Available online at www.sciencedirect.com
ScienceDirect
Physica B 403 (2008) 2450–2460
PHYSICA B
www.elsevier.com/locate/physb

A new approach to estimate refractive index, electronic polarizability, and optical basicity of binary oxide glasses

Xinyu Zhao[a,*], Xiaoli Wang[a], Hai Lin[b], Zhiqiang Wang[b,**]

[a]School of Petrochemical Engineering, Shenyang University of Technology, Liaoyang 111003, PR China
[b]Department of Material Science and Engineering, Dalian Institute of Light Industry, Dalian 116034, PR China

Received 31 August 2007; received in revised form 23 November 2007; accepted 5 January 2008

Abstract

In this paper, we introduce the optical electronegativity $\Delta\chi^*_{glass}$ to predict basic properties of binary oxide glasses. Optical electronegativity $\Delta\chi^*_{glass}$ of numerous binary oxide glasses has been evaluated on the basis of two different properties: the linear refractive index n and energy gap E_g, which have demonstrated remarkable correlation. Furthermore, we also calculate the refractive index n through the energy-gap-based optical electronegativity $\Delta\chi^*_E$, and obtain a perfect linear correlation between the calculated refractive index n_{cal} and the n_0 values of Dimitrov and Komatsu. The average electronic oxide polarizability $\alpha_{O^{2-}}$ and the optical basicity Λ of binary oxide glasses have been estimated on the basis of the optical electronegativity $\Delta\chi^*_{glass}$ calculated from the refractive index n. The estimated values are in good agreement with the available experimental data. The present method needs only one original experimental parameter to estimate the optical electronegativity $\Delta\chi^*_{glass}$, which is the refractive index n.

PACS: 42.70.Ce; 42.70.Qs; 78.20.Ci; 61.43.Fs

Keywords: Binary oxide glasses; Optical electronegativity; Refractive index; Optical basicity; Electronic polarizability

1. Introduction

Photon-based systems have a great potential because of the large demand for ultra-high-speed information transfer and processing, and the development of photonic materials is being driven by such a demand. For designing photonic systems, the application of nonlinear optical (NLO) properties is one of the strong candidates. Glasses are promising materials for NLO applications because of their high transparency, ease of fabrication into fibers and waveguides, high thermal and chemical durability, ease of doping, flexibility of composition, and low cost of fabrication [1]. Oxide glasses are also stable hosts for obtaining efficient luminescence in rare-earth ions [2–4]. All these applications indicate the need for a basic understanding of the relationship between optics and electronics in glass matrixes.

One of the most important properties of materials that is closely related to NLO applications is the electronic polarizability of ions. Optical nonlinearity is caused by the electronic polarization of a material on exposure to intense light beams. Hence the nonlinear response of the material is governed by electronic polarizability [5]. For this purpose, materials of high optical nonlinearity have to be found or designed on the basis of correlations of optical nonlinearity with some other electronic properties, which are easily understandable and accessible.

Inorganic oxide materials in the crystalline, vitreous, or molten state have properties that can be accounted for in terms of the electronic "state" of oxygen atoms. Furthermore, the polarizability of oxide ions is closely related to the optical basicity of oxide materials. Optical basicity, proposed by Duffy and Ingram [6,7], is used as a measurement of acid–base properties of oxide glasses and

*Corresponding author. Tel.: +86 4196860128; fax: +86 4195311989.
**Also for correspondence.
E-mail address: zhaoxydq@hotmail.com (X. Zhao).

0921-4526/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2008.01.009

expresses the basicity of a glass in terms of the electron density carried by oxygen. Since its introduction, many physical and chemical properties of oxidic media in vitreous or molten state have been related to the optical basicity [8,9].

There has been some interest [10–16] in using the refractivity of glasses to measure their basicity or oxygen electron donor power, based on the Lorentz–Lorenz equation. For this method, the refractive index, density, cation polarizability, molecular weight and molar volume parameters are needed to calculate the electronic polarizability. Recently the expressions given by Duffy [17,18] and Reddy et al. [19–22] correlate the average electronic oxide polarizability, refractive index, and optical electronegativity for simple oxides and crystals. However, there is no systematic data about the correlation between the average electronic oxide polarizability $\alpha_{O^{2-}}$, optical basicity Λ, refractive index n, and optical electronegativity $\Delta\chi^*_{glass}$ for binary oxide glasses.

