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Calculation of the structure and physical properties of ternary glasses via the phase diagram approach

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ABSTRACT

Despite great advances in glass science and technology, the debate on the predominant feature of the glass structural model, especially the structure-property relationship, has lasted for more than half a century. Recently, the phase diagram approach has shown to be an effective method for investigating the physical properties of glass but it is restricted to the binary glass systems. Herein, the phase diagram approach was popularized to a series of ternary glass systems with a quantitative prediction of their structure and physical properties, including the density, refractive index, thermal expansion coefficient, elastic modulus and shear modulus. Furthermore, the structure-property relationship of ternary glass and the borate anomaly are reasonably described via the phase diagram approach. Detailed error analysis for the predicted results is also performed. The good agreement between the calculated results and experimental data indicates that the phase diagram approach is a promising method for investigating the structure and physical properties of glasses, providing a novel insight into the study of glass science and technology.

1. Introduction

Glass as a representative amorphous material is playing an increasingly important role in both science and technology [1–5]. Although remarkable achievements have been made in the applications of glass, the nature of the glassy state is still one of the most challenging problems in condensed matter physics, especially the laws of the structure and properties of glassy matter [6,7]. Two classical theories, Zachariasen's continuous network theory [8] and Lebedev's microcrystallite theory [9], have been applied to the qualitative interpretation of the glass structure, but they cannot predict the structure and properties quantitatively. Actually, the composition-property relationship of glass has been studied since early times. Several important theories were proposed successively by Huggins-Sun [10], Appen [11], Gan [12–14], Volf [15], Priven [16] and Inaba [17]. According to Huggins-Sun's method [10], the addition of oxides to glass would lead to special structural changes, and the calculation coefficients of twelve oxides were given by this method. Shortly afterwards, Appen [11] proposed a calculation approach based on the oxide molecular ratios and some oxide properties obtained by differential method. And the properties of the glass are determined by the additive law. Later, Gan's theory [13] improved the computing model and provided more than fifteen kinds of physical properties of oxides via the additivity rule, differential method and substitution method. In 1984, Volf [15] also proposed a chemical approach to answer the question of how the properties of glass change after the substitution of one component by another. Similarly, the method from Priven [16] was built on the equations of chemical reactions and chemical equilibria, as well as the equations of material balance. Subsequently, Inaba [17] established the relationship between the physical properties of oxide glasses and ionic packing rate, with the aim of getting an empirical equation to calculate the properties of glass. Nevertheless, there are deficiencies in these computing systems, such as the lack of theoretical basis and failure in calculating the physical properties of non-oxide glasses, and a more serious problem is that the glass structure is not considered when predicting the glass properties. Another method to combine the final properties with a set of chemical objects is the quantitative structure-property relationship (QSPR) analysis [18], which is on the strength of the hypothesis that reflects the structure changes in macroscopic properties of materials. However, by means of molecular dynamics (MD) simulations, the required structural descriptors for the prediction of different kinds of properties are diverse even for the same glass. Thus, the QSPR fitting formulas vary from one to another and the optimal formula is hard to determine. To solve these problems, Jiang proposed a phase diagram approach to further understand the structural characteristics and physical properties of glass, glass formation

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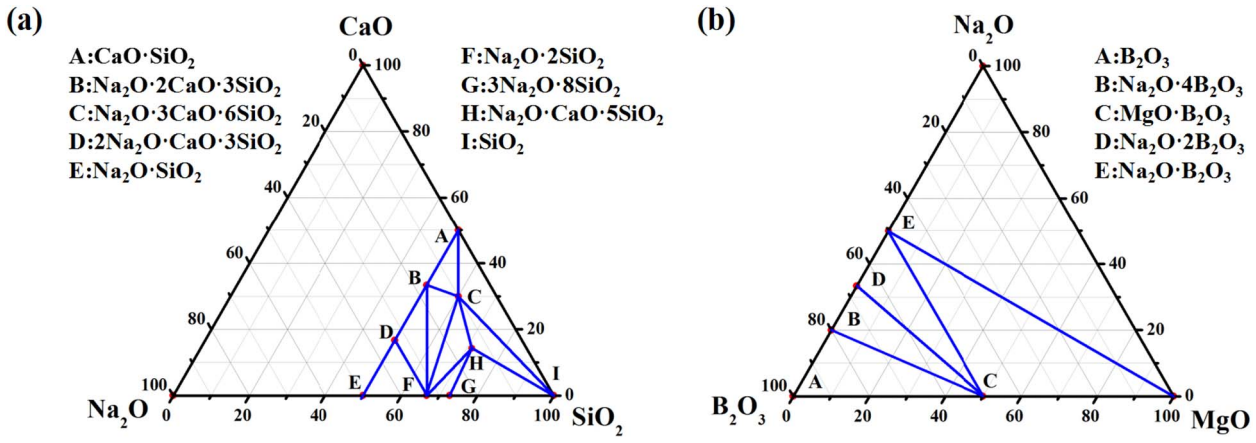

Fig. 1. Example of the determination of compatibility triangles: (a) Na_2O-CaO-SiO_2 system (mol%) and (b) Na_2O-B_2O_3-MgO system (mol%).

Table 1
The density, refractive index, thermal expansion coefficient, elastic modulus and shear modulus of the oxide glasses with congruently melting compounds.

