Rotational invariants of network former and modifier cations in silicate glasses

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ABSTRACT

The structure of oxide glasses is described in terms of the local atomic environment of cations, and a key role is played by cation-oxygen coordination numbers (CN) and coordination polyhedra. There are no preferred axes in an isotropic material like a glass, so the description of coordination polyhedra must be rotationally invariant. Here a new analysis is presented using the second order rotational invariant Q_l which are based on the spherical harmonic coefficients C_{lm} of the coordination polyhedra. The Q_l are related to crystal field strength parameters which are reported in the studies of rare earth luminescence. There are few previous studies of rotational invariants and they tend to focus on hard sphere and Lennard–Jones models, and to focus on Q_l with l even. Here results are presented for Q_l of Si, Na, Mg, Ca, Ba, and Eu cations in molecular dynamics models of silicate glasses including a 15,100 atom model of Eu-doped sodium silicate glass. For Si with CN = 4 the Q_l are very similar to those for tetrahedra, and variations in tetrahedral distortion are apparent in different glasses. For Na with CN = 5 the Q_l are similar to those for a random distribution, except for l = 1 and 2 where the non-overlap of neighbouring atoms prevents a truly random distribution. The values of Q_l for Mg cations with CN = 4 and CN = 5 show similarities to those for Al cations with CN = 4 and Na cations with CN = 5 respectively. The values of Q_l for Ca and Ba cations with CN = 6 differ from those for a random distribution for Q_l with l ≤ 4. For Eu with CN = 6 the Q_l are between those for octahedral and for a trigonal prism geometries. For all cations there are significant values for Q_l with l odd.

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1. Introduction

The structures of crystalline solids are appropriately described using concepts of exact symmetry, e.g. the space group of the unit cell, which are inappropriate for non-crystalline materials. Instead, the structures of glasses are appropriately described using functions which focus on short range order, and can quantify the degree of order on continuous scale (i.e. varying from completely random to crystalline). Short range order in the form of bond lengths and coordination numbers (CN) results from chemical interactions, can be measured using structural techniques such as diffraction, and can be represented by the pair distribution function [1]. Coordination geometries of atoms can be described using the bond angle distribution function, readily obtained from atomistic models but more difficult to obtain from experiments [1]. Here we look at the use of alternative parameters, referred to as rotational invariant Q_l, for describing the type of and degree of order in coordination geometries.

The use of rotational invariants to describe non-crystalline structures has been reported in previous studies, where the same parameters

may also be referred to as "spherical invariants" or "bond orientational order parameters". (The definition of rotational invariants will be given in Section 2). Probably the most well-known study is by Steinhardt et al. [2]. That study used bond orientational order parameter Q_l to characterise the order in coordination geometries of atoms in Lennard–Jones (LJ) liquids and dense random packed models, and a resemblance to icosahedral geometry was proposed. Interestingly, though, the values of Q_l were only presented for l even, despite the fact that values of Q_l for l odd will be non-zero when there is no centrosymmetry. A later study [3] reported values of Q_l for l even and odd for LJ liquids, and since Q_l with l odd were found to be large, that study questioned the hypothesis of icosahedral geometry (which has zero values for Q_l with l odd). The present study reports values of Q_l including l odd for cations in silicate glasses, and to our knowledge, is the first such report for non-crystalline structures which are not dense packed.

Silicate glasses are the main representative of oxide glasses, and the structural organisation of oxide glasses is based on cations with different structural roles (e.g. [4]). Network formers have well-defined short range order, the archetypal example being Si, which always has a tetrahedral coordination with a relatively undistorted geometry. Network modifiers, such as Na, have variable CNs with less well-defined coordination geometry. These differences follow from the different

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interatomic interactions of Si and Na with oxygen, and are observed in both sodium silicate crystals and glasses. Some cations fall on a spectrum between the clearcut cases of Si and Na, and may sometimes be considered "intermediates". Fig. 1 illustrates these differences by showing typical bond angle distribution functions for Si cations [5], Na cations [6] and dopant Eu cations [7] in sodium silicate glasses. The present study explores the potential for rotational invariant parameter Q_l to reveal the type and degree of order present in coordination geometries of cations in oxide glasses.

2. Method

In a glass with atom positions $R_i = (x_i, y_i, z_i)$ the information about the positions of neighbouring atoms j relative to a given atom i can be expressed using

$$T_i(x, y, z) = \sum_{j \neq i} \delta(x - x_{ij}) \delta(y - y_{ij}) \delta(z - z_{ij}) \quad (1)$$

where $x_{ij} = (x_j - x_i)$. In isotropic materials like glasses it is common to describe separately the correlations in radial positions of neighbouring atoms r_{ij} using the pair distribution function $T(r)$ which is the orientational average of $T_i(x, y, z)$ over all atoms i, i.e.

