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Investigations on the local structures of Cu^{2+} at various BaO concentrations in $59B_2O_3$–$10K_2O$–$(30-x)ZnO$–xBaO–$1CuO$ glasses

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ABSTRACT

The local structures and electron paramagnetic resonance (EPR) parameters for Cu^{2+} in $59B_2O_3$–$10K_2O$–$(30-x)ZnO$–xBaO–$1CuO$ (BKZBC) glasses are theoretically investigated with distinct modifier BaO concentrations x (= 0, 6, 12, 18, 24 and 30 mol %). The $\left[CuO_6\right]^{10-}$ clusters are found to undergo the relative tetragonal elongations of about 13.5 and 5.0% at zero and higher BaO concentrations. The concentration dependences of the measured d–d transition bands, g factors and $A_{//}$ are suitably reproduced from the Fourier type functions or sign functions of the relevant quantities with x by using only six adjustable parameters. The features of the EPR parameters and the local structures of Cu^{2+} are analysed in a consistent way by considering the differences in the local ligand field strength and electronic cloud admixtures around Cu^{2+} under addition of Ba^{2+} with the highest ionicity and polarisability. The present theoretical studies would be helpful to the researches on the structures, optical and EPR properties for the similar potassium barium zinc borate glasses containing copper with variation concentration of modifier BaO.

1. Introduction

Borate glasses exhibit novel photonic and optical properties [1]. Addition of ZnO and BaO brings forward barium zinc borate (BaO–ZnO–B_2O_3) glasses, which afford interesting thermal and electrical properties [2], IR and Raman spectroscopic behaviours [3] and radiative shielding features [4]. The properties of these borate glasses can be modified with addition of some network modifiers (especially alkali (e.g. K_2O) and alkaline earth oxides (e.g. BaO)) [5], e.g. potassium

zinc borate glasses exhibit unique luminescence properties [6–8]. On the other hand, the above borate glasses can be taken as the suitable hosts for some transition-metal dopants for the optoelectronic and optical fibre devices [9]. Among the transition-metal dopants, copper (Cu^{2+}) is an ideal probe to reveal the structural and electron paramagnetic resonance (EPR) properties of the glass systems due to the relatively simpler energy level structure and the convenience of remarkable optical absorption and EPR signals recordable at room temperature [10]. Therefore, optical and EPR investigations on the potassium barium zinc borate glasses containing copper dopants have been important and attractive subjects. Recently, optical adsorption and EPR experiments were performed for $59B_2O_3$–$10K_2O$–$(30-x)ZnO$–$xBaO$–$1CuO$ ($0 \leq x \leq 30$ mol %) (BKZBC) glasses with 1 mol % Cu^{2+}, and the copper d–d transition bands and the EPR parameters, g factors and hyperfine structure constants, were measured for distinct barium concentrations x [11]. The g factors were quantitatively discussed in Ref. [11] from the simple g formulas with the adjustable bonding parameters α^2, β_1^2 and fixed β^2 ($= 1$) and orbital reduction factor K ($= 0.77$). But comprehensive investigations of the d–d transition bands, the EPR parameters and the defect structures for Cu^{2+} in BKZBC glasses and their concentration dependences have not been made until now. Nor have the optical basicities been studied for different concentrations x.

It is known that the properties of materials are closely correlated to the local structures around the transition-metal impurities. And the systematic studies on the defect structures, EPR parameters, d–d transitions for Cu^{2+} in BKZBC glasses with distinct BaO concentrations are of special importance. In the present article, the g factors and hyperfine structure constants and defect structures of the Cu^{2+} dopants and their concentration dependences are theoretically studied from the perturbation calculations of these parameters for tetragonally elongated $3d^9$ clusters. Further, the local optical basicities of the systems are also calculated so as to illustrate the covalency or electronic cloud admixtures of the octahedral $\left[CuO_6\right]^{10-}$ clusters at various BaO concentrations. The results are discussed.

2. Theory and calculations

In this section, the g factors and hyperfine structure constants as well as the defect structures and their concentration dependences are theoretically analysed for impurity Cu^{2+} in BKZBC glasses from the perturbation formulas of the EPR parameters for tetragonally elongated octahedral $3d^9$ clusters.

