Spectroscopic studies of Cu²⁺ spin probe in sodium niobium based tellurite glasses

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Differential scanning calorimetry (DSC), electron spin resonance (ESR), Raman, infrared (IR) and optical absorption studies on $10Na_2O-xNb_2O_5-(89-x)TeO_2-1CuO$ glasses (where x =0, 5, 10, 15 and 20 mol%) containing Cu²⁺ spin probe have been carried out. Glass transition temperature (T_g) and thermal stability of glass samples have been estimated from the DSC measurements and it has been found that both increase with increasing the Nb₂O₅ content. From Raman and IR spectra, it is clear that present glass system consists of structural units of TeO₃ (tp) and TeO₄ (tbp) and NbO₆ octahedra. Also, TeO₄ units convert into TeO₃ units with change in Nb₂O₅ content. The hyperfine splittings in the parallel features of ESR spectra of Cu²⁺ are recorded for all compositions. ESR results show that $g_{\parallel > g_{\perp}}$ indicating that the Cu²⁺ ion is in tetragonal distorted octahedral site and its ground state is d_{x2-y2} . There is considerable variation in Hamiltonian parameters for the different compositions. The