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Theoretical and experimental investigations on the temperature dependence of the refractive index of amorphous silica

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ABSTRACT

Though people have experimentally studied the temperature dependence of the refractive index (RI) of optical fibers made of amorphous silica (a-SiO_2), the temperature ranges in the previous experiments are usually below 800 K, and a rigorous theoretical model for the experimental results has still been absent. In this paper, the temperature dependence of the RI of a-SiO_2 is studied theoretically and experimentally, where by means of an optical fiber delay line, the experiment is carried out in the temperature range of 301–1275 K for the first time, and the theoretical result agrees well with the experimental one. Our work has potential application in temperature sensors by means of optical fiber delay lines.

1. Introduction

It is significant for us to study the temperature dependence of the RI of a-SiO_2. For example, a fiber optic sensor can be devised by means of the temperature dependence of the RI of the optical fiber [1,2]. Historically, many experimental investigations on the temperature dependence of the RI of a-SiO_2 have been presented [3–6], while a satisfying theoretical explanation has still been absent. On the other hand, some theoretical models have been presented for the temperature dependence of the RI of monatomic crystals or diatomic ionic crystals (e.g., Refs. [7–13]), but they are not valid for the material of a-SiO_2. In the previous paper [14], we have presented a theoretical study on temperature dependence of the refractive index of optical fibers. However, we are not satisfied with the starting point of the theoretical model in Ref. [14]. Here we will present a theoretical and experimental investigations on the temperature dependence of the RI of a-SiO_2, where the theoretical model is more rigorous and the experiment will be carried out in the temperature range of 301–1275 K by means of an optical fiber delay line, for the first time.

As we know, the amorphous phase of SiO_2 differs from the crystalline phase only by the missing long-range order, however there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms. One example of this ordering is found in the preference of the network to form rings of 6-tetrahedra [15]. From comparison of the properties of materials in a crystalline and an amorphous state we have learned the essential features of the electronic structure, and thereby also macroscopic properties, are determined by short-range order. Thus these properties are similar for solids in crystalline and amorphous states.

Amorphous SiO_2 under consideration is solid and dielectric, it only possesses two types of dielectric behavior, that is, the polarization of the electronic cloud around the atoms and the polarization stemming from the motion of the charged ions. More generally, the fluctuations of electron density distribution can induce a time-varying electric dipole moment, which can be regarded as, equivalently, being caused by a fixed ion core with positive charges and a vibrating electron cloud with negative charges. All mentioned here can be taken as the starting point that one will study the temperature dependence of the RI of a-SiO_2.

2. Theoretical investigation starting from the first principle

The main purpose of this work is to present a theoretical basis for temperature sensors based on optical fiber delay lines, where the optical fiber has a core made of high-purity silica in amorphous form, i.e., a noncrystalline form of SiO_2. As the amorphous phase of SiO_2, the amorphous silica exhibits both ionic and covalent bonding (where the fraction of the covalent bonding is about 0.486), and consists of a non-repeating network of tetrahedra (in the form of 6-tetrahedron rings), such that in which the simplifications associated with periodicity are absent. To be specific, the building block of the amorphous silica is the SiO_4 unit, where each individual SiO_4 tetrahedron is connected with adjacent tetrahedrons at the corners, forming a three-dimensional structure.

Seeing that a-SiO_2 is a non-magnetic material, its refractive index can be expressed as $n = \sqrt{1+\chi}$ (where χ is the electric susceptibility of the medium). For a Si–O bond being parallel to a local electric field