2.1. Perturbation formulas of g factors and hyperfine structure constants for a tetragonally elongated octahedral 3d⁹ cluster

The local structures of Cu^{2+} in the octahedral sites of BKZBC glasses can be described as the tetragonal elongation distortions along the fourfold axis by a relative elongation ratio ρ due to the Jahn–Teller effect by means of the vibration

interactions [12–14]. Then the original ground orbital doublet ^2E_g of a regular octahedral $3d^9$ cluster may be split into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$ (the former lying lowest), and the twofold orbital degeneracy is entirely cancelled. On the other hand, the original excited orbital triplet $^2T_{2g}$ is separated into an orbital singlet $^2B_{2g}$ and an orbital doublet ^2E_g. Normally, the energy differences E_1 and E_2 are adopted to illustrate the separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states, respectively. They can be represented by using the cubic CF parameter Dq and the teteagonal CF parameters Ds and Dt [15–17]:

$$E_1 = 10Dq$$

$$E_2 = 10Dq - 3Ds + 5Dt \tag{1}$$

In order to analyse the EPR parameters for Cu^{2+} in BKZBC glasses, the fourth order perturbation formulas of the EPR parameters for a tetragonally elongated octahedral $3d^9$ cluster [15–17] are utilised here:

$$g_{//} = g_s + 8k\zeta/E_1 + k\zeta^2/E_2^2 + 4k\zeta^2/E_1E_2 - g_s\zeta^2\left[1/E_1^2 - 1/(2E_2^2)\right] + k\zeta^3(4/E_1 - 1/E_2)/E_2^2$$
$$- 2k\zeta^3(2/E_1E_2 - 1/E_2^2)/E_1 + g_s\zeta^3\left[1/(E_1E_2^2) - 1/(2E_2^3)\right],$$

$$g_\perp = g_s + 2k\zeta/E_2 - 4k\zeta^2/(E_1E_2) + k\zeta^2\left[2/(E_1E_2) - 1/E_2^2\right] + 2g_s\zeta^2/E_1^2 + k\zeta^3(2/E_1 - 1/E_2)$$
$$\times(1/E_2 + 2/E_1)/2E_2 - k\zeta^3(1/E_1^2 - 1/E_1E_2 + 1/E_2^2)/2E_2,$$

$$A_{//} = P[-\kappa - 4H/7 + (g_{||} - g_s) + 3(g_\perp - g_s)/7],$$

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

Here g_s (≈ 2.0023) is the g value of pure spin. k stands for the orbital reduction factor, reflecting covalency of the systems. ζ is the spin-orbit coupling coefficient, and P is the dipolar hyperfine structure parameter for the copper centres. They can be determined in terms of the respective free-ion values ζ_0 and P_0 as: $\zeta = k \zeta_0$ and $P = k P_0$. κ is the core polarisation constant, characteristic of the Fermi contact interactions due to the isotropic central ion 3d-3s (4s) orbital admixtures in the studied systems. H is the reduction factor characteristic of the anisotropic central ion 3d-3s (4s) orbital admixtures due to tetragonal elongation [15,18].

2.2. Superposition model formulas of the tetragonal CF parameters

Applying the superposition model [19–21] and the local geometry (i.e. the relative tetragonal elongation ratios ρ) of the copper centres, the tetragonal CF parameters are expressed as:

$$Ds = 4\bar{A}_2[(1 + 2\rho)^{-t2} - (1-\rho)^{-t2}]/7 ,$$

$$Dt = 16\bar{A}_4[\,(1 + 2\rho)^{-t4} - (1-\rho)^{-t4}]/21. \tag{3}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [19]. The relationships $\bar{A}_4 \approx (3/4)$ Dq and $\bar{A}_2 \approx 10.8\,\bar{A}_4$ [22–24] suitable for octahedral $3d^n$ clusters in many systems are adopted here.

