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Local electric field investigation of Si_2N_2O and its electronic structure, elastic and optical properties

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ABSTRACT

This paper demonstrates that the Clausius–Mosotti equation cannot be used for Si_2N_2O since the Lorenz approximation is invalid therein. Therefore a modified definition for the Lorenz electric field is suggested which can be derived from the optical dielectric constant calculated using the plane-wave pseudopotential method. In addition, other parameters of Si_2N_2O such as the energy band gap, density of states, elastic and optical properties are also given in this paper. Based on the new expression for local electric field, the modified Clausius–Mosotti equation is suggested, and then the dielectric constant of Si_2N_2O is discussed by using the additivity rule. It is found that the result of the phenomenological analysis of the dielectric constant is basically consistent with the experimental data and the first principles results, which explain the experimental observation that the dielectric constant of Si_2N_2O is enhanced with the increase of Li content. Also, the modified Clausius–Mosotti equation and the additivity rule are suggested to be used in predicting the dielectric behaviors of the new and complex compounds.

1. Introduction

Silicon oxynitride (Si_2N_2O) is a unique compound in the SiO_2–Si_3N_4 quasi-binary [1]. Like Si_3N_4, Si_2N_2O, it is a engineering material which can keep excellent oxidation resistance in air of up to 1600 °C and high flexural strength up to 1400 °C without degradation [2–5]. It is also an important link between two major classes of materials of great technological importance, Si_3N_4 and SiO_2. Many theoretical studies have concerned on the electronic structure of Si_2N_2O due to the fact that the electronic structure calculations have become more important in the fields of physics and chemistry. On the basis of the first principles of orthogonalized-linear-combination-of-atomic-orbitals (OLCAO) method, Ching et al. [6] has predicted that the indirect band gap of Si_2N_2O is 5.97 eV whereas its valence-band DOS can be approximately regarded as a superposition of α-SiO_2 and β-Si_3N_4 crystals with an exception at the top of the valence-band edge, which is derived from the oxygen lone-pair orbitals. Because of the feasibility of using SiO_xN_y glass as a gradient index optical material [7], understanding on the intrinsic optical properties of the Si_2N_2O solids is certainly a matter of great importance. Xu and Ching [8] have calculated the optical dielectric function of Si_2N_2O by the means of self-consistent LDA calculations of the first principles. But limited reports have concerned on other optical properties such as reflectivity, loss function and conductivity by using the calculation method of the first principles.

Recently, a new synthesizing method to prepare Si_2N_2O with Li_2O additive gives good dielectric properties ($\varepsilon' = 6.17$, $\tan\delta = 0.0008$) [9]. Thus, the good dielectric properties of Si_2N_2O mean that it can be used for many potential applications such as high temperature electric insulator, nuclear-reactor moderator or reflector, and materials for solid electrolytes. However, little work has been carried out on the theoretical prediction of the dielectric constant of Si_2N_2O based on the investigation of its local electric field.

As is well known, the Clausius–Mosotti formula gives a remarkably good approximation to the effective dielectric constant of mixtures and materials containing several phases [10,11]. This equation can be given as [12],

$$\frac{\varepsilon - 1}{\varepsilon - 1 + (4\pi/L)} = \frac{L}{V_m}\alpha_m \qquad (1)$$

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$$\alpha_m = \sum_i N_i \alpha_i \tag{2}$$

where V_m represents the molecular volume, ε, the dielectric constant, L, the Lorenz factor taken equally to $L_0 = 4\pi/3$. This expression is of importance for dielectric material as it provides a physical description of the interaction of electromagnetic field with the materials.

However, until now there has been a wide controversy in the literature with arguments both for and against the Clausius–Mosotti limit [13–15]. Moreover, the proposal of this formula is based on the symmetry structure of the cubic crystal, and it would be desirable to consider if this type of equation could be extended to predict the dielectric constant of non-cubic materials such as Si_2N_2O solids.

Consequently, the aim of this paper is to make theoretical analysis of the dielectric constant of Si_2N_2O with a view of its local electric field. Firstly, first principles calculations are performed on the band structure, density of states, elastic and optical properties of Si_2N_2O by using the plane-wave pseudopotential method, which are used as reference data for analyzing the optical properties of more complicated SiO_xN_y compounds. And the calculated optical dielectric constant is used for the key parameter to obtain a modified definition of the local electric field for the reason that the Lorenz approximation is invalid therein. Then the dielectric constant of Si_2N_2O is mainly studied according to the modified Clausius–Mosotti and the additivity rule.

