Chun-Rong Feng, Jun Jian, Xiao-Hong Chen*, Quan Du and Ling Wang

Investigations on the Local Structures and the Spin Hamiltonian Parameters for Cu$^{2+}$ in (90–x) TeO$_2$–10GeO$_2$–xWO$_3$ Glasses

https://doi.org/10.1515/zna-2017-0308
Received September 3, 2017; accepted October 9, 2017; previously published online November 9, 2017

Abstract: The local structures and the spin Hamiltonian parameters (SHPs) for Cu$^{2+}$ in (90–x)TeO$_2$–10GeO$_2$–xWO$_3$ glasses are theoretically investigated at various WO$_3$ concentrations (x=7.5, 15, 22.5 and 30 mol%). Subject to the Jahn-Teller effect, the [CuO$_6$]$^{10-}$ groups are found to experience the small or moderate tetragonal elongation distortions (characterised by the relative tetragonal elongation ratios ρ = 0.35–3.09 %) in C$_2$ axis. With only three adjusted coefficients $a$, $b$ and $α$, the relevant model parameters (D$_q$, k and ρ) are described by the Fourier type and linear functions, respectively, and the measured concentration dependences of the d–d transition bands and SHPs are reproducible. The maximum of $g$ and the minimum of $|A_||$ and the minimum of $|A_\perp|$ and the lowest $|A_\perp|$ at $x = 15$ mol% are illustrated from the abrupt decrease of the copper–oxygen electron cloud admixtures or covalency and the obvious decline of the copper 3d–3s (4s) orbital admixtures due to the decreasing electron cloud density around oxygen ligands spontaneously bonding with Cu$^{2+}$ and Te$^{4+}$ (W$^{6+}$), respectively.

Keywords: Cu$^{2+}$; Defect Structures; Electron Paramagnetic Resonance (EPR); TeO$_2$–GeO$_2$–WO$_3$ Glasses.

1 Introduction

Tellurite glasses have unique irradiation shielding [1, 2], optical spectral [3], thermal and structural properties [4] as well as photon upconversion behaviour [5]. Tellurite glasses partially substituted by germinate can form germinate-tellurite glasses with interesting emission [6–9] and fluorescence [10–12] properties. Addition of WO$_3$ can lead to the novel tellurite germanate tungstate TeO$_2$–GeO$_2$–WO$_3$ (TGW) glasses, which exhibit useful DC conductivity as well as optical [13, 14] and thermal performances [15].

Normally, the above properties and performances of TGW glasses depend strongly on the local structures of the network, which can be conveniently investigated with the aid of electron paramagnetic resonance (EPR) and optical absorption techniques by transition-metal (particularly, Cu$^{2+}$ (3d$^9$)) as a representative system with the simple electron level structure) probes. To study the influences of heavy metal oxide (WO$_3$) on the local structures of copper dopants in TGW glasses, infrared (IR), d–d transition optical and EPR experiments were performed for (90–x) TeO$_2$–10GeO$_2$–xWO$_3$ (TGW) (7.5 ≤ x ≤ 30 mol%) glasses with 1 mol% CuO dopants [16]. And the copper d–d transition bands and the spin Hamiltonian parameters (SHPs, $g$ factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$ and $A_\perp$) were measured at different WO$_3$ concentrations $x$ [16]. Based on the simple $g$ formulas and the orbital reduction factor $K = 0.77$ [16], the experimental $g$ factors were quantitatively analysed to obtain the optimal bond parameters $\alpha^2$, $\beta^\parallel$, and $\beta^\perp = 1$ in the previous work [16]. Nevertheless, the hyperfine structure constants have not been uniformly studied for the various concentrations. Nor has the quantitative information has been acquired about the concentration dependence of the local structure around Cu$^{2+}$ dopants. In essence, the observed d–d transition bands and SHPs (especially $g_\parallel$ and $A_\parallel$) exhibit an overall declining rule accomplished by some fluctuations, with the largest $g_\parallel$ and the lowest $|A_\parallel|$ at $x = 15$ mol% [16]. Therefore, the above concentration dependences of the optical and EPR spectra for Cu$^{2+}$ in TGW glasses are worthy to be further investigated in a consistent way.