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$\boldsymbol{E}_c$, its induced dipole moment is $\mathbf{p}=\alpha\mathbf{E}_c$, where α is the polarizability; however, if the angle between the direction of $\boldsymbol{E}_c$ and the one of a Si–O bond is $\theta\in[0,\pi/2]$, the induced dipole moment should be $\alpha\mathbf{E}_c\cos\theta$. Or equivalently, if the angle between the direction of $\boldsymbol{E}_c$ and the one of a Si–O bond is $\theta\in[0,\pi/2]$, the number of the Si–O bond can be taken as $\cos\theta$. In such a sense, let N denote the average number of Si–O bonds along the direction of $\boldsymbol{E}_c$ per unit volume, then the intensity of polarization is $\mathbf{P}=N\mathbf{p}=N\alpha\mathbf{E}_c$. Although obtaining an exact equation describing the local electric field is difficult, for convenience, let us assume that $\boldsymbol{E}_c$ is expressed as $\mathbf{E}_c=\mathbf{E}+b\mathbf{P}$ [16,17], where b is a constant which may be considered as a measure of the overlap of the total polarization $\boldsymbol{P}$, then using $\mathbf{P}=\varepsilon_0\chi\mathbf{E}$ (where ε_0 is the vacuum permittivity) one can obtain the following formula:

$$\frac{n^2-1}{1+b\varepsilon_0(n^2-1)}=\frac{N\alpha}{\varepsilon_0}. \tag{1}$$

The proposed potentials describing the interactions between the ions in silica are (for our purpose, we will just take into account the interactions between the Si and O ions within a Si–O bond in silica) [18–20],

$$u(r)=\frac{e^2}{4\pi\varepsilon_0}\frac{q_{\mathrm{Si}}q_{\mathrm{O}}}{r}+A\exp(-Br)-\frac{C}{r^6}, \tag{2}$$

where $q_{\mathrm{O}}=-1.2$, $q_{\mathrm{Si}}=2.4$, and $r=|\mathbf{r}_{\mathrm{Si}}-\mathbf{r}_{\mathrm{O}}|$ is the distance between the Si and O ions in a Si–O bond ($\mathbf{r}_{\mathrm{Si}}$ and $\mathbf{r}_{\mathrm{O}}$ are the position vectors of the Si and O ions, respectively). The values of the parameters A, B and C can be found in Refs. [18,19], that is: A = 18,003.7572 (eV), B = 4.87318 (Å^{-1}), C = 133.5381 (eV Å^6).

As we know, a-SiO$_2$ consists of positively charged ion cores and negatively charged valence electrons and as a whole it is electrically neutral. Because of thermal vibrations, these two regions of charge can deviate from their equilibrium positions ($r=r_0$), which will induce electric dipole moments. When the distance between two adjacent Si and O atoms becomes $r=r_0+R$, where $R=r-r_0$ is very small, by means of a Taylor expansion the interaction energy $u(r)$ can be written as, approximately

$$u(r)\approx u(r_0)+\frac{1}{2}u''(r_0)R^2+\frac{1}{6}u'''(r_0)R^3, \tag{3}$$

where $u'(r_0)=0$ because of $r=r_0$ being the equilibrium position. Using Eq. (2) one has

$$u''(r_0)=\frac{e^2q_{\mathrm{Si}}q_{\mathrm{O}}}{2\pi\varepsilon_0}\frac{1}{r_0^3}+AB^2\exp(-Br_0)-\frac{42C}{r_0^8}, \tag{4}$$

$$u'''(r_0)=-\frac{3e^2q_{\mathrm{Si}}q_{\mathrm{O}}}{2\pi\varepsilon_0}\frac{1}{r_0^4}-AB^3\exp(-Br_0)+\frac{336C}{r_0^9}. \tag{5}$$