In this paper, we introduce the optical electronegativity $\Delta\chi^*_{glass}$ to more complex oxide glass compositions and extend the approach proposed for simple oxides. We have estimated the refractive index n, average electronic oxide polarizability $\alpha_{O^{2-}}$, and optical basicity Λ on the basis of the optical electronegativity $\Delta\chi^*_{glass}$ for binary oxide glass systems. This type of approach has not been found earlier in the literature. Hence the inclusion of optical electronegativity has a wide scope in predicting many physical properties of optical materials.

2. Results and discussion

2.1. Optical electronegativity of binary oxide glasses based on the energy gap and refractive index

Optical electronegativity is one of the most important parameters in understanding the nature of chemical bonding, and several important physical parameters can be predicted by using it. Duffy [17,18] has made an attempt to describe the metallic character of chemical bonding for compounds that are inadequately described in a solely "ionic/covalent" framework from the point of view of band gap electronegativity. Optical absorptions for a semiconductor or insulator arise through electron transfers from the valence band to the conduction band. The transfer of electrons from an anion to a cation and the associated optical absorption is known as "electron transfer" or "charge transfer absorption". Duffy [17,18] has well established the above concept and introduced it in terms of the "optical electronegativity". It has been recently suggested that a simple model based on the concept of optical electronegativity and some other parameters should be good enough to study the main properties of ionic crystals and semiconductors with the use of only a few numerical constants.

The concept of optical electronegativity and its use in estimating physicochemical parameters of simple oxides has been well establishes in the literature. The purpose of the present paper is an attempt to introduce optical electronegativity to binary oxide glass systems and study the dependence of average electronic oxide polarizability $\alpha_{O^{2-}}$, optical basicity Λ, refractive index n, and optical electronegativity $\Delta\chi^*_{glass}$.

The correlation between energy gap E_g and optical electronegativity $\Delta\chi^*$ has been elucidated by Duffy [17,18] and his proposed relation reads as follows:

$$\Delta\chi^* = 0.2688E_g, \tag{1}$$

where $\Delta\chi^*$ is the optical electronegativity. For simple oxides, optical electronegativity is calculated by $\Delta\chi^* = \Delta\chi^*_{anion} - \Delta^*_{cation}$, $\Delta\chi^*_{anion}$ and $\Delta\chi^*_{cation}$ being the optical electronegativity of the anion and the cation, respectively. In the case of binary oxide glasses, $\Delta\chi^*$ estimation is somewhat difficult. In order to overcome the difficulty, we have chosen Eq. (1) for the calculation of optical electronegativity of binary oxide glasses. The data on the energy gap are collected in Ref. [10], and the detailed data are listed in Table 1 (column 5). The optical electronegativity $\Delta\chi^*_E$ values estimated from the E_g using Eq. (1) are given in Table 1 (column 6).

The refractive index n is one of the fundamental properties of materials, because it is closely related to the average electronic oxide polarizability $\alpha_{O^{2-}}$ of ions and local fields inside the material [20]; n for glasses is easily determined experimentally. Recently, Reddy and Ahammed [23] have proposed an empirical relationship between the refractive index n and optical electronegativity $\Delta\chi^*$ and is as follows:

$$\Delta\chi^* = 9.8e^{-n}. \tag{2}$$

The refractive indices n are taken from the literature [10], which are presented in Table 1 (column 8). For binary oxide glasses, the calculated optical electronegativity $\Delta\chi^*_n$ based on the refractive index n are given in Table 1 (column 7).

Taking into account the optical electronegativity $\Delta\chi^*$, first introduced for binary oxide glasses, we have plotted the calculated values of $\Delta\chi^*_E$ against $\Delta\chi^*_n$ in Fig. 1. A remarkable correlation is found between them ($R^2 = 0.9975$, the correlation equation and the square of the correlation coefficient R^2, which can be used to measure the effectiveness of the least-squares fitting, are also shown in the potted figure). This means that the determination of optical electronegativity $\Delta\chi^*$ by means of the energy gap E_g and refractive index n is very promising.

Reddy et al. [20] have estimated the refractive index n based on the optical electronegativity $\Delta\chi^*$ for various simple oxide materials. In the present paper, we also make an attempt to calculate the refractive index n of binary oxide glasses using a new experiential equation based on Eq. (2).

$$n_{cal} = -0.73\ln(0.102\Delta\chi^*_E) + 0.5511. \tag{3}$$