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An investigation of the local distortions and the EPR parameters for Cu^{2+} in 40MgO–(10–x)PbF_2–50SiO_2–xCuO glasses

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ABSTRACT

The local distortions and electron paramagnetic resonance (EPR) parameters for Cu^{2+} in 40MgO–(10–x)PbF_2–50SiO_2–xCuO (MPSC) glasses are theoretically studied at various impurity CuO concentrations x (= 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 mol %) in a consistent way. Due to the Jahn-Teller effect, the $[CuO_6]^{10-}$ clusters are found to experience the moderate tetragonal elongation distortions (characterized by the moderate relative tetragonal elongation ratios $\rho \approx 3\%$) along C_4 axis. With only five adjusted coefficients a_1, a_2, b_1, b_2 and ω, the relevant model parameters (Dq, k, ρ, κ and H) are described by the Fourier type functions, which suitably reproduce the corresponding overall varying tendencies and fluctuations of the measured d–d transition bands and EPR parameters with x. The microscopic mechanisms of the varying rules of the relevant quantities with x are discussed in view of the whole decreasing ability of Si^{4+} to accept electrons and the reverse tendencies due to partial Cu^{2+} reduced to Cu^{+} at $x \geq 0.7$ mol %. The monotonically increasing tendency of the calculated optical basicity reveals decreasing covalency of the whole glass systems with x.

1. Introduction

Glasses are the basic materials in various fields such as industry, medicine and science due to the unusual physical and optical properties [1–4]. Especially, magnesium lead silicate glasses can afford a broad range of commercial applications because of novel mechanical, bioactive [5] and dielectric properties and high thermal stability [6]. In particular, studies on the glasses containing transition-metal impurities (e.g., Cu^{2+}) can reveal unique structural properties and impurity behaviors by means of electron paramagnetic resonance (EPR) and optical absorption techniques with the paramagnetic copper probes [7,8]. For example, addition of CuO can make the glass electrically semiconducting and superparamagnetic [9,10], with two possible valence states (i.e., Cu^{+} and Cu^{2+}) forming CuO_4 and CuO_6 groups in the glass network [11,12]. In order to study the structural and spectroscopic properties of the glass systems with copper oxide modifier, EPR and d–d transition optical measurements were employed for 40MgO–(10–x)PbF_2–50SiO_2–xCuO (MPSC) glasses, and the copper d–d transition bands and the EPR parameters (anisotropic g factors $g_{//}$ and $g_{\perp}$ and hyperfine structure constants $A_{//}$ and $A_{\perp}$) were obtained for different CuO concentrations x [13]. In detail, the observed d–d transition bands and EPR parameters (especially $g_{//}$ and $A_{//}$) show the whole decreasing and increasing tendencies, respectively, and the moderate fluctuations with x, as illustrated by the reversing rules at $x \geq 0.7$ mol % due to partial Cu^{2+} reduced to Cu^{+} [13]. Although the g factors were quantitatively analyzed from the simple g formulae with various adjustable molecular orbital coefficients α^2 and β_1^2 as well as the fixed β^2 (= 1) and orbital reduction factor K (= 0.77 [13]), the comprehensive studies have not been carried out for the concentration dependences of the d–d transition bands and the EPR parameters. Neither has the information been obtained for the local structures of impurity Cu^{2+} at different concentrations.

Normally, the properties of materials are sensitive to local environments (e.g., occupation, coordination number, local symmetry, strength of crystal-fields (CFs)) in the vicinity of the doped impurities. Therefore, a detailed investigation of the EPR parameters, d–d transition bands and defect structures for Cu^{2+} in MPSC glasses at various CuO concentrations x are of fundamental and applied significance. In this paper, the concentration dependences of d–d transition band and EPR parameters as well as optical basicity values are calculated for Cu^{2+} in MPSC glasses in Section 2. In

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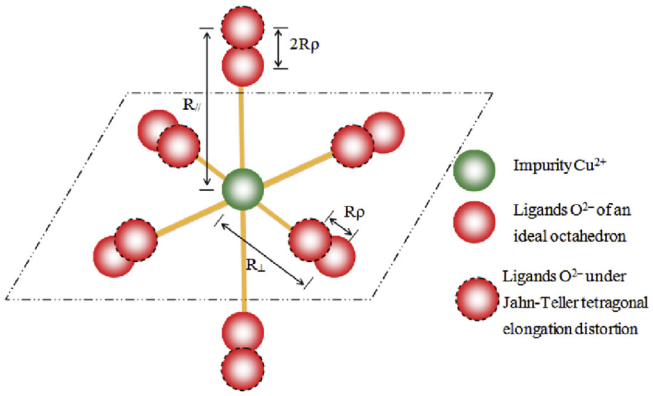

Fig. 1. Local distortion of the $[CuO_6]^{10-}$ cluster in MPSC glasses due to the Jahn–Teller effect with respect to an ideal octahedron.

Section 3, the properties of the EPR parameters and local structures are analyzed for different x, and the microscopic mechanisms of the varying rules of the relevant quantities with x are discussed from the overall decreasing ability of Si^{4+} to accept electrons and the reverse tendencies due to partial Cu^{2+} reduced to Cu^{+} at $x \geq 0.7$ mol %.