2. Computational details

First principles calculations are performed on Si_2N_2O crystal based on density-functional theory through the Cambridge Sequential Total Energy Package (CASTEP) with the Vanderbilt-type ultrasoft pseudopotential and local density approximations (LDA), respectively. This Method has shown a great success in describing and predicting the properties of materials [16–21]. For the CASTEP computer code, the Kohn–Sham equations are solved within the framework of density functional theory by expanding the wave functions of the valence electrons in a basis set of plane waves with a kinetic energy smaller than a specified cut-off energy E_{cut}. The kinetic energy cutoff for the plane waves is 450 eV, and the Brillouin-zone sampling mesh parameters for the k-point set are $6 \times 6 \times 6$. Before any electronic structure calculations are carried out, the cell parameters and the atomic positions within a unit cell are optimized by employing BFGS (proposed by Broyden, Fletcher, Goldfarb, and Shannon) minimization algorithm.

3. Results and discussion

3.1. Ground state behaviors

X-ray powder diffraction data is used as a starting point for geometry optimization. The Si_2N_2O has an orthorhombic crystalline structure [22,23] with lattice constants of $a = 8.843$ Å, $b = 5.437$ Å, and $c = 4.853$ Å. The building block of this crystal is a slightly distorted SiN_3O tetrahedral unit which links together to form a three-dimensional network. The energy scale is measured in ev and the top of the valence band (VB) is set to zero on this energy scale. The direct band gap is found to be 5.08 ev between the maximum of the valence-band at Γ and the minimum of the conduction-band at Γ. In this work, the band structure for Si_2N_2O is in agreement with Xu and Ching's results calculated by a OLCAO method [8]. Fig. 1 shows that the total density of state (TDOS) and the partial density of state (PDOS) of Si_2N_2O. One may note from the Fig. 1 that the valence bands actually consist of three groups of bands of widths roughly 1.96, 4.43, 9.80 ev, separated by gaps of 0.05 and 2.12 ev. And it can be seen from Fig. 1 that the lowest lying states of N and O *2p* states overlap with the Si *3s* states locating at around −10.21 to −8.06 eV. The states extending from −8.06 ev to the Fermi level originated mainly from N and O *2p* orbitals with slight contributions from Si *3p* states. The electronic states above the Fermi level are dominated by the Si *s*–*p* hybridization. The features are in good consistence with those reported by other researchers [8,24].

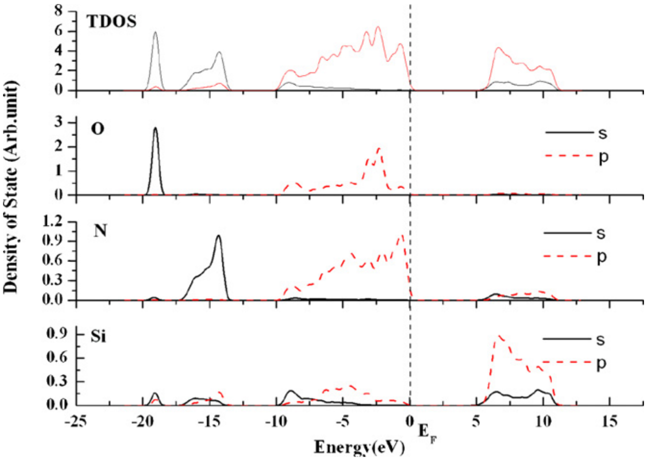

Fig. 1. The density of states and partial density of states for Si_2N_2O.

It is well known that the Bulk modulus is related to the average atomic bond strength, which is strongly correlated to cohesive energy, whereas the shear and young's modulus are associated with material intrinsic hardness. And the theoretical polycrystalline elastic modulus for Si_2N_2O may be calculated from these independent elastic constants, shown in Table 1. In contrast, we list the results calculated by other methods [25] and the measured data [26]. However, small deviations are noted in C_{11}, C_{12}, C_{22}, $C_{23.}$ But the measured shear modulus for Si_2N_2O matches very well with our calculated values.