2.3. Concentration dependence of Dq

In view of the overall non-linearly increasing trend of the d–d transition bands E_1 (= 10 Dq) with BaO concentration x [11], the Fourier type function is adopted to describe the concentration dependence of Dq:

$$Dq = Dq_0\big[1 + \big(a\,\cos\,(\omega_1 x) + b\,\sin\,(\omega_1 x)\big)\big] \tag{4}$$

Here the adjusted coefficients a, b and ω_1 are obtained by matching the measured d–d transition bands for various concentrations x. The reference (initial) value Dq_0 ≈ 1314 cm^{-1} may be determined in light of the optical absorption experiments for Cu^{2+} in some oxide glasses [25,26]. According to the observed concentration dependence of Dq [11], the optimal coefficients

$$a \approx -0.011796,\ b \approx 0.011035,\ \omega_1 \approx 2100 \tag{5}$$

are determined for the studied systems. The concentration dependence of E_1 is compared with experiment in Table 1.

Table 1. The d–d transition bands E_1 (= 10 Dq) (in cm^{-1}), g factors and hyperfine structure constants (in 10^{-4} cm^{-1}) for Cu^{2+} in BKZB glasses at various BaO concentrations x.

x (mol %)		0	6	12	18	24	30
E_1	Cal.	12,985	13,042	13,109	13,180	13,247	13,301
	Expt. [11]	12,987	13,037	13,089	13,175	13,262	13,333
$g_{//}$	Cal. [a]	2.310	2.300	2.306	2.309	2.302	2.298
	Cal. [b]	2.339	2.327	2.331	2.337	2.321	2.326
	Expt. [11]	2.333	2.323	2.331	2.337	2.331	2.329
$g_{\perp}$	Cal. [a]	2.044	2.062	2.061	2.060	2.063	2.058
	Cal. [b]	2.050	2.064	2.065	2.066	2.063	2.064
	Expt. [11]	2.047	2.067	2.066	2.065	2.069	2.064
$A_{//}$	Cal. [a]	–	–	–	–	–	–
	Cal. [b]	−141	−147	−142	−137	−139	−139
	Expt. [11]	−142	−149	−141	−136	−135	−139
$A_{\perp}$	Cal. [a]	–	–	–	–	–	–
	Cal. [b]	14	19	20	21	20	20
	Expt. [11]	–	–	–	–	–	–

[a]Calculations of g factors based on the simple g formulas and the fitted bonding parameters α^2 and β_1^2 as well as the fixed $\beta^2 = 1$ and orbital reduction factor $K = 0.77$ in the previous work [11].
[b]Calculations of the EPR parameters based on the perturbation formulas of this work.

2.4. Concentration dependences of g factors

2.4.1. Concentration dependence of $g_{//}$

From Equation (2), $g_{//}$ is largely proportional to the square of k and inverse of Dq, respectively. In view of the concentration dependences of $g_{//}$ and Dq [11], the varying rule of orbital reduction factor is written as:

$$k = k_0\left[1 + \left(-a\ \cos(\omega_2 x) - b\ \sin\left(\omega_2 x\right)/3\right)\right],\qquad(6)$$

Here the factor 1/3 is introduced in view of the much slighter fluctuations of k than Dq, and the frequency ω_2 denotes the more delicate variations (much higher frequency) with concentration. The reference value k_0 (≈ 0.803) can be obtained from the optical absorption measurements for Cu^{2+} in the oxides [26]. By inputting the free-ion spin-orbit coupling coefficient ζ_0 ($\approx 829\ cm^{-1}$ [27]) for Cu^{2+} and fitting the experimental concentration dependence of $g_{//}$, we have

$$\omega_2 \approx 15{,}115.\qquad(7)$$

The corresponding concentration dependence of $g_{//}$ (Cal. [b]) is shown in Table 1. In order to further evaluate the variation of covalency of the systems at distinct concentrations, the values of k and the averages $\chi\ (= \alpha^2 + \beta_1^{\ 2})$ of the fitted bonding parameters as well as the averages $\Gamma\ (= \Gamma_\pi + \Gamma_\sigma)$ of the normalisation covalency factors in the previous studies [11] are collected in Table 2. Meanwhile, the concentration dependences of these quantities are plotted in Figure 1 for visualisation.