2. Theoretical calculations

The doped CuO in MPSC glasses usually acts as the modifier and can induce non-bridging oxygen (NBO) in the glass network [13]. The modifier CuO enters the glass network by breaking up the Si–O–Si bonds and introduces coordinated defects known as dangling (broken) bonds [14]. As pointed out in Refs. [13,15], impurity Cu^{2+} normally occupies an appropriate octahedral site in the glass network and forms the tetragonally elongated octahedral $[CuO_6]^{10-}$ cluster, corresponding to positive g anisotropy $\Delta g (= g_{\|} - g_{\perp})$. So, the local structure of impurity Cu^{2+} in MPSC glasses can be characterized by the relative tetragonal elongation ratio ρ (see Fig. 1).

2.1. Calculations of copper d–d transition bands and EPR parameters

The tetragonal elongation distortions of the octahedral $[CuO_6]^{10-}$ clusters in MPSC glasses can be ascribed to the Jahn-Teller effect [13]. In detail, the ground state ^2E_g for a $3d^9$ ion in an ideal octahedron would be separated into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$, with the original two-fold orbital degeneracy completely removed. Meanwhile, the excited state $^2T_{2g}$ for an ideal octahedral $3d^9$ cluster may split into an orbital doublet ^2E_g and a singlet $^2B_{2g}$ [16,17]. Thus, the new lowest level is $^2B_{1g}$. Experimentally, the measured d–d transition bands and EPR spectra [13] can be explicitly assigned to the transitions between Cu^{2+} CF 3d levels under tetragonal elongation distortion and Zeeman levels under external magnetic field, respectively.

Table 1
The concentration dependence of d–d transition band E_1 (in cm^{-1}).

x (mol %)	0.1	0.3	0.5	0.7	0.9	1.0
Cal.	14,148	14,009	13,650	13,790	13,764	13,816
Expt. [13]	14,204	14,124	13,458	13,869	13,642	13,698

2.1.1. Calculations for Cu^{2+} d–d transition bands

Conventionally, the energy separations E_1 and E_2 can describe the differences between the excited $^2B_{2g}$ and ^2E_g states and the ground $^2B_{1g}$ state, which are written in terms of the cubic CF parameter Dq and the tetragonal CF parameters Ds and Dt [18]:

$$\begin{aligned} E_1 &= 10Dq, \\ E_2 &= 10Dq - 3Ds + 5Dt. \end{aligned} \tag{1}$$

From the optical absorption measurements of MPSC glasses [13], the energy denominator E_1 and the cubic CF parameter Dq exhibit the whole decreasing (from 1420 cm^{-1} at 0.1 mol % to 1369.8 cm^{-1} at 1.0 mol %) tendency and moderate fluctuations with concentration x. For convenience, a Fourier type function is applied to manifest the above rule with delicate fluctuations. Thus, we have:

$$\begin{aligned} Dq = Dq_0[1 &+ (a_1 \cos(\omega x) + b_1 \sin(\omega x) + a_2 \cos(2\omega x) \\ &+ b_2 \sin(2\omega x))] \end{aligned} \tag{2}$$

Here the adjusted coefficients a_1, a_2, b_1, b_2 and ω can be determined by fitting the experimental d–d transition bands. The reference value $Dq_0 \approx 1393$ cm^{-1} can be obtained from the optical spectral measurements for Cu^{2+} in various oxide glasses [15,19,20]. By fitting the theoretical E_1 to the experimental data for various concentrations x, the optimal quantities in Eq. (2) can be obtained:

$$\begin{aligned} &a_1 \approx -0.0072,\ b_1 \approx 0.0014, \\ &a_2 \approx -0.0180,\ b_2 \approx 0.0002,\ \omega \approx 1325. \end{aligned} \tag{3}$$

The corresponding d–d transition bands E_1 are compared with the experimental values [13] in Table 1.

2.1.2. Calculations for the EPR parameters

Unlike the simple g formulae based on various adjustable molecular orbital coefficients in the previous calculations of g factors [13], the fourth order perturbation formulae of EPR parameters for $3d^9$ ions in tetragonally elongated octahedra are adopted here. Thus, we have [18]:

$$\begin{aligned} g_{\|} &= g_s + 8k\zeta/E_1 + k\zeta^2/E_2^2 + 4k\zeta^2/E_1E_2 - g_s\zeta^2\left[1/E_1^2 - 1/\left(2E_2^2\right)\right] + k\zeta^3(4/E_1 - 1/E_2)/E_2^2 \\ &\quad - 2k\zeta^3\left(2/E_1E_2 - 1/E_2^2\right)/E_1 + g_s\zeta^3\left[1/\left(E_1E_2^2\right) - 1/\left(2E_2^3\right)\right], \\ g_{\perp} &= g_s + 2k\zeta/E_2 - 4k\zeta^2/(E_1E_2) + k\zeta^2\left[2/(E_1E_2) - 1/E_2^2\right] + 2g_s\zeta^2/E_1^2 + k\zeta^3(2/E_1 - 1/E_2) \\ &\quad (1/E_2 + 2/E_1)/(2E_2) - k\zeta^3\left(1/E_1^2 - 1/(E_1E_2) + 1/E_2^2\right)/(2E_2), \\ A_{\|} &= P\left[-\kappa - 4H/7 + \left(g_{\|} - g_s\right) + 3(g_{\perp} - g_s)/7\right], \\ A_{\perp} &= P\left[-\kappa + 2H/7 + 11(g_{\perp} - g_s)\right]. \end{aligned} \tag{4}$$