The elastic anisotropy (A) of crystals can exert a great influence on the properties of physical mechanisms, such as anisotropic plastic deformation, crack behavior, and elastic instability. Thereby, it is important to calculate elastic anisotropy in order to obtain a comprehensive understanding on the properties of such material. For orthorhombic Si_2N_2O, the result of the anisotropy factor A calculated by a equation of $A = 2C44/(C_{11} - C_{12})$ [27] is 1.20. In addition, the percentages of anisotropy in compressibility and shear are also calculated by bulk modulus factors $A_B = (B_V - B_R)/(B_V + B_R)$ and shear modulus factors $A_G = (G_V - G_R)/(G_V + G_R)$ [28], respectively, in which B and G represent the bulk and shear modulus, and the subscripts V and R denote the Voigt and Reuss approximations. For

Table 1
Elastic constants for Si_2N_2O.

	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E
This work	330.4	104.3	66.4	278.2	51.5	329.2	135.5	62.3	75.0	152.3	92.4	242.4
LDA/UPP [25]	316.0	81.3	51.5	241.6	31.0	320.7	139.1	59.7	76.2	132.7	97.1	234.2
GGA/UPP	313.9	84.0	53.6	252.3	36.5	320.3	136.7	61.6	76.0	136.4	97.3	235.8
Experiment [26]											93.1	221.6

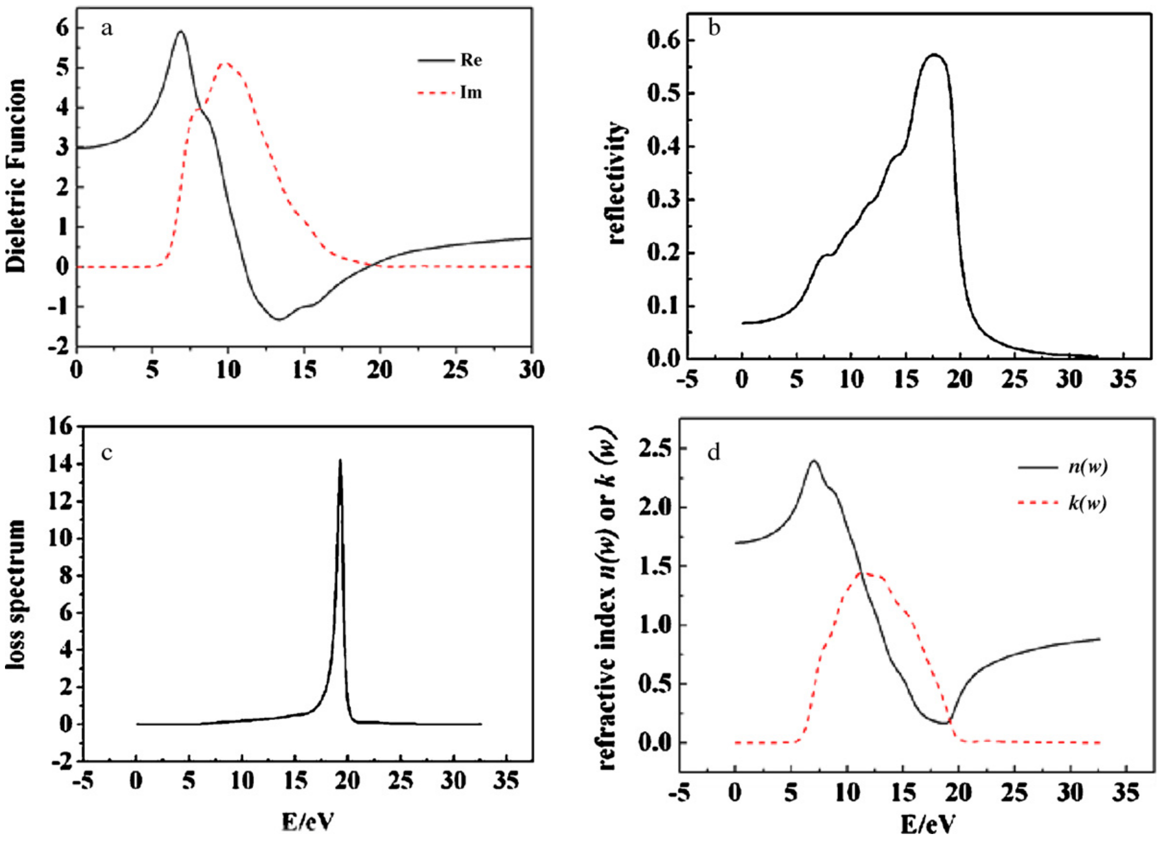

Fig. 2. The calculated optical properties for Si_2N_2O.