The concentration variations of the optical and EPR spectra may reveal the modifications of the local structures (e.g. local symmetry, strength of crystal-fields and electron cloud distributions) around impurities Cu$^{2+}$. Thus, a systematic investigation of the local structures, SHPs and d–d transition bands for Cu$^{2+}$ in TGW glasses at distinct CuO concentrations is of scientific and practical importance. The arrangement of this paper is as follows.

*Corresponding author: Xiao-Hong Chen, School of Science and Research Center for Advanced Computation, Xihua University, Chengdu 610039, P.R. China, E-mail: xhchen65@163.com
Chun-Rong Feng: School of Science, Xihua University, Chengdu 610039, P.R. China
Jun Jian: Department of Applied Physics, School of Science, Xihua University, Chengdu 610039, P.R. China
Quan Du and Ling Wang: School of Science and Research Center for Advanced Computation, Xihua University, Chengdu 610039, P.R. China
In Section 2, the concentration dependences of d–d transition bands, SHPs and local structure are theoretically calculated for Cu²⁺ in TGW glasses. Then the local optical basicity \( \Lambda_{\text{loc}} \) is analysed and compared with the previous conventional optical basicity \( \Lambda_{\text{th}} \) for the various concentrations in Section 3. The features of the SHPs and local structures are discussed in Section 4, and the microscopic mechanisms of the concentration dependences of these properties are also analysed in a consistent way.

### 2 Theoretical Calculations

For the studied TGW glasses, increases in the concentration of the modifier WO₃ may bring about increase in non-bridging oxygen (NBO) concentration in the glass network. The impurity Cu²⁺ can dominantly occupy some suitable octahedral site and construct the octahedral \([\text{CuO}_6]^{10-}\) group. Importantly, the Jahn-Teller effect for this 3d⁹ group can lead to a tetragonal elongation distortion by means of the vibrational interactions [17–20]. So, the local structure around impurity Cu²⁺ may be described as two longer axial bonds and four shorter perpendicular ones, characterised by the relative tetragonal elongation ratio \( \rho \) and the positive anisotropy \( \Delta g = g_\perp - g_\parallel \).

For the \([\text{CuO}_6]^{10-}\) groups undergoing the Jahn-Teller elongation distortions, the copper–oxygen distances parallel and perpendicular to the \( C_4 \) axis can be written in terms of the reference distance \( R_0 \) and the relative tetragonal elongation ratio \( \rho \) as:

\[
\begin{align*}
R &= R_0 (1 + 2 \rho), \\
R_\perp &= R_0 (1 - \rho).
\end{align*}
\]

For a tetragonally elongated 3d⁹ group, the original cubic ground orbital doublet \( ^3E_g \) can split into two orbital singlets \( ^2B_{1g} \) and \( ^2A_{1g} \), with the former lying lowest. And the original two-fold orbital degeneracy is entirely cancelled. On the other hand, the original cubic excited orbital triplet \( ^3T_{1g} \) can be separated into an orbital singlet \( ^3B_{2g} \) and an orbital doublet \( ^3E_g \) [18–20].

#### 2.1 Calculations for Cu²⁺ d–d Transition Bands

The measured copper d–d transition bands [16] were explicitly ascribed to the transitions between the lowest \( ^2B_{1g} \) and the excited \( ^3B_{2g} \) states under the tetragonal crystal-fields, while the anisotropic EPR signals can be assigned to the transitions between the electronic Zeeman levels under external magnetic field. Normally, the energy separations \( E_1 \) and \( E_2 \) are used to label the separations between the excited \( ^3B_{2g} \) and \( ^3E \) states and the ground \( ^2B_{1g} \) state, in terms of the cubic crystal-field parameter \( D_q \) and the tetragonal crystal-field parameters \( D_s \) and \( D_t \) [18]:

\[
\begin{align*}
E_1 &= 10D_q, \\
E_2 &= 10D_q - 3D_s + 5D_t, \tag{2}
\end{align*}
\]

