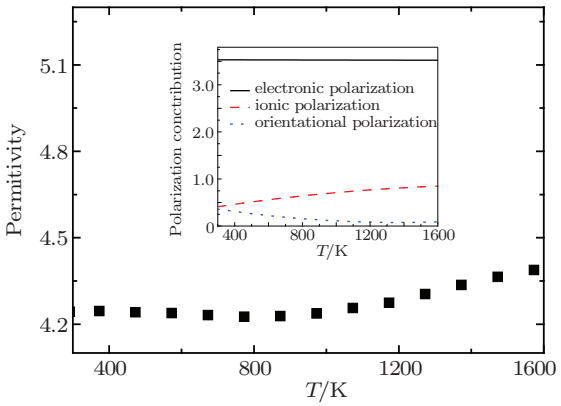


Fig. 2. (colour online) Measured permittivity of h-BN (at 10 GHz). The inset shows, respectively, the contributions of electronic polarization, ionic polarization, and orientational polarization.

It is also found that the C term is mainly affected by the ionic contribution term $C_{\rm a}$. From Eq. (35), it is obvious that the $C_{\rm a}$ term depends on the value of $[3.15/(z-1)]P - Q$, which can be expressed as a function of n and z

$$\frac{3.15}{z-1}P - Q = \frac{3.15(n^2+2n+7)(n+2)^2}{(z-1)(n-1)^3} - \frac{(n+1)(n+2)}{(n-1)}. \quad (39)$$

If the value of the C term is positive, the following expression is obtained:

$$\frac{3.15(n^2+2n+7)(n+2)^2}{(z-1)(n-1)^3} - \frac{(n+1)(n+2)}{(n-1)} > 0. \quad (40)$$

Hence

$$z < \frac{3.15(n^2+2n+7)(n+2)}{(n^2-2n+1)(n-1)} + 1. \qquad (41)$$

Similarly, in the case of the ionic crystal, the repulsive potential is described by the Born–Mayer function, and if the value of the C term is positive, it is deduced that

$$z < \frac{3.15((n+1)^4+6(n+2)^2}{(n+1)^2(n-3)} + 1. \qquad (42)$$

This means that the C term really is a structural effect, which is affected by the repulsive term n and the number of nearest neighbors z. So, we can draw the conclusion that the temperature dependence of the permittivity, i.e., $\mathrm{d}\varepsilon/\mathrm{d}T$, may depend on the structure parameters, i.e., n and z. Table 4 also gives the n and z values of h-BN, NaCl, and CsCl compounds to study how the structure parameters n and z affect the C term. In the case of h-BN, the value of n is approximately equal to 8.68, and it is deduced from Eq. (41) that $z < 8.5$ when the value of the C term is positive. For NaCl and CsCl compounds, $z < 6.6$ is obtained from Eq. (42) when the value of the C term is positive. The larger value of the number of nearest neighbors in CsCl ($z = 8$) than that in NaCl ($z = 6$) and in h-BN ($z = 3$) may result in the negative value of its C term. The physical nature of the influence of z on the C term is discussed with the use of the potential energy. For CsCl, the sum of the potential energy under the equilibrium condition is

$$\psi_{\mathrm{E}_0} = -\frac{Ae^2}{4\pi\varepsilon_0 R_0}\{1-\exp[(-(n+1)]\}, \qquad (43)$$

where the Madlung constant A is also a structure factor, which is known to be proportional to the number of nearest neighbors z. Hence, it can be seen from Eq. (43) that the greater number of nearest neighbors of the CsCl structure compounds may result in the higher potential energy. If this potential energy is larger than the energy caused by temperature, it may hinder the displacements of the polarized ions when the temperature increases. Consequently, this may lead to the decrease in the polarizability α, and the value of the C term may be negative.

5. Conclusion

In summary, based on the determination of the modified definition of the local electric field of h-BN, the microwave permittivity and its temperature dependence are studied.

Three effects contribute to the temperature dependence of the permittivity of h-BN. Our analyses show that the microwave permittivity increases with increasing temperature, which is attributed to the positive temperature coefficient of the ionic polarizability at a constant volume.

The C term really is a structural effect, which is affected by the ionic repulsive term n and the number of nearest neighbors z. A greater value of z may result in a large ionic potential energy, which may hinder the displacements of the polarized ions when the temperature increases, thus leading to a decrease in the polarizability α, and the value of the C term may be negative.

The comparison between the calculated permittivity of h-BN and the experimental data reveals that our calculation method is reliable in obtaining the microwave permittivity. This work is of importance with regard to applications that employ h-BN at high temperature and high frequency.

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