Si_2N_2O, $A_B = 0.43\%$ and $A_G = 5.04\%$ with our DFT calculation. These results indicate that Si_2N_2O is slightly anisotropic in compressibility while it is greatly anisotropic in shear modulus. Moreover, the ratio B/G can be used to estimate the ductility of the material [28–30], and from the bulk and shear modulus calculated in this work for Si_2N_2O, one obtains $B/G = 1.65$. This B/G ratio suggests that the Si_2N_2O crystal has an increasing toughness of more than 98% compared with diamond.

3.2. Optical properties

Fig. 2 shows the calculated optical properties are at the equilibrium lattice constant in an energy ranging from 0 to 35 eV. To account for the structures observed in the optical spectra, it is customary to consider transitions from the occupied to unoccupied bands in the electronic energy band structure especially at high symmetry points in the Brillouin zone. The calculated real and imaginary parts of dielectric function for Si_2N_2O from the Krames–Kronig analysis are shown in Fig. 2(a). The zero frequency limit of $\varepsilon_1(\omega)$ is the electronic part of the static optical dielectric constant $\varepsilon_1(0)$, which is sometimes denoted as ε_∞. Obviously, it is noted from the Fig. 2(a) that the calculated static optical dielectric constant ε_∞ of Si_2N_2O is 2.98. This value is in excellent consistent with the results of other methods [6,8]. Also, it is seen that the real and imaginary parts of dielectric function have one peak at about 6 eV and 5 eV, respectively. This energy peak is attributed to the transition of electron excitation from the VB to the CB in the electronic energy band structure. The calculated reflectivity spectrum, i.e., $R(\omega)$ and loss spectrum, i.e., $L(\omega)$, are shown in Fig. 2(b) and (c). The electron energy loss function $L(\omega)$ is an important factor describing the energy loss of a fast electron traversing in a material. Prominent peaks in $L(\omega)$ spectra represent the characteristics associated with the plasma oscillations and the corresponding frequencies are the so-called bulk plasma frequency $\omega(p)$, which occurs where $\varepsilon_2 < 1$ and ε_1 reaches zero point [31]. Obviously, one may note from the Fig. 2(b) and (c) that the peak of $L(\omega)$ is at about 17.58 eV, which corresponds to an abrupt reduction of $R(\omega)$. The refractive index provides useful information about the optical properties of the material. The extinction coefficient directly describes the attenuation of electromagnetic waves within the material and is also known as a damping constant or attenuation coefficient. The refractive index and the extinction coefficient are given in Fig. 2(d). The static refractive index $n(0)$ is found to have a value of 1.70. This value increases with the energy increasing in the transparency region and reaches its peak in the ultraviolet at about 2.40 eV. It is decreased to the minimum at 0.17 eV. The origin of the structures in the imaginary part of the dielectric function also explains the structures in the refractive index. The local maxima of the extinction coefficient $k(\omega)$ corresponds to the zero of $\varepsilon_1(\omega)$. Our calculated optical constants of the dielectric function, absorption spectrum, refractive index, extinction coefficient, reflectivity, and energy loss coefficient are in good agreement with the results of other calculation methods [8] and can be used as reference data for analyzing the optical properties of more complicated SiO_xN_y compounds.

3.3. Local electric field

It is assumed that the actual electric field E is seen by a dipole, i.e., its local electric field, E_{local}, is given by the following:

$$E_{\mathrm{local}} = E_{\mathrm{a}} + E_{\mathrm{LOR}} + E_{\mathrm{near}} \tag{3}$$

where, E_{a} stands for the external electric field, E_{LOR} for the contribution of the atoms or ions outside the sphere (called as Lorenz electric field), and E_{near} for the contribution of the sources inside the sphere while excluding the central dipole (on the principle that the electric field of the central dipole does not act on itself).

Table 2
The value of ε_∞ of different γ.