2.4.2. Concentration dependence of $g_\perp$

From Ref. [11], $g_\perp$ exhibits a sudden increase from 2.050 at $x = 0$ mol % to 2.064 at $x = 6$ mol % and then approximately keeps unchanged at higher concentrations [11]. In the light of Equations (2) and (3), the perpendicular g-shift ($g_\perp - g_s$) is roughly inversely proportional to the denominator E_2, which decreases with decreasing the relative tetragonal elongation ratio ρ and hence the magnitude of the negative Ds. Thus, the concentration dependence of ρ can be expressed as follows:

$$\rho = \rho_0\left[1 + c\ \mathrm{Sgn}\ (x)\right].\qquad(8)$$

Table 2. The concentration dependences of the orbital reduction factor k as well as the averages $\chi\ (= (\alpha^2 + \beta_1^{\ 2})/2)$ of the bonding parameters and $\Gamma\ (= (\Gamma_\pi + \Gamma_\sigma)/2)$ of the normalisation covalency factors in the previous studies [11] as well as the general optical basicity Λ_{th} and the local optical basicity Λ_{loc} for Cu^{2+} in BKZBC glasses at various BaO concentrations x.

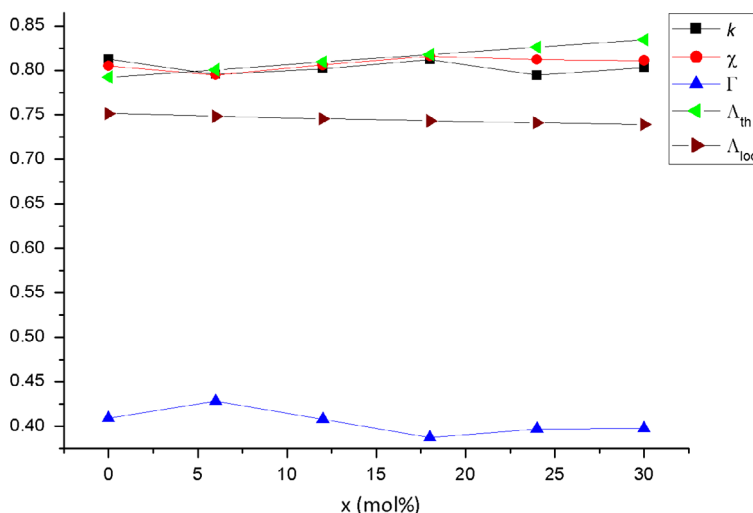| x (mol %)	0	6	12	18	24	30
k	0.813	0.795	0.802	0.812	0.795	0.803
χ	0.805	0.795	0.805	0.816	0.811	0.811
Γ	0.409	0.429	0.408	0.388	0.397	0.397
Λ_{th}	0.7924	0.8008	0.8092	0.8176	0.8260	0.8344
Λ_{loc}	0.7513	0.7483	0.7457	0.7433	0.7411	0.7391

Figure 1. (colour online) The concentration dependences of the orbital reduction factor k, the averages χ (= $(\alpha^2 + \beta_1^2)/2$) of the bonding parameters and Γ (= $(\Gamma_\pi + \Gamma_\sigma)/2$) of the normalisation covalency factors in the previous studies [11] as well as the general optical basicity Λ_{th} and the local optical basicity Λ_{loc} for Cu^{2+} in BKZBC glasses at various BaO concentrations x.

Here the reference value $\rho_0 \approx 13.5\%$ is determined by fitting the calculated $g_\perp$ to the experimental result (≈ 2.047 [11]) at $x = 0$. By matching the theoretical $g_\perp$ to the observed values at other concentrations, one can obtain the coefficient

$$c \approx -0.63. \qquad (9)$$

The corresponding relative elongation ratios are approximately 5.0% for $x = 6 - 30$ mol %. The theoretical $g_\perp$ (Cal. [b]) are compared with the experimental data [11] in Table 1. For comparison, the calculated g factors (Cal. [a]) based on the simple g formulas with three bonding parameters α^2, β^2 and β_1^2 in Ref. [11] are collected in Table 1.

