



Complex refractive index of silica, silicate, borosilicate, and boroaluminosilicate glasses – Analysis of glass network vibration modes with specular-reflection IR spectroscopy

Jiawei Luo^{a,b}, Nicholas J. Smith^c, Carlo G. Pantano^{b,d}, Seong H. Kim^{a,b,d,*}

^a Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

^b Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA

^c Science and Technology Division, Corning Incorporated, Corning, NY 14830, USA

^d Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Keywords:

Glass
Vibrational spectroscopy
Complex refractive index

ABSTRACT

A novel mathematical algorithm was developed to calculate refractive index ($n + ik$) from specular reflectance infrared (SR-IR) spectra in the strongly-absorbing glass network vibration region. The method is named as two-angle SR-IR (TASR-IR), since it is based on the Fresnel equations of specular reflectance at two incidence angles (10° and 45°). The results obtained from TASR-IR are comparable with the values obtained from spectroscopic ellipsometry. The TASR-IR method allows one to obtain the peak positions and intensities of fundamental network vibration modes of glass from the imaginary component (k) of complex refractive index without convolutions from the dispersion effect due to chains in the real component (n) of refractive index. The TASR-IR method is applied to silica, silicate, borosilicate, and boroaluminosilicate glasses; tentative peak assignments of glass network vibrations are proposed. The origin and concept of *peaks* in the vibrational spectra of glasses is discussed.

1. Introduction

The distribution of bond parameters such as Si–O bond length, Si–O–Si dihedral bond angle, and O–Si–O tetrahedral bond angle in silicate-based glass materials are believed to influence their chemical durability, mechanical property, and mechano-chemical reactivity (for example, stress corrosion and wear in humid environments) [1–6]. The bond length and angle distributions could be obtained from neutron scattering or extended X-ray absorption fine-structure (EXAFS) analyses [7–9]. However, such experimental techniques are not readily available; thus, a simple and routine experimental technique applicable to various compositions of glass would be practically useful. We recently reported that the peak position of the Si–O–Si asymmetric stretching vibration mode ($\nu_{\text{Si-O-Si,as}}$; typically $1000\text{--}1100\text{ cm}^{-1}$) correlates with the average Si–O bond length ($\bar{d}_{\text{Si-O}}$) [10]. This correlation works best in the absorbance spectrum where the peak intensity, $A(\omega)$, at a given wavenumber (ω) can be converted to the absorptivity, $a(\omega)$, using the Beer-Lambert law: $A(\omega) = a(\omega) \cdot b \cdot c$ where b is the length of beam path and c is the concentration of species of interest within the beam path. Then, $a(\omega)$ is directly related to the imaginary component of the complex refractive index, $n(\omega) + ik(\omega)$, through the relationship $a(\omega) = 4\pi k(\omega)/\lambda$ where λ is wavelength ($=1/\omega$) [11].

In transmission IR analysis, the intensity ratio of transmitted (I_t) and incident (I_o) beam at the surface normal direction is defined as transmittance $T(\omega) = I_t/I_o$. Absorbance is then calculated as: $A(\omega) = -\log T(\omega)$. Here, the dispersion effect arising from the real part of the complex refractive index, $n(\omega)$, is usually negligible in $T(\omega)$ measurements at normal incidence ($\theta_i = 0$ in Fig. 1a); at least, this is the case for a weakly absorbing medium. Unfortunately, the transmission IR analysis of typical silicate glass networks is not possible unless the sample thickness is $< 1\ \mu\text{m}$ because of the extremely high absorptivity of glass in the stretching mode region [11,12]. For this reason, IR analysis of glass is often performed by measuring the intensity of a reflected beam (I_r) at the specular reflection direction ($\theta_i = \theta_r$ in Fig. 1a) and reflectance $R(\omega) = I_r/I_i$ is plotted. Calculation of $-\log R(\omega)$ provides a spectrum that is *dimensionally equivalent* to $A(\omega)$. However, it should be noted that $R(\omega)$ is convoluted by the dispersion of $n(\omega)$ and the absorption of $k(\omega)$; thus, it cannot be considered to truly reflect $k(\omega)$ [11,13].