γ	0	0.2	0.5	0.8	1.0
ε_∞	3.04	3.38	4.09	6.82	7.35

There are two assumptions introduced to the Lorenz approximation. Firstly, the spatial dimension of a molecule is assumed to be small enough that the local electric field can be taken to be consistent with the whole molecule. In this premise, the polar particle is treated as a point-dipole. However, if the distance of the ions is short, the point-dipole approximation is invalid therein, and the interaction between the particles cannot be ignored. Secondly, it is assumed that the near electric field (E_{near}) can be approximately considered as the sum of the contributions from the point dipoles at the lattice points inside the auxiliary sphere. If the crystal has a cubic symmetry, the electric field of the sources inside the sphere would be zero, i.e., $E_{\text{near}} = 0$. It is known that Si_2N_2O has an asymmetric structure which belongs to the space group C_{2v}^{12}. Hence, the contributions of the sources inside the sphere may not be ignored. Accordingly, it is necessary to consider the contributions of the overlap electron clouds to the local electric field, simple to say, a modified definition should be introduced to the local electric field of Si_2N_2O. Eq. (1) is accordingly replaced by,

$$\frac{\varepsilon - 1}{\gamma(\varepsilon - 1) + (4\pi/L)} = \frac{L}{\varepsilon_0 V_m}\alpha_m \tag{4}$$

where γ stands for the modified definition for the local electric field, $0 \le \gamma \le 1$.

Also, the optical dielectric constant ε_∞ is given by,

$$\frac{\varepsilon_\infty - 1}{\gamma(\varepsilon_\infty - 1) + (4\pi/L)} = \frac{L}{\varepsilon_0 V_m}\alpha_e \tag{5}$$

where α_e represents electronic polarizability of Si_2N_2O. Correspondingly, one may note from Eq. (5) that the value of γ can be determined by ε_∞ and α_e. The value of electronic polarizability α_e of Si_2N_2O is known as,

$$\begin{aligned}\alpha_e(Si_2N_2O) &= 2\alpha_e(Si^{4+}) + 2\alpha_e(N^{3-}) + \alpha_e(O^{2-}) \\ &= 10.45 \times 10^{-40} F \cdot m^2\end{aligned} \tag{6}$$

Therefore, we can obtain the value of ε_∞ by combining Eqs. (5) and (6) with different value of γ, seen in Table 2. And ε_∞ can be obtained by a plane-wave pseudopotential method in the Section 3.2, which is equal to 2.98. Therefore, it is deduced that an appropriate factor of γ is approximately equal to zero from Table 2. If $\gamma = 0$, the expression (5) has the following form,

$$\frac{\varepsilon - 1}{4\pi} = \frac{\alpha_m}{\varepsilon_0 V_m} \tag{7}$$

It means the polarized field of Si_2N_2O generated by the polarized ions is equal to the external applied electric field for the reason that the overlapping electronic clouds of Si_2N_2O are so great that they would make the Lorenz electric field, i.e., $E_{LOR} = P/3\varepsilon_0$ be counteracted by the electric field generated by the polarized ions (E_{near}).

3.4. *Dielectric constant and the additivity rule*

The concept of additivity of molar dielectric polarizabilities according to,

$$\alpha_m(\text{complex mixture}) = \sum \alpha_m(\text{oxide components}) \tag{8}$$

has been discussed by Lasaga and Cygan [32]. In the above expression, the molecular polarizabilities (α_m) of the complex crystal can be expressed as the summation of the polarizabilities of the constituent crystal. Thus the dielectric polarizabilities and the dielectric constants of new materials or compounds whose dielectric constants have not been measured are potentially predictable by the polarizability additivity rules. On the basis of the dielectric constants of 129 oxides and 25 fluorides, Shannon [33] has derived a set of 61 ion dielectric polarizabilities from a least squares refinement procedure by using the ion additivity rule and calculated dielectric constants for about a hundred compounds in conjunction with the Clausius–Mosotti equation. Excellent agreement between the calculated polarizability values and those measured data is shown for many ternary systems such as borates, aluminates, gallates, silicates, germinates, phosphates, and vanadates, etc. So, the Clausius–Mosotti equation, and the additivity rule can be used in combination as a powerful tool for predicting the dielectric constant of any hypothetical materials. However, these discussions are based on the Clausius–Mosotti equation and here it should be necessary to ask if this additivity rule can be used for Si_2N_2O. According to the above concept of the additivity rules of molecular polarizabilities, the molecular polarizabilities Si_2N_2O can be obtained from a sum of the molecular polarizabilities of the Si_3N_4 and SiO_2,

$$\alpha_m(Si_2N_2O) = \frac{1}{2}\alpha_m(SiO_2) + \frac{1}{2}\alpha_m(Si_3N_4) \tag{9}$$

