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Critical transition of conductance and dielectric relaxation of synthesized fused silica investigated by electrical impedance spectroscopy

Mankang Zhu [a,*], Xingxuan Wu [a], Yudong Hou [a], Guowu Zhang [b]

[a] College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China
[b] Yaohua Quartz Glass Scientific Development Co. Ltd, Qinhuangdao, Hebei, China

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ABSTRACT

In this work, a critical transition at about 500 °C in alternate-current (a.c.) conductance and dielectric relaxation of synthesized fused silica is first observed. The synthesized fused silica sample demonstrates the features of high hydroxyl content and low metal impurities through infrared absorption and ultraviolet transmittance analyses. The dispersion profiles of conductivity at different temperatures demonstrate the feature of the thermally-activated, long-range conduction. Besides, the temperature dependence of a.c. conductivity and dielectric relaxation shows different behaviors in high or low temperature range, thus lead to a critical transition occurring around 500 °C. It is believed that the occurrence of the critical transition is ascribed to the heterogeneous crystallite domains, which go through a transformation of stacking structure when the sample was subjected upon a heating.

1. Introduction

Synthesized fused silica is widely used in high-tech fields due to its high purity and a consequence of physicochemical property, especially in inertial navigation, microwave communication and so on. In these applications, the electrical property of synthesized fused silica is of great importance. Studies on the electrical conduction of silica were performed in the latest decades, mainly focusing on the types and models of conduction to explain their observations.

A few of researchers studied the electric behavior of crystal quartz [1,2,3]. Jain and Nowick [1] suggested that electrical conduction in the quartz crystals belongs to ionic ones by alkali ions (M^+) moving in channels parallel to the c axis. Lazzari et al. [2] and Martini et al. [4] reported a critical transition of electric conductance around 500 °C. In the lower temperature range ($250\ °C < T < 500\ °C$), the sample shows an activation energy $E = 1.32$ eV while at higher temperatures ($500 < T < 950$ °C), a lower E (0.67 eV) is found [2,4]. They attributed it to the opening of channels for conduction along the z-axis in the crystalline structure. Campone et al. [3] further investigated the effect of hydrogen on the ionic transport in crystalline SiO_2, and also observed the critical transition of the electric conductance around 520 °C.

As to fused silica, every effort was made to understand the nature of its electrical conduction. Several researchers suggested that the conduction in fused silica is resulted from the metal cations moving through the glass network of the fused silica [5,6,7]. Stamminger et al. [8] researched the electrical impedance spectroscopy (EIS) of quartz glass grades with a variety of lithium and hydroxyl contents at temperatures between 600 °C and 1000 °C, and found that the plots of conductivity versus temperature yielded good Arrhenius dependencies. Recently, our research on EIS of synthesized fused silica illustrated that the temperature dependence of conductance and relaxation matches well with the Arrhenius law in the temperature range 175–300 °C [9]. In a word, all these researchers found that the conduction of fused quartz is consistent with an Arrhenius law in their measuring temperature ranges. Whether does a critical transition of conductance in synthesized fused silica exist, as observed in the crystal silica, is of great interest in glass science.

In this paper, we investigated the a.c. electric impedance of synthesized fused silica at temperatures between 250 °C and 700 °C. The dependencies of a.c. conductivity, bulk conductance and dielectric modulus on frequency and temperature were investigated extensively. A critical transition at about 500 °C was first observed in the temperature dependent conductance and relaxation behavior. The relevance between critical transition and glass structure of synthesized fused silica was dug deeper to discussion.

2. Experiments

The synthesized fused silica sample, manufactured by Yaohua Quartz Technology Development Co., Ltd., Qinhuangdao, China, though flame hydrolysis process of $SiCl_4$, was cut into a dimension of $\Phi 20 \times 0.7$ mm, and polished on both sides. The density was measured by a precision balance (XS104, Mettler Toledo, Switzerland) equipped with density kits based on Archimedes' principle. The refractive index was measured by an Abe refractometer (Abbemat MW, Anton Paar, Germany). Optical absorption/transmittance spectrum was recorded

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* *Corresponding author.
E-mail address: zhumk@bjut.edu.cn (M. Zhu).

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by a scanning spectrophotometer (UV-2101PC, Shimadzu, Japan) in the wavelength range from 180 nm to 4000 nm. To measure the electric behavior, platinum electrodes were magnetron sputtered on both sides of the sample. The electrical impedance spectrum was recorded by a wide-frequency impedance tester (Concept 40, Novocontrol, Germany) in the temperature range from 250 °C to 700 °C. All the errors are derived from the fitting process by the least square method.

3. Results

3.1. Basic physical properties and optical transmittance spectrum

First, the basic physical parameters of synthesized fused silica sample, including the density and refraction indices at different wavelengths, are measured at room temperature. Table 1 lists these values and demonstrates the well match to those of fused silica published by other manufacturers.

Generally, high hydroxyl content and low metal impurity are typical features of synthesized fused silica manufactured by flame hydrolysis of $SiCl_4$. Fig. 1 shows the experimental infrared (IR) absorption spectrum of the sample in the wavelength range 800–3000 nm. As seen from the figure, three distinct absorption bands were observed at the 2.73 μm, 2.20 μm and 1.39 μm, respectively, as previously reported [10]. The hydroxyl content C_{OH} in glass bulk is determined by following equation [11]:

$$C_{OH} = 96.5 \times \frac{1}{d}\lg\frac{I_0}{I} \tag{1}$$

here, C_{OH} is the hydroxyl content in ppm (10^{-6} by weight), d the thickness of the sample in cm, I_0 is the apparent transmittance of the baseline at 2.73 μm, I is the apparent transmittance of the absorption band at 2.73 μm. The calculation gives out the hydroxyl content of the sample to be 1071 ± 5 ppm, showing one of the features of the synthesized fused silica made by the flame hydrolysis of $SiCl_4$. Further, the absorption band at 2.73 μm (3672 cm^{-1}) could be attributed to stretching vibration of the hydroxyls [12,13,14,15]. Fig. 2 presents the absorption band at 2.73 μm in the range from 2.6 μm to 2.9 μm. Plotnichenko suggested that the absorption band around 2.73 μm for O–H stretching vibration is composed by four Gaussian components, corresponding to four bonding status of the hydroxyl [10]. Similarly, the absorption band around 2.73 μm in our work is also evoluted into four components, as shown in Fig. 2: the υ_1 is at 2.70 μm, the υ_2 at 2.72 μm, the υ_3 at 2.75 μm, and the υ_4 at 2.81 μm, respectively, which is in good consistence with Plotnichenko's. In a word, the IR analysis presents the feature of synthesized fused silica with high the hydroxyl content. Such high hydroxyl content may affect the electrical behavior of the synthesized fused silica [8].

The metal impurity in synthesized fused silica has a great influence on the ultraviolet (UV) transmittance spectrum. The absorption edge of synthesized fused silica will shift to long wavelength as the metal impurities increases, [16] and will further affect the conduction behavior of the fused silica. Fig. 3 shows the UV transmittance spectrum of the sample. The transmittance falls sharply at about 190 nm, which implies the very fewer metal impurity in the sample. To be more quantitative, the indirect allowed optical band gap of the sample is determined by the Tauc equation according to the UV transmittance spectrum in the wavelength range from 180–400 nm, as shown in the insert of Fig. 3. The indirect allowed optical band gap is estimated to be about 5.9 eV for the sample, much larger than that of commercially-available fused silica (5.1–5.3 eV). Briefly, the UV absorption spectrum indicates another feature of the synthesized fused silica with low metal impurities. All in all, the sample is such a type of synthesized fused silica with high hydroxyl contents and low metal impurities.

Table 1
Density and refractive index.

Property	Value
Density g/cm^3	$2.195 \pm 2 \times 10^{-3}$
Refractive index	$1.4565 \pm 2 \times 10^{-4}$@ λ = 656.3 ($n_c$) $1.4586 \pm 2 \times 10^{-4}$@ λ = 587.6 ($n_d$) $1.4632 \pm 2 \times 10^{-4}$@ λ = 486.1 ($n_f$) $1.4668 \pm 2 \times 10^{-4}$@ λ = 435.8 ($n_g$)

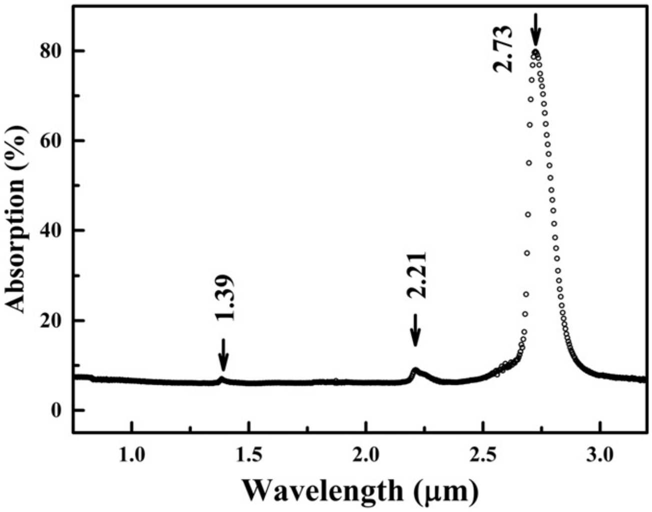

Fig. 1. IR absorption spectrum of synthesized fused silica, showing the characteristic absorption of hydroxyl at 2730, 2210, and 1390 nm, respectively.

3.2. Dispersion of a.c. conductivity

Fig. 4 shows the dispersion of a.c. conductivity σ_{ac} at different temperatures, where the σ_{ac} shows two distinct stages at a certain temperature within the measured frequency range. At low frequency stage, the σ_{ac} emerges into a plateau, corresponding to the frequency independent conductivity σ_{dc}; and the σ_{dc} increases with temperature, meaning the conduction is thermally activated. Meanwhile, at the high frequencies, the σ_{ac} presents a dispersion region for different temperatures, which obey the Jonscher's power law given by the following equation:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n \tag{2}$$

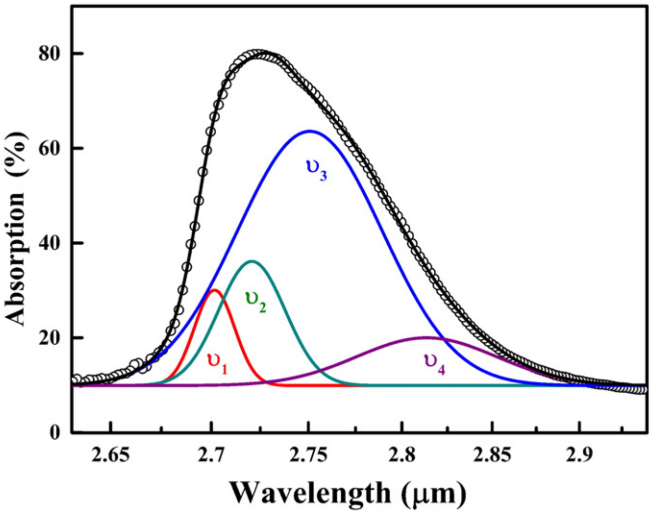

Fig. 2. IR absorption band of hydroxyl for the stretching vibration at 2.73 μm (3670 cm^{-1}), which is devoluted into four Gaussian components as the solid lines shown.