From the optical absorption spectra for Cu²⁺ in TGW glasses [16], the energy denominator \( E_1 \) or the cubic crystal-field parameter \( D_q \) exhibits the whole decreasing (from 1240.7 cm⁻¹ at 7.5 mol% to 1191.9 cm⁻¹ at 30 mol%) tendency and moderate fluctuations with concentration \( x \). For convenience, a Fourier type function is applied to manifest the above rule with moderate fluctuations. Thus, we have:

\[
D_q = D_q \left[ 1 + a \cos(\omega x) - \sin(\omega x) \right]. \tag{3}
\]

Here the adjusted coefficients \( a \) and \( \omega \) can be determined by fitting the experimental d–d transition bands.

<table>
<thead>
<tr>
<th>( x )</th>
<th>7.5</th>
<th>15</th>
<th>22.5</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_1 )</td>
<td>Cal.</td>
<td>12,405</td>
<td>12,250</td>
<td>12,084</td>
</tr>
<tr>
<td></td>
<td>Expt. [16]</td>
<td>12,406</td>
<td>12,210</td>
<td>12,077</td>
</tr>
<tr>
<td>( g_1 )</td>
<td>Cal.</td>
<td>2.413</td>
<td>2.420</td>
<td>2.425</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>2.356</td>
<td>2.388</td>
<td>2.359</td>
</tr>
<tr>
<td></td>
<td>Expt. [16]</td>
<td>2.355</td>
<td>2.386</td>
<td>2.362</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>Cal.</td>
<td>2.413</td>
<td>2.420</td>
<td>2.425</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>2.356</td>
<td>2.388</td>
<td>2.359</td>
</tr>
<tr>
<td></td>
<td>Expt. [16]</td>
<td>2.355</td>
<td>2.386</td>
<td>2.362</td>
</tr>
<tr>
<td>( \Lambda_{\text{loc}} )</td>
<td>Cal.</td>
<td>0.975</td>
<td>0.981</td>
<td>0.987</td>
</tr>
<tr>
<td>( \Lambda_{\text{th}} )</td>
<td>Cal.</td>
<td>0.5779</td>
<td>0.5750</td>
<td>0.5739</td>
</tr>
</tbody>
</table>

*Calculations of \( g \) factors based on the simple \( g \) formulas and the fitted bonding parameters \( \alpha, \beta, \gamma = 1 \) and the orbital reduction factor \( K = 0.77 \) in the previous analysis [16].

*Calculations of the SHPs based on the higher order perturbation formulas of these parameters in this work.

*Calculations of the local optical basicity in this work.
The reference value $D_{q0} = 1210 \text{ cm}^{-1}$ can be obtained from the optical spectral measurements for $\text{Cu}^{2+}$ in various oxide glasses [17, 19]. By fitting the theoretical $E_i$ to the experimental data for various concentrations $x$, the optimal quantities in (3) are obtained as:

$$a = 0.0362, \quad \omega = 2098.$$  

The corresponding d–d transition bands $E_i$ are compared with the experimental values [16] in Table 1.

### 2.2 Calculations for the SHPs

In order to perform further theoretical analysis on the EPR spectra for $\text{Cu}^{2+}$ in TGW glasses at various concentrations, the higher order perturbation formulas of the SHPs for tetragonally elongated octahedral 3d$^9$ groups are utilised here, which is dissimilar to the previous treatments of $g$ factors based on the simple $g$ formulas with various adjustable bond parameters [16]. These formulas are expressed as follows [21-23]:

$$g_{||} = g_s + 8k\zeta / E + k\zeta^2 / E^2 + 4k\zeta^2 / EE,$$

$$- g_s^2[1/E^2 - 1/(2E^2)] + k\zeta^2[4/E - 1/E] / E^2,$$

$$- 2k\zeta^2(2/E^2 - 1/E^2) / E + g_s^2[1/(E^2 - 1)/(2E^2)],$$

$$g_\perp = g_s + 2k\zeta / E^2 - 4k\zeta / (EE) + k\zeta^2[2/(EE) - 1/E^2]$$

$$+ 2g_s\zeta^2 / E^2 + k\zeta^2[2/E - 1/E] / EE(1/E^2 + 2/E) / (2E),$$

$$- k\zeta^2(1/E^2 - 1/(EE) + 1/E^2) / (2E),$$

$$A_{||} = P\gamma \kappa - 2H / 7 + (g_{||} - g_s) + 3(g_\perp - g_s) / 7,$$

$$A_\perp = P\gamma \kappa + 2H / 7 + 11(g_{||} - g_s) / 14.$$  

Here $g_s = 2.0023$ is the spin only value. $k$ represents the orbital reduction factor, characteristic of the covalency or electron cloud admixtures between the central ion and ligands in the studied systems. $\zeta$ and $P$ are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the 3d$^9$ ion in glasses, which are expressed by the corresponding free-ion values $\zeta_0$ and $P_0$, multiplying $k \kappa$ is the core polarisation constant, characteristic of the Fermi contact interactions related to the isotropic central ion 3d–3s (4s) orbital admixtures. $H$ is the reduction factor relevant to the anisotropic central ion 3d–3s (4s) orbital admixtures arising from the tetragonal elongation distortion [24].

According to the local structural properties of the studied $[\text{CuO}_x\beta]$ groups, the tetragonal crystal-field parameters can be determined from the superposition model [22, 25, 26]:

$$D_s = -(4/7)\bar{A}_2(R_0)[(R_0^5 / R_0^5)^3 - (R_0^5 / R_0^5)^d],$$

$$D_t = -(16/21)\bar{A}_2(R_0)[(R_0^5 / R_0^5)^3 - (R_0^5 / R_0^5)^d]$$

Here the superscripts $t_1 = (3)$ and $t_2 = (5)$ are the power-law exponents [25]. With the reference distance $R_0$, $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, satisfying the relationships $\bar{A}_2(R_0) = (3/4) D_q$ and $\bar{A}_4(R_0) = 10.8 \bar{A}_2(R_0)$ for octahedral 3d$^9$ groups [27, 28]. Therefore, the local distortions are closely correlated with the tetragonal crystal-field parameters and thus quantitatively involved in the theoretical analysis of the SHPs for $\text{Cu}^{2+}$ in TGW glasses.

In the light of (3) and (5), similar but less significant fluctuations of orbital reduction factor $k$ than $D_q$ can be expected in view of the whole increasing $g$ factors (especially $g_s$) and moderate fluctuations with $x$. For convenience, a factor $(-1/5)$ is added to the terms except 1 in the square bracket of (3). Then, the concentration dependence of orbital reduction factor can be similarly expressed as the Fourier type function:

$$k = k_0[1 - a\cos(\omega x) + \sin(\omega x)] / 5.$$  

Here the reference value $k_0 = 0.81$ is obtained from the optical spectral analysis for $\text{Cu}^{2+}$ in some oxide glasses [17, 19]. Utilizing (7), $k = 0.8082, 0.8372, 0.7961$ and 0.7836 are calculated for $x = 7.5, 15, 22.5$ and 30 mol%, respectively. The above values are qualitatively in consistence with the averages $(-0.8$ [16]) of the fitted bonding parameters $\alpha^2$ and $\beta^2$ and can be regarded as reasonable.

From (5), the anisotropy $\Delta g = g_{||} - g_{\perp}$ is relevant to the tetragonal crystal-field parameters $D_s$ and $D_t$ and hence with the relative tetragonal elongation ratio $\rho$. From the overall decreasing (from 0.278 at 7.5 mol% to 0.255 at 30 mol%) tendency and the moderate fluctuations of the measured $\Delta g$ with $x$ [16], the relative elongation ratio can be expressed by the following linear function:

$$\rho = \rho_0 (1 + bx),$$

where $\rho_0$ is the reference value of the relative elongation ratio. Inserting the above values and the spin-orbit coupling coefficient $\zeta_0 = 829 \text{ cm}^{-1}$ [29]) for free $\text{Cu}^{2+}$ into the $g$ formulas and matching the theoretical $\Delta g$ to the observed results, we have

$$\rho_0 = 4\% , \quad b = -3.0.$$  

The corresponding tetragonal elongation ratios $\rho = 3.09, 2.18, 1.26$ and 0.35% are obtained for $x = 7.5, 15, 22.5$ and 30 mol%, respectively. The theoretical $g$ factors (Cal. a) for various concentrations $x$ are shown in Table 1. For comparison, the calculated $g$ factors (Cal. a)
based on the simple $g$ formulas and the fitted bonding parameters $\alpha^2, \beta^2$, and $\beta^2 (= 1)$ as well as the orbital reduction factor $K = 0.77$ in the previous analysis [16] are also shown in Table 1.

From (5), it is seen that hyperfine structure constants depend mainly upon the isotropic contributions from core polarisation constant $\kappa$ and the anisotropic ones related to reduction factor $H$. Thus, the almost constant observed $A_i$ (except a sudden decrease in magnitude at 15 mol% [16]) may suggest that the concentration dependences of $\kappa$ and $H$ should obey the piecewise horizontal lines:

$$
\kappa = \begin{cases} 
\kappa_0 (x = 15 \text{ mol%}) \\
\kappa_0 (x = 15 \text{ mol%})^{*} 
\end{cases}
$$

$$
H = \begin{cases} 
H_0 (x = 15 \text{ mol%}) \\
H_0 (x = 15 \text{ mol%})^{*} 
\end{cases}
$$

where $\kappa_0 = -2\chi/(3 <r^3>)$, where $\chi$ is characteristic of the density of unpaired spins at the nucleus of the central ion and $<r^3>$ is the expectation value of the inverse cube of the 3d radial wave function of the impurity ion [30], which can be obtained from the corresponding free-ion value $<r^3>_o$ multiplying $k_0$. Utilising the data $<r^3> = 8.252$ a.u. [31] and $\chi = 2.91$ a.u. [30] for Cu$^{2+}$ in the oxides, one can obtain $\kappa_0 = 0.29$, which is comparable with the expectation ($= 0.3$ [29]) for 3d transition-metal ions in oxides and can be regarded as suitable. In view of the sudden decrease of $|A_i|$ at 15 mol%, the lower value of $\kappa_0 = 0.27$ is adopted for this concentration. The reference value $H_0$ of the reduction factor can be reasonably taken as 0.805 in view of the anisotropic Cu$^{2+}$ 3d–3s (4s) orbital admixtures, which lowers this quantity by about 20% from the ideal value of unity [28]. Similarly, the lower value of $H_0 = 0.786$ is applied in consideration of the abrupt decline of $|A_i|$ at $x = 15$ mol%. Substituting these values and the dipolar hyperfine structure parameter $P_o (= 402 \times 10^{-6}$ cm$^{-1}$ [30]) for a free Cu$^{2+}$ ion into (4), the concentration dependences of hyperfine structure constants (Cal.) are obtained and compared with the experimental data in Table 1.

### 3 Calculations of Local Optical Basicity $\Lambda_{\text{loc}}$

Reflecting the acid–base property of oxide glasses, the conventional optical basicity $\Lambda_{\text{con}}$ indicates the ability of the glasses to contribute negative charge to the probe ion (e.g. Cu$^{2+}$). In the light of the previous analysis, $\Lambda_{\text{con}}$ shows an increasing rule with WO$_3$ concentration [16] (see Table 1). This point was illustrated by the increase in polarisability of NBOs with the modifier concentration [16].