In theory, $R(\omega)$ can be deconvoluted into $n(\omega)$ and $k(\omega)$ using the Kramers-Kronig (KK) transformation [14–16]. However, in practice the KK conversion does not work well for evaluating the network stretching modes of silicate glass materials. One limitation arises from the fact that, in theory, the KK algorithm requires integration from $-\infty$ to $+\infty$

* Corresponding author at: Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA.
E-mail address: shkim@engr.psu.edu (S.H. Kim).

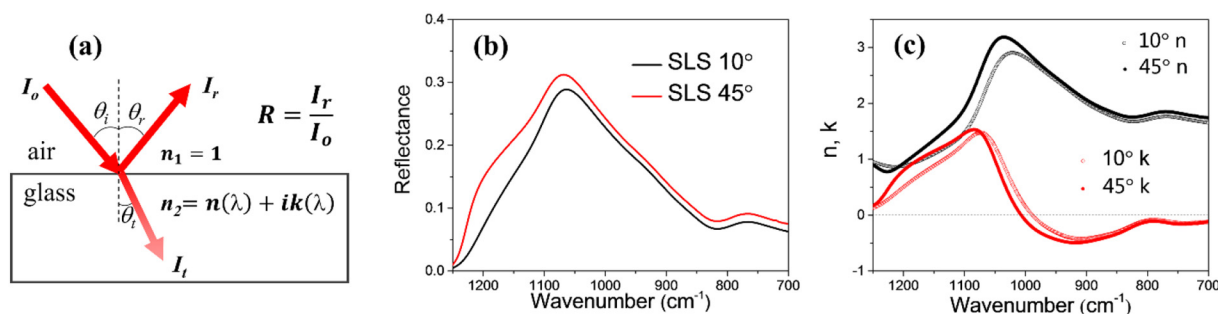


Fig. 1. (a) Schematic representation of SR-IR analysis of glass. (b) SR-IR of soda lime silica (SLS) glass spectra collected at an incidence angle of 10° and 45° . (c) Complex refractive index (n and k) values of SLS glass obtained using the Kramers-Kronig transformation algorithm of the built-in software of a FTIR instrument.

in the wavenumber (ω) domain. The reality is that IR spectra obtained with typical mid-IR instruments are truncated on the low-wavenumber end near $200\text{--}400\text{ cm}^{-1}$ due to beam splitter and detector limitations; this spectral region contains various low-frequency vibrational modes. Without definitive knowledge of the spectral features at $\omega < 400\text{ cm}^{-1}$, errors propagate in the KK transform into the network stretching mode region, and often manifest in artifacts such as negative backgrounds and artificial peak shifts. Another issue is that the KK algorithm available in many commercial instruments is derived for non-polarized reflection at the normal incidence angle ($\theta_i = \theta_r = 0^\circ$). Accordingly, errors will be inevitable if non-polarized specular reflectance (SR) IR spectra are measured at an oblique angle ($\theta_i = \theta_r > 0^\circ$). Fig. 1b and c shows an example of converting the SR-IR spectra of a soda lime silica (SLS) float glass – collected at incidence angles of 10° and 45° – to the corresponding $n(\omega)$ and $k(\omega)$ spectra using the built-in KK conversion function of a commercial spectrometer. Note that $k(\omega)$ values are negative at $\omega < 1000\text{ cm}^{-1}$, which is physically not feasible.

In order to overcome these limitations, in this paper we describe a new algorithm that allows calculation of $n(\omega)$ and $k(\omega)$ from non-polarized SR-IR spectra collected at two incidence angles – 10° and 45° ; hereafter, this method will be referred to as the “two-angle SR (TASR)” IR method. The method was validated by processing a data set simulated with known $n(\omega)$ and $k(\omega)$ spectra, and comparing with the data obtained from variable-angle spectroscopic ellipsometry (VASE) [17]. The TASR-IR method was subsequently applied to flat glass samples with different types of glass networks, specifically silica, silicate, borosilicate, and boroaluminosilicate glasses. The peaks observed in the $k(\omega)$ spectra of these glasses were deconvoluted into multiple components, and the physical origins of individual components are discussed.