$$T(r) = \frac{1}{N} \sum_i \sum_{j \neq i} \partial(r - r_{ij}). \quad (2)$$

For radial distances r corresponding to cation-oxygen nearest neighbours, i.e. bond lengths, it is common to describe separately the correlations in angular positions of nearest neighbour atoms (θ_{ij}, ϕ_{ij}) using the bond angle distribution function (where θ_{ij} means the angular position of atom j when atom i is at the origin). Alternatively, the part of the function $T_i(x, y, z)$ which depends on (θ_{ij}, ϕ_{ij}) is

$$\tau_i(\theta, \phi) = \sum_{j \neq i} \delta(\theta - \theta_{ij}) \delta(\phi - \phi_{ij}). \quad (3)$$

A function $f(\theta, \phi)$ can be represented as an expansion in spherical harmonics $Y_{lm}(\theta, \phi)$ with coefficients C_{lm} such that

$$f(\theta, \phi) = \sum_l \sum_m C_{lm} Y_{lm}(\theta, \phi). \quad (4)$$

From the properties of completeness and orthogonality, the values of C_{lm} are given by

$$C_{lm} = \iint f(\theta, \phi) Y_{lm}^*(\theta, \phi) \sin\theta \, d\theta \, d\phi \quad (5)$$

where * denotes the complex conjugate. If the function $f(\theta, \phi)$ is normalised such that the integral of the modulus squared is equal to one then the coefficients C_{lm} will be normalised such that the sum of the moduli squared is equal to one. However, the values of C_{lm} depend on the axis orientation which cannot be important in an isotropic material. The values of C_{lm} can be used to calculate the second order rotational invariants

$$Q_l = \left(\frac{1}{2l+1} \sum_m C_{lm}^2 \right)^{1/2} \quad (6)$$

which do not dependent on the axis orientation. This is illustrated in Fig. 2 by using the example function

$$f(\theta, \phi) = \cos(2\theta) = \cos(2\hat{z}) \quad (7)$$

which has the spherical harmonic coefficients $C_{00} = 0.489$ and $C_{20} = 0.874$. In comparison, the example function

$$f(\theta, \phi) = \sin(2\theta)\cos(2\phi) = \cos(2\hat{x}) \quad (8)$$

has the spherical harmonic coefficients $C_{00} = 0.489$, $C_{20} = -0.438$, and $C_{22} = C_{2-2} = 0.536$. These two functions differ only in the axis orientation and both functions have the same rotational invariants $Q_0 = 0.489$ and $Q_2 = 0.391$.

Returning to the distribution of N nearest neighbour atoms it is necessary to consider the discrete function $f(\theta, \phi) = \tau_i(\theta, \phi)$ rather than the continuous functions of the kind used in the above examples. The presence of delta functions in $\tau_i(\theta, \phi)$ complicates the normalisation, and for convenience we do not normalise $\tau_i(\theta, \phi)$. Substituting $\tau_i(\theta, \phi)$ into the expression for C_{lm} gives

$$C_{lm} = \sum_{j \neq i} Y_{lm}^*(\theta_{ij}, \phi_{ij}). \quad (9)$$

This is illustrated in Fig. 3 using the example function consisting of four points in a "square" in the (x,y) plane which for $l \leq 5$ has non-zero values of $C_{00} = 1.128$, $C_{20} = -1.262$, $C_{44} = C_{4-4} = 1.770$, and $C_{40} = 1.269$. In comparison the example function consisting of four points in a "square" in the (x,z) plane has non-zero values of $C_{00} =$
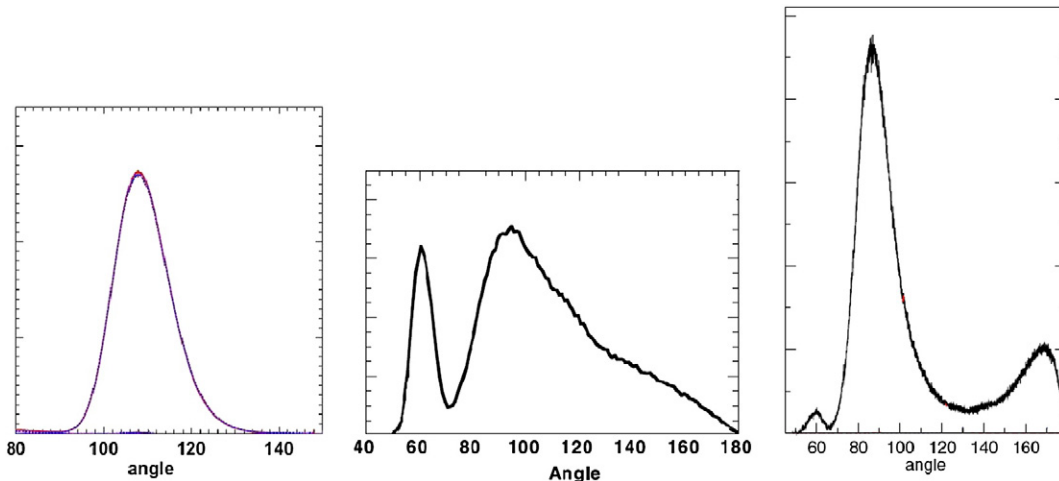

Fig. 1. Typical bond angle distribution functions for (left) Si cations [5], (middle) Na cations [6] and (right) dopant Eu cations [7] in sodium silicate glasses.