In order to further explore the electron cloud distribution and covalency of the [CuO$_4$] tetrahedra groups, the local optical basicity $\Lambda_{\text{loc}}$ is applied here to characterise the variations of the local environments around the impurities (e.g. Cu$^{2+}$) in TGW glasses at various WO$_3$ compositions. The local optical basicity can be expressed as follows [32]:

$$
\Lambda_{\text{loc}} = 1 - \sum_{i=1}^{n} \frac{O_i}{N_i} \left[ \frac{Z_{ij} \left(1 - \frac{1}{\gamma_{ij}} \right)}{N_{ij}} \right],
$$

with the normalisation condition [32]

$$
\sum_{i=1}^{n} \frac{O_i}{N_i} = 1.
$$

Here $\gamma_{ij}$ is the basicity moderating parameter of the $j$th cation in $i$th unit [33]:

$$
\gamma_{ij} = 1.36(x_j - 0.26),
$$

where $x_i$ is the Pauling’s electronegativity [34] of the $i$th cation. In the studied TGW glasses, the Pauling’s electronegativity $x_i$ values are 2.36, 2.10 and 1.90 [34] for W$^{6+}$, Te$^{4+}$ and Cu$^{2+}$, respectively.

In (11), $N_i$ is the sort number of oxyanion units, $N_i$ is the highest coordination number of central ion, $N_{ij}$ is the coordination number of oxygen in $i$th unit and $o_i$ is the average number of the $i$th unit involved in the coordination. $n$ is the number of cations in $i$th unit, $Z_{ij}$ is the oxidation number of the $j$th cation in $i$th unit and $r_{ij}$ is the ionic ratio related to the total number of oxides.

For the studied ($90-x$)TeO$_2$–10GeO$_2$–xWO$_3$ systems, the octahedral [CuO$_4$]$_{10}$ groups tend to situate into the decentralised area, largely exposed to two kinds of oxyanion units Cu–O–W (Te) and Cu–O–Cu (Te). Therefore, $N_o = 2$, and the occupied ratios $o_i/N_i$ are 1/$(1+x)$ and $x$/ $(1+x)$ for Cu–O–W (Te) and Cu–O–Cu (Te) units, respectively. Thus, the local optical basicity $\Lambda_{\text{loc}}$ for Cu$^{2+}$ in TGW glasses can be further expanded as:

$$
\Lambda_{\text{loc}} = x/(1+x)[1-[(1/4)(1-1/\gamma_{\text{Cu}}) + (1/3)(1-1/\gamma_{\text{Cu}})] + (1/9)(1-1/\gamma_{\text{Cu}})] + 1/(1+x)[1-[(1/4)(1-1/\gamma_{\text{Te}}) + (1/3)(1-1/\gamma_{\text{Te}})] + (2/9)(1-1/\gamma_{\text{Te}})].
$$

The calculated local optical basicities for Cu$^{2+}$ in TGW glasses at distinct $x$ values are also given in Table 1.
4 Discussion

The experimental d–d transition bands and SHPs for Cu\(^{2+}\) in TGW glasses at various WO\(_3\) concentrations are satisfactorily interpreted in a consistent way based on the Fourier type functions of the cubic field parameter Dq and the orbital reduction factor k as well as the linear function of the relative tetragonal elongation ratio \(\rho\) with concentration \(x\) of the modifier WO\(_3\), with only three adjusted coefficients \((a, b\) and \(\omega)\). The local structures and the SHPs as well as their concentration dependences can be analysed as follows.