2.5. Concentration dependences of hyperfine structure constants

The measured $A_{//}$ exhibits the roughly harmonic form variations with x and declines significantly in magnitude at $x = 12$ mol % [11]. In the light of Equation (2), the isotropic and anisotropic parts of $A_{//}$ depend mainly on the core polarisation constant κ and the reduction factor H, respectively. So, the varying rules of κ and H with x are shown as:

$$\kappa = \kappa_0 \left[1 - \left(a \cos\left(\omega_2 x\right) + b \sin\left(\omega_2 x\right)\right)/3 + d \, \text{Sgn}\left(x - 0.12\right)\right],$$

$$H = k_0 \left[1 + d \, \text{Sgn}\left(x\right)\right]. \qquad (10)$$

Here the reference value κ_0 is taken as 0.293, which is close to the expectation value 0.3 [27] for transition-metal ions in crystals. From the above relationships and the free-ion dipolar hyperfine structure parameter $P_0 \approx 402 \times 10^{-4}$ cm^{-1} [28] for Cu^{2+}, the coefficient d can be determined by fitting the measured concentration dependence of $A_{//}$:

$$d \approx 0.05. \tag{11}$$

The corresponding hyperfine structure constants are listed in Table 1. The calculated core polarisation constants and reduction factors are $\kappa \approx 0.33, 0.33, 0.32, 0.30, 0.30, 0.30$ and $H \approx 0.80, 0.84, 0.84, 0.84, 0.84, 0.84$ for $x = 0, 6, 12, 18, 24$ and 30 mol %, respectively.

2.6. Calculations of general optical basicity Λ_{th} and local optical basicity Λ_{loc}

In order to further evaluate the concentration dependence of covalency for the studied $[CuO_6]^{10-}$ clusters, not only the general optical basicity Λ_{th} but also the local optical basicity Λ_{loc} are analysed for the various concentrations x of the BKZBC glasses in this section.

2.6.1. Calculations of general optical basicity Λ_{th}

Characteristic of acid-base property of oxide glasses, the general optical basicity demonstrates the ability of the glasses to contribute negative charge to the probe ion (e.g. Cu^{2+}). This quantity is conventionally determined as follows [29–31]:

$$\Lambda_{th} = 1 - \sum_{i=1}^{n} \frac{Z_i r_i}{2} \left(1 - \frac{1}{\gamma_i} \right). \tag{12}$$

Here n is the total number of cations, Z_i is the oxidation number of the ith cation and r_i is the ionic ratio of the ith cation related to the total number of oxides. γ_i is the basicity moderating parameter of the ith cation [29]:

$$\gamma_i = 1.36(x_i - 0.26), \tag{13}$$

where x_i is the Pauling electronegativity [32] of the ith cation. Utilising the Pauling electronegativity $x_i \approx 0.89, 0.82, 1.65, 2.04$ and 1.90 [32] for Ba^{2+}, K$^+$, Zn^{2+}, B^{3+} and Cu^{2+}, respectively, the general optical basicities Λ_{th} are calculated for BKZBC glasses with distinct x and given in Table 2. For the present Cu^{2+} doped BKZBC glasses, Λ_{th} is found to increase with x, indicating overall decreasing covalency of the whole glass systems due to the highly ionic Ba^{2+}.

2.6.2. Calculations of local optical basicity Λ_{loc}

In Ref. [33], the local optical basicity Λ_{loc} was proposed to describe the variations of local environments in the vicinity of the impurities (e.g. Cu^{2+}) at different modifier concentrations. The local optical basicity can be defined as [33]:

$$\Lambda_{\text{loc}} = 1 - \sum_{i=1}^{N_u} \sum_{j=1}^{n_i} \frac{o_i}{N_c} \left[\frac{Z_{ij}\, r_{ij}}{N_{oi}} \left(1 - \frac{1}{\gamma_{ij}} \right) \right], \tag{14}$$

with the normalisation condition

$$\sum_{i=1}^{N_u} \frac{o_i}{N_c} = 1. \tag{15}$$

Here N_u is the sort number of oxyanion units, N_c is the highest coordination number of central ion. N_{Oi} is the coordination number of oxygen in ith unit, and o_i is the average number of the ith unit involved in the coordination. n_i is the number of cations in ith unit, Z_{ij} is the oxidation number of the jth cation in ith unit and r_{ij} is the ionic ratio related to the total number of oxides. γ_{ij} is the basicity moderating parameter of the jth cation in ith unit.