The potential energy of an oscillator with the equilibrium position of $R=0$ is

$$V(R)=u(r)-u(r_0)=\kappa R^2/2-\beta R^3, \tag{6}$$

where $\kappa=u''(r_0)>0$ and $\beta=-u'''(r_0)/6>0$, the former results in an attractive potential energy for atoms to vibrate about their equilibrium positions, while the latter represents a repulsive potential to keep the stability of the lattice. The anharmonic term of $-\beta R^3$ in Eq. (6) comes from a repulsive energy. To guarantee the result of $\beta=-u'''(r_0)/6>0$, we take the parameter C = 132.3225 (eV Å^6), instead of C = 133.5381 (eV Å^6), while the parameters A = 18,003.7572 (eV) and B = 4.87318 (Å^{-1}) are still the same as those in Refs. [18,19]. In terms of SI, they are, $A = 2.884526\times10^{-15}$ (J), $B = 4.87318\times10^{10}$ (m^{-1}), and $C = 2.120045\times10^{-77}$ (Jm^6). Using $u'(r_0)=0$ one has $r_0=1.384316\times10^{-10}$ (m). Then using $\kappa=u''(r_0)$, $\beta=-u'''(r_0)/6$ and Eqs. (4)–(5) one can obtain $\kappa=9.49171\times10^2$ (Jm^{-2}) and $\beta=1.979\times10^8$ (Jm^{-3}).

Under the local electric field $\boldsymbol{E}_c$, the total energy of an oscillator can be expressed as

$$H=p^2/2m+V(R)-qE_cR, \tag{7}$$

where $E_c=|\mathbf{E}_c|$ and $p=|\mathbf{p}|$, $\boldsymbol{p}$ is the momentum of the oscillator, m is the mass. According to statistical mechanics, by means of the derivation processes similar to those in Ref. [14], one can show that the average intensity of polarization is, approximately,

$$P\approx N(q^2/\kappa+3\beta qk_BT/\kappa^2E_c)E_c\equiv N\alpha E_c, \tag{8}$$

where k_B is Boltzmann's constant and T is the absolute temperature, and the polarizability is

$$\alpha=q^2/\kappa+3\beta qk_BT/\kappa^2E_c\equiv A+BT, \tag{9}$$

where

$$A=q^2/\kappa,\quad B=3q\beta k_B/\kappa^2E_c. \tag{10}$$

Using Eqs. (1) and (9), one has

$$\frac{n^2-1}{1+b\varepsilon_0(n^2-1)}=\frac{N(A+BT)}{\varepsilon_0}. \tag{11}$$

We will show that $BT\ll A$, and then using Eq. (11) one has

$$\begin{aligned}n^2&=1+\frac{N(A+BT)}{\varepsilon_0[1-bN(A+BT)]}\approx1+\frac{N(A+BT)}{\varepsilon_0(1-bNA)}\\&=1+\frac{NA}{\varepsilon_0(1-bNA)}+\frac{NBT}{\varepsilon_0(1-bNA)}.\end{aligned} \tag{12}$$

Under the condition of $BT\ll A$, one has

$$\frac{NBT}{\varepsilon_0(1-bNA)}\ll1+\frac{NA}{\varepsilon_0(1-bNA)}. \tag{13}$$

Using Eq. (13), it follows from Eq. (12) that

$$n\approx\sqrt{1+\frac{NA}{\varepsilon_0(1-bNA)}}+\frac{NB}{2\sqrt{\varepsilon_0(1-bNA)[\varepsilon_0-(\varepsilon_0b-1)NA]}}T. \tag{14}$$

Substituting Eq. (10) into Eq. (14), Eq. (14) becomes

$$n\approx n_0+aT, \tag{15}$$

where

$$n_0=\sqrt{\frac{\varepsilon_0\kappa+(1-b\varepsilon_0)Nq^2}{\varepsilon_0\kappa-b\varepsilon_0Nq^2}}, \tag{16}$$

$$a=\frac{3Nq\beta k_B}{2\kappa E_c\sqrt{\varepsilon_0(\kappa-bNq^2)[\varepsilon_0\kappa+(1-b\varepsilon_0)Nq^2]}}. \tag{17}$$

Eqs. (15)–(17) imply that, the RI of a-SiO$_2$ is directly proportional to the temperature T. Obviously, the temperature-dependent term vanishes for β = 0, and then it is related to the anharmonic term in Eq. (6), which implies that, in terms of quantum field theory, the temperature-dependent term arises from the phonon–phonon interactions.

Let us present a quantitative consideration. Using Eqs. (16) and (17), one can rewrite Eq. (17) in terms of n_0,

$$a=\frac{3\beta k_B(n_0^2-1)}{2\kappa qE_cn_0}. \tag{18}$$