Compounds	Density (g/cm^3)	Refractive (n_D)	Thermal expansion coefficient (10^{-7}/°C)	Elastic modulus (GPa)	Shear modulus (GPa)
SiO_2	2.2 [29]	1.46 [29]	11.098 [29]	69.58 [30]	31 [30]
$Na_2O·2SiO_2$	2.486 [30]	1.5072 [30]	158.28 [30]	60.3 [30]	22.9 [30]
$Na_2O·SiO_2$	2.56 [30]	1.517 [30]	–	–	–
$3Na_2O·8SiO_2$	2.449 [30]	1.498 [30]	136 [30]	55.9 [30]	22 [30]
$K_2O·2SiO_2$	2.468 [30]	1.513 [30]	183.41 [30]	48.9 [30]	18 [30]
$K_2O·4SiO_2$	2.387 [30]	1.495 [30]	113 [30]	48 [30]	19.35 [30]
$CaO·SiO_2$	2.898 [30]	1.628 [30]	105 [29]	–	–
$BaO·SiO_2$	3.506 [30]	1.646 [30]	–	–	–
$BaO·2SiO_2$	3.734 [30]	1.609 [30]	103.5 [29]	–	–
$2BaO·3SiO_2$	3.998 [30]	1.632 [30]	–	–	–
$MgO·SiO_2$	2.75 [30]	–	–	–	–
B_2O_3	1.843 [29]	1.463 [29]	151 [29]	17 [31–33]	7 [31]
$K_2O·2B_2O_3$	2.3023 [29]	1.502 [29]	130 [34]	–	18 [34]
$Na_2O·4B_2O_3$	2.216 [29]	1.502 [29]	78 [34]	–	17 [35]
$Na_2O·2B_2O_3$	2.374 [29]	1.517 [29]	–	–	–
$Na_2O·B_2O_3$	2.379 [29]	1.525 [29]	–	–	–
$BaO·4B_2O_3$	2.82 [12]	1.558 [12]	70 [12]	–	–
$BaO·2B_2O_3$	3.54 [12]	1.62 [12]	80 [12]	–	–
$BaO·B_2O_3$	4.1 [12]	1.66 [12]	–	–	–
$MgO·B_2O_3$	2.51 [29]	–	–	–	–
$Na_2O·CaO·5SiO_2$	2.522 [29]	1.529 [29]	97 [34]	71.5 [34]	30.5 [34]
$Na_2O·2CaO·3SiO_2$	2.776 [29]	1.584 [29]	103 [34]	–	–
$Na_2O·3CaO·6SiO_2$	2.723 [29]	1.567 [29]	116.3 [34]	78.5 [34]	33.5 [34]
$2Na_2O·CaO·3SiO_2$	2.668 [29]	1.549 [29]	134 [34]	–	–
$MgO·CaO·2SiO_2$	2.854 [30]	1.604 [29]	–	–	–
$Na_2O·B_2O_3·2SiO_2$	2.545 [30]	1.529 [29]	109 [34]	76 [34]	26.9 [34]
$Na_2O·B_2O_3·6SiO_2$	2.448 [30]	1.509 [29]	68.3 [34]	73.5 [34]	28 [34]
$3BaO·3B_2O_3·2SiO_2$	3.87 [30]	1.65 [29]	–	–	–

Table 2
The density and structure of congruently melting compounds in the Na_2O-CaO-SiO_2 glass system.

Label	Congruent compound	Density (g/cm^3)	Compound structure
A	$CaO·SiO_2$	2.898 [30]	Ring
B	$Na_2O·2CaO·3SiO_2$	2.776 [29]	Ring [36]
C	$Na_2O·3CaO·6SiO_2$	2.723 [29]	Layer-band [37]
D	$2Na_2O·CaO·3SiO_2$	2.668 [29]	Ring
E	$Na_2O·SiO_2$	2.56 [30]	Chain [38]
F	$Na_2O·2SiO_2$	2.486 [30]	Layer [39]
G	$3Na_2O·8SiO_2$	2.449 [30]	Layer-framework
H	$Na_2O·CaO·5SiO_2$	2.522 [29]	Layer-framework
I	SiO_2	2.2 [29]	Framework [40]

and glass transitions [19]. In this approach, glass possesses a structure similar to a congruently crystalline compound of the same composition. Furthermore, the model considered that the glass structure is a mixture of the melts of the nearest neighbor congruent compounds in the phase diagram, suggesting that the structure and properties of the resulting glass can be calculated quantitatively from the reasonable data of these congruent compounds by using the lever rule [19–26]. Therefore, the formula would be in a more concise and explicit way. In contrast to previous methods, this approach not only makes it possible to calculate the glass structure and properties quantitatively, but also can be used to interpret the glass structure, addressing the situation that the structure of glass is isolated from the properties, which was the case in previous studies.

We have recently applied this phase diagram approach to investigate the physical properties of a series of binary glasses, and the results show that the calculated values agree well with the experimental ones [27], confirming that the phase diagram approach is applicable to binary glass systems. Herein, the phase diagram approach is used to quantitatively predict the structure and physical properties (i.e. density, refractive index, thermal expansion coefficient, elastic modulus and shear modulus) of several ternary glass systems based on a small amount of reasonable data. By virtue of the phase diagram model, the