For BKZBC glasses, the octahedral $[CuO_6]^{10-}$ clusters tend to situate in the decentralised area and may be exposed to two kinds of oxyanion units Cu–O–R(B) and Cu–O–Cu (B) (R = K and Ba). Therefore, $N_u = 2$, and the occupied ratios o_i/N_c are $1/(1+x)$ and $x/(1+x)$ for Cu–O–R(B) and Cu–O–Cu (B) units, respectively. Thus, the local optical basicity Λ_{loc} for Cu^{2+} in BKZBC glasses can be further expanded as:

$$\Lambda_{\text{loc}} = 1 / (1+x) \{1 - [(1/4)(1 - 1/\gamma_B) + (1/6)(1 - 1/\gamma_K) + (1/9)(1 - 1/\gamma_{Ba}) + (1/9)(1 - 1/\gamma_{Cu})]\}$$
$$+ x / (1+x)\{1 - [(1/4)(1 - 1/\gamma_B) + (1/6)(1 - 1/\gamma_K) + (1/9)(1 - 1/\gamma_{Ba}) + (1/9)(1 - 1/\gamma_{Cu})\}. \tag{16}$$

The calculated local optical basicities of BKZBC glasses with distinct x are given in Table 2. For visualisation, the concentration dependences of the general and local optical basicities for the studied systems are plotted in Figure 1.

3. Discussion

From Tables 1 and 2, the experimental d–d transition bands and the EPR parameters and their concentration dependences [11] are suitably reproduced in this work for Cu^{2+} in BKZBC glasses from Equations (4), (6), (8) and (10) for cubic CF parameter Dq, orbital reduction factor k, relative elongation ratio ρ as well as the core polarisation constant κ and the reduction factor H with BaO concentration x by using only six adjustable parameters (a, b, c, d, ω_1 and ω_2).

  (1) In the light of Equation (4), the d–d transition band or the cubic CF parameter Dq demonstrates the non-linearly increasing tendency with x. This is in accordance with the similar increasing rule of the density of BKZBC systems [11] and the decreasing copper–oxygen distance or the increasing CF strength of the $[CuO_6]^{10-}$ clusters. This is also supported

by the blue shifts of the IR peaks from 696 to 719 cm^{-1} [11], corresponding to the bending vibration of the B–O–B linkage of the glass network [34]. Importantly, the increasing glass transition temperature T_g with x also reflects the more rigid and highly cross-linked network and the higher thermal stability under addition of BaO with high polarisability, which makes BKZBC glasses promisingly applicable in fibre drawing [11]. The non-linear (i.e. Fourier type) variation of Dq can be ascribed to the modifications of the ligand fields around the copper dopants arising from the changes of distribution of non-bridging oxygens (NBOs) as well as the variations of the differences in field strength and polarisability between Ba^{2+} and Zn^{2+} with x. So, the present fitting of Dq based on the Fourier type function in Equation (4) can suitably illustrate the variations of the local CFs around impurity Cu^{2+} in the studied glasses.

(2) The Fourier type varying orbital reduction factor k in Equation (6) reveals the overall increasing covalency of the $\left[\text{CuO}_6\right]^{10-}$ clusters with some fluctuations. In detail, k declines from $x = 0$ to 6 mol %, and increases from $x = 12$ to 18 mol %, then decreases at 24 mol % and finally slightly increases at the highest $x = 30$ mol %, which accounts for the similar varying rule of $g_{//}$ [11] under the increasing Dq. From Table 2 and Figure 1, the present concentration dependence of k is largely consistent with that of the average χ $(= (\alpha^2 + \beta_1^2)/2)$ of the fitted bonding parameters and roughly opposite to that of the average Γ $(= (\Gamma_\pi + \Gamma_\sigma)/2)$ of the normalisation covalency factors in the previous analysis [11] and can be regarded as reasonable. Meanwhile, the overall decreasing tendency of k is also in accordance with the decreasing local optical basicity Λ_{loc}, despite the increasing general optical basicity Λ_{th}. This means that the local environments and covalency around transition-metal dopants in the glasses can be more conveniently evaluated by local optical basicity. The covalency of the studied systems is dominantly characterised by the in-plane π bonding between copper 3d and oxygen 2p orbitals. Physically, the increase of the concentration of Ba^{2+} with the highest ionicity and polarisability may depress the electronic cloud density around Ba^{2+} and bring forward an increase of the electronic cloud admixtures between Cu^{2+} and the ligand oxygen bonding with Ba^{2+}, resulting in the overall increasing covalency of the $\left[\text{CuO}_6\right]^{10-}$ clusters. Meanwhile, the increasing density of BKZBC glasses with x also indicates the increasing bonding strength of the systems and indirectly supports the slightly decreasing copper–oxygen distances and the roughly increasing covalency or decreasing k. In addition, the fluctuations of covalency with x can be illustrated by the variations of the field strengths and polarisabilities in the vicinity of Cu^{2+} when Zn^{2+} is gradually replaced by Ba^{2+}.