The static polarizablitiy values for SiO_2 which is 4.28×10^{-40} F m^2 [33] utilizing the Clausius–Mosotti equation with the dielectric data, and the static polarizablitiy values for Si_3N_4 is found to be 42.89×10^{-40} F m^2 according to the measured dielectric constant [34]. Correspondingly, the calculated dielectric constant is 5.63 according to Eqs. (7)–(9), which may not be consistent with the measured value 6.17 by Tong et al. [9]. However, it is found that in their experiment, some Li_2O has been used for additive to prepare Si_2N_2O, and it is observed that the dielectric constant of Si_2N_2O is enhanced with the increase of residual Li content [9]. Therefore, when a comparison is made between the predicted value and the measured value from Tong et al, the effect of Li on the dielectric constant of Si_2N_2O should be considered. Since Li easily introduces Si_2N_2O to form the point defects due to its small size, the impact of Li on the polarization of Si_2N_2O may result in the orientation polarization. The total polarizablity α_m and the dielectric constant of Si_2N_2O with Li_2O additive $\varepsilon_{\text{dope}}$ thus should be expressed as follows:

$$\alpha_m = \alpha_m(\text{pure}) + \alpha_d \tag{10}$$

$$\frac{\varepsilon_{\text{dope}} - 1}{4\pi} = \frac{\alpha_m(\text{pure})}{\varepsilon_0 V_m} + \frac{N_d \alpha_d}{4\pi\varepsilon_0} \tag{11}$$

Where the orientation polarizablity α_d and the number N_d of impurity ions or defects can be given as,

$$\alpha_d = \sum \frac{(q\delta)^2}{12KT} \tag{12}$$

$$N_d = \sum \frac{p_{im}\rho_0 N_A}{m_{im}} \tag{13}$$

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_{im} is the molar mass, and p_{im} is the concentration and the value is from the measurement [9]. Using Eqs. (11)–(13), it is found that the polarization contribution caused by Li is 0.53. Thus the calculated value of Si_2N_2O with Li_2O additive is 6.16, which agrees with the measured value 6.17 within the approximation of 0.16% uncertainty. Also, it is seen from Eqs. (11)–(13) that more concentration of Li would lead to higher dielectric constant due to the fact that more polarized ions are generated. The conclusions is key to explain the experimental observation by Tong et al. [9], who has found that the polycrystalline dielectric constant of Si_2N_2O is enhanced with the increase of residual Li content.

Recently, the effects of impurity Li atom on crystal structure, electronic and dielectric properties of Si_2N_2O are calculated by Liu et al. [35] using a Plane-wave pseudopotential total energy method and it is found that the dielectric constant of Li-doped Si_2N_2O is increased by 0.60 compared to that of pure one, which can be attributed to a reduction of band gap. Obviously, our phenomelogical analysis of dielectric constant is very well consistent with their results, which reveals that our calculation method is reliable to predict the dielectric constant of Si_2N_2O. Also, the consistence demonstrates that the modified Clausius–Mosotti equation and the additivity rule are suggested to be used in predicting the dielectric constant of Si_2N_2O, which means that the dielectric behaviors of the new and complex compounds with asymmetric structures can be obtained from those of the simple materials by adopting this method.

4. Conclusions

In summary, it is found that the Lorenz approximation cannot be used in Si_2N_2O, which shows that the interaction between the polar particles cannot be ignored. Therefore, the local electric field of the Si_2N_2O is analyzed by introducing a modified definition for the Lorenz electric field since it may dominate the polar particles motion. The modified definition parameter of local electric field is found to be equal to zero by using its optical dielectric constant, which shows that the overlap electron clouds of Si_2N_2O would make the Lorenz electric field, i.e., $E_{LOR} = P/3\varepsilon_0$ counteract by the electric field of the polar ions (E_{SPH}). And based on the determination of the modified definition of local electric field of Si_2N_2O and the additivity rule, its dielectric constant is studied. By making the comparison of the calculated results with that of other researchers, it is found that the modified Clausius–Mosotti equation and the additivity rule can be used to obtain the dielectric behaviors of the new and complex compounds.

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