2. Methods

2.1. Experimental analysis

SR-IR spectra were collected using a V70 spectrometer (Bruker) equipped with a DTGS detector and a Seagull™ variable-angle reflection accessory (Harrick Scientific). It should be noted that a small misalignment of the incidence angle in data collection can cause a large error in calculation; thus, it is important to accurately align the incidence angle to 45° (see Fig. S1 in Supporting information, SI). Also, the divergence of the incidence angle should be minimized; this can be done by reducing the IR beam diameter (see Fig. S1 in SI). A gold mirror was used as a reference for background. One hundred scans with a resolution of 6 cm^{-1} were collected and averaged. Spectra were collected under N_2 environment. No atmospheric correction was used during the data collection. The incidence angle was calibrated under the manufacturer's instruction. The aperture size was set to be 50% to minimize the divergence of the IR beam.

For comparison, VASE measurements were performed using an IR-VASE instrument (J.A. Woollam) equipped with a DTGS detector (working range $8000\text{--}250\text{ cm}^{-1}$). Spectra were collected at a 16 cm^{-1}

resolution at 50° and 55° incidence angles. The latter represents the Brewster angle for most silicate glasses in the mid-IR region where VASE data exhibits the highest signal-to-noise ratio. Although most data discussed in this paper refer to the strongly-absorbing IR region $< 1200\text{ cm}^{-1}$ wherein backside surface reflections are virtually eliminated, efforts were nevertheless made to evaluate any deleterious effects of backside reflections on the VASE data. Accordingly, VASE data were collected using both a backside-index-matching method (i.e. using transparent tape [18]) and a more rigorous backside-roughening-plus-index-matching method. The latter was found to be identical with the former, verifying the negligible impact of backside reflections in this spectral region. IR-VASE data were processed using the WVASE® software platform (J.A. Woollam). The same program was also used to model Ψ and Δ for a SLS glass based on published $n(\omega)$ and $k(\omega)$ data.

Commercial flat glass samples were used in this study. The glass samples were cut into a square pieces of $\sim 25\text{ mm} \times \sim 25\text{ mm}$. Fused quartz slides were obtained from Technical Glass Products (GE124 grade), and used as a model system for “pure” silica glass. As a model system for sodium calcium silicate glass, two SLS float glass panels were analyzed: (1) $700\text{ }\mu\text{m}$ thick panels provided by Asahi Glass Co. and (2) 4 mm thick panels obtained from the PPG Industries Works #6 plant (now Vitro Architectural Glass, Carlisle, PA). In order to minimize spectral artifacts due to a dealcalized surface layer, the SLS glass samples were annealed at 600°C for 2 h and slowly cooled down to room temperature over 10 h [19]. The 4 mm thick panel was thermally tempered at United Plate Glass (Butler, PA). A Borofloat®33 panel from Schott Inc. was used to represent a typical alkali borosilicate glass. Two types of alkaline earth boroaluminosilicate glass were analyzed: AF45 from Schott Inc. and Willow® from Corning Incorporated. Unless specified, commercial glass samples were measured on air-side or melt surfaces in their as-received condition. Another type of boroaluminosilicate glass is the International Simple Glass (ISG), which was produced as a model nuclear waste glass by MoSCI Corporation [20]. A small disk of ISG glass was cut from a boule and polished to an optically clear finish with SiC slurry.

2.2. Mathematical algorithm to obtain $n(\omega) + ik(\omega)$ from TASR-IR data

The SR-IR method utilizes a few specific mathematical conditions within the polarization-dependent Fresnel equations, namely that (i) the polarization dependence of SR-IR vanishes at $\theta_i = 0^\circ$, and (ii) the s-polarized spectrum can be analytically calculated from the non-polarized spectrum at $\theta_i = 45^\circ$. Subsequent conversion of the $R(\theta_i = 0^\circ)$ and $R(\theta_i = 45^\circ)$ spectra to the $n(\omega)$ and $k(\omega)$ spectra is thus equivalent to solving two algebraic equations for two unknowns; so, the degrees of freedom are zero and, in principle, an exact solution can be obtained. Practically, it is not possible to collect the $R(\omega)$ spectrum at $\theta_i = 0^\circ$; the lowest θ_i is about 10° in typical commercial FTIR instruments. Since the $R(\theta_i = 10^\circ)$ value is very close to the $R(\theta_i = 0^\circ)$ value (as shown in the simulation plot in Fig. 2), it can be assumed that $R(\theta_i = 0^\circ) \approx R(\theta_i = 10^\circ)$ initially and the error introduced by this assumption can be

Download English Version:

<https://daneshyari.com/en/article/7899727>

Download Persian Version:

<https://daneshyari.com/article/7899727>

[Daneshyari.com](https://daneshyari.com)