(3) The local structures of impurities Cu^{2+} are characterised by the large relative elongation ratio ρ ($\approx 13.5\%$) at zero BaO concentration and smaller ρ ($\approx 5.0\%$) at higher concentrations, as described by the sign function of Equation (8) with the negative coefficient c. From Equations (1), (3) and (4), the above abrupt decrease of ρ at $x = 6$ mol % can reduce the magnitude of the negative tetragonal CF parameter Ds. and hence the denominator E_2, yielding the sudden increase of $g_\perp$ at this concentration. The overall decreasing tendency of ρ can be ascribed to the increasing force constant of the Cu^{2+}–O^{2-} bonds, characterised by the increasing cubic CF parameter Dq. The present lower relative tetragonal elongations at $x > 0$ can be regarded as another evidence of the higher stability of BKZBC glasses with more rigid and highly cross-linked network due to BaO addition.

(4) For hyperfine structure constants, the whole decreasing core polarisation constant κ based on the roughly harmonic function and the overall increasing reduction factor H based on the sign function in Equation (10) can suitably reproduce the variations of $A_{//}$ with x. The magnitude of $A_{//}$ first increases at $x = 6$ mol %, then declines from 12 to 24 mol % and increases slightly at the higher concentration 30 mol %. From Equation (2), the isotropic contributions from the core polarisation constant influence mainly the magnitudes of hyperfine structure constants, while the anisotropic contributions from H and g-shifts lead to the discrepancy between the parallel and perpendicular components. Since the deviation of H from unity usually reflects the degree of tetragonal elongation distortion in the impurity centres [18], the larger H at $x \geq 6$ mol % than $x = 0$ are suitably associated with the lower ρ at higher concentrations. The signs of $A_{//}$ and $A_\perp$, which were normally difficult to be determined experimentally [11], are found to be negative and positive, respectively. Of course, the present calculated $A_\perp$ remain to be verified by further experimental measurements. Finally, the microscopic mechanisms of the concentration dependences of κ and H can be roughly ascribed to the decreasing copper 3d-3s(4s) electronic cloud admixtures with increasing Ba^{2+} of the highest ionicity and polarisability due to the increasing electronic cloud density around the oxygen ligands simultaneously bonding to Cu^{2+} and Ba^{2+}.

4. Conclusion

This work performs the theoretical studies on the defect structures and the EPR parameters as well as their concentration dependences for Cu^{2+} in BKZBC glasses based on the relevant quantities (Dq, k, ρ, κ and H) at various BaO concentrations x. The $\left[CuO_6\right]^{10-}$ clusters are found to undergo the relative tetragonal elongations

of about 13.5 and 5.0% at zero and higher x. The features of EPR parameters and the local structures of the impurities Cu^{2+} are uniformly analysed from the variations of the local ligand field strength and electronic cloud admixtures in the vicinity of Cu^{2+} with increasing Ba^{2+} of the highest ionicity and polarisability. The concentration dependences of the measured d–d transition bands, g factors and $A_{//}$ are suitably reproduced from the Fourier type functions or sign functions of the relevant quantities with x. The present theoretical studies would be helpful to the further studies on the structures, optical and EPR properties for similar potassium barium zinc borate glasses containing copper with varying modifier concentration.

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