(i) The features of the SHPs can be illustrated as follows. First, the overall unchanging \(g_\parallel\) with some fluctuations (i.e. a sudden increase at 15 mol\%, then an obvious decrease at 22.5 mol\% and a moderate decrease at 30 mol\%) can be ascribed to the fact that the competitive influences of the non-linearly decreasing Dq (from 1240.7 to 1191.9 cm\(^{-1}\) [16]) and the moderately decreasing \(k\) with some fluctuations (i.e. a sudden increase at 15 mol\%, then obvious decreases at higher concentrations) may largely cancel each other. The highest \(g_\parallel\) at 15 mol\% is mainly attributable to the largest \(k\) and the significant decrease in Dq at this concentration. Second, the slightly increasing \(g_\perp\) can be illustrated as the decreasing relative elongation ratio \(\rho\) and hence the decreasing magnitude of the negative tetragonal crystal-field parameter Ds, which induces decreasing denominator \(E\) in the perpendicular component of the \(g\) factors. Thus, the relatively higher \(g_\perp\) for Cu\(^{2+}\) in the present TGW glasses may be ascribed to the smaller tetragonal elongation distortions. As regards the anisotropy of \(g\) factors, the whole declining \(\Delta g\) arising from the overall unchanging \(g_\parallel\) and the increasing \(g_\perp\) is also assigned to the linearly decreasing \(\rho\), while the fluctuations of \(\Delta g\) are similar to those of \(g_\parallel\). Third, the abrupt decline of the magnitude for \(A_\parallel\) at 15 mol\% with respect to the other concentrations can be attributed to the sudden decreases (by 3–7%) of the core polarisation constant \(\kappa_0\) and the reduction factor \(H_0\) related to \(\kappa_0\) and \(H_0\). Additionally, the hyperfine structure constants in the EPR measurements are normally given as the absolute values [16, 30]. According to the present calculations, \(A_\parallel\) and \(A_\perp\) are found to be negative and positive, respectively. This is ascribed to the dominant negative contributions relevant to \(\kappa\) and \(H\) and the much smaller positive contributions relevant to \(g\)-shifts for the parallel component, and the negative contributions related to \(\kappa\) and the comparable but slightly larger positive contributions due to \(H\) and \(g\)-shifts for the perpendicular component, respectively. Although the present calculated \(A_\parallel\) remains to be further checked with the experimental measurements; the very low magnitudes of the perpendicular hyperfine structure constants are somewhat qualitatively in agreement with the absence of the observed \(A_\perp\).

(ii) The moderate or small relative elongation ratio \(\rho\) (=0.35–3.09%) with linearly decreasing rule for copper in TGW glasses is of the Jahn-Teller character by means of the vibration interactions in the octahedral [CuO\(_6\)]\(^{10-}\) groups. Similar moderate or small relative tetragonal elongations (\(\rho = 3\% \) and 7% or 0.4%) were also reported for Cu\(^{2+}\) in xLi\(_2\)O·(30–x)·K\(_2\)O·70B\(_2\)O\(_3\) \((0 \leq x \leq 25 \text{ mol\%})\) [35] and LiRbB\(_4\)O\(_7\) [36] or xMgO·(30–x)·Na\(_2\)O·69B\(_2\)O\(_3\) \((5 \leq x \leq 17 \text{ mol\%})\) glasses [37], respectively. The above positive tetragonal elongation ratios yield longer axial copper–oxygen bond lengths than the perpendicular ones, and the resultant tetragonal elongation distortions are associated with the lowest \(\Gamma^\perp\) state and positive anisotropy \(\Delta g\) [19–21]. Thus, the local structure and its concentration dependence are quantitatively correlated to the anisotropy of the experimental EPR spectra for Cu\(^{2+}\) in TGW glasses.

(iii) The calculated \(g_\parallel\) and \(g_\perp\) (Cal.) by using the simple \(g\) formulas and the fitted bonding parameters \(\alpha^\perp\), \(\beta^\perp\) and \(\alpha^\parallel\) (1.009–1.059) as well as the orbital reduction factor \(K = 0.77\) in the previous analysis [16] are higher and lower than the experimental data, respectively, inducing larger \(\Delta g\) than the measured results [16]. On the other hand, both the present orbital reduction factors \(k = 0.8082, 0.8372, 0.7961\) and 0.7836 based on (7) and the averages (0.815, 0.848, 0.812 and 0.824) of the fitted \(\alpha^\parallel\) and \(\beta^\parallel\) at distinct concentrations in [16] display their respective maxima at 15 mol\%, reflecting the lowest covalency (or highest ionicity) of the copper–oxygen bonds for this concentration. This point is further supported by the largest \(\beta^\parallel = 0.958\) [16] and the lowest normalised covalency \(\Gamma^\perp = 8.5\%\) [16] characterised by the predominant ionicity of the in-plane \(\pi\) bonding at this concentration. In addition, the overall decreasing tendency of \(k\) is largely consistent with the decreasing local optical basicity \(\Lambda_{\text{loc}}\) with the increase in WO\(_3\) concentration, whereas the conventional optical basicity \(\Lambda_{\text{ch}}\) demonstrates an increasing tendency due to the increasing polarisability of NBOs [16], So, local optical basicity seems more suitable to describe the local environments and covalency around the transition-metal dopants in glasses.

(iv) The concentration dependences of d–d transition bands and SHPs can be largely illustrated as the
modifications of the local crystal-fields and the electron cloud admixtures around the impurity Cu2+ in the [CuO4]16− groups due to the variations of the concentration of the modifier-induced NBOs and the difference in field strength between W6+ and Te4+ cations. First, the increases in the concentration of WO3 bring about increasing NBOs with much higher polarisability which mainly act as the ligands of the Cu2+ dopants and lead to the fluctuations of the local crystal-fields and the SHPs. As Te4+ is gradually replaced by W6+ with higher field strength, the original Te–O–Te linkages in the glass network are partially substituted by the new Te–O–W or W–O–W ones through some TeO4 groups, as supported by the decreases in the electron cloud density around the oxygen ligands bonding with both Cu2+ and Te4+ due to the Te–O bonding with stronger covalency, leading to the decrease in the copper–oxygen electron cloud admixture and covalency of the [CuO4]16− groups. This is also supported by the higher conventional optical basicity values of the present TGW glasses than those of various borate glasses (e.g. \( \Lambda_{\text{in}} \approx 0.69–0.77 \) [38] and 0.76 [39]) for Cu2+ in R2B4O7 · 9PbO · CuO (R = Li, Na and K) and xLi2O · (30–x) · Na2O · 69.5B2O3 (5 ≤ x ≤ 25 mol%) glasses, respectively. This point may be understood. Second, the covalency of the present TGW:Cu2+ glasses is weaker than the conventional borate glasses (e.g. values about 0.76–0.77 [38] and 0.76 [39] for Cu2+ in R2B4O7 · 9PbO · CuO (R = Li, Na and K) and xLi2O · (30–x) · Na2O · 69.5B2O3 (5 ≤ x ≤ 25 mol%) glasses, respectively). On the one hand, the increases in polarizability with much higher (about twice) field strength which yields the lower \( k'_{\text{o}} \) and \( H'_{\text{o}} \) and hence the smallest \( |A_{\text{f}}| \). Finally, linearly declining relative tetragonal elongation ratio of the Jahn-Teller character can be ascribed to the weakening Cu–O bonding and hence the vibration interactions of the [CuO4]16− groups with increasing x, in accordance with the decreasing rule of cubic field parameter Dq.

5 Conclusion

The local distortions and SHPs for Cu2+ in TGW glasses are theoretically studied for various WO3 concentrations from the perturbation calculations of these parameters. Owing to the Jahn-Teller effect, the [CuO4]16− groups are found to undergo the moderate or small tetragonal elongation distortions (characterised by the moderate or small relative tetragonal elongation ratios \( \rho = 0.35–0.39 \% \)) along C4 axis. With only three adjusted coefficients \( a, b \) and \( \omega \), the relevant model parameters (Dq, \( k \) and \( \rho \)) are described by the Fourier type and linear functions, and the measured concentration dependences of the d–d transition bands and SHPs are soundly reproduced. The maximum of \( g_{\text{is}} \) and the minimum of \( |A_{\text{f}}| \) at x = 15 mol% are illustrated from the obvious decreases of the copper–oxygen electron cloud admixtures (covalency) and the cubic field parameter as well as the abrupt decreases in the copper 3d–3s (4s) orbital admixtures due to the decreasing electron cloud density of the oxygen ligands spontaneously bonding with Cu2+ and Te4+ (W6+), respectively.

Acknowledgements: This work was financially supported by the Funds for Sichuan Distinguished Scientists (Grant No. 2015Q0042) in China, and the Funds for the Youth Innovation Team of the Education Department of Sichuan Province (Grant No. I4TD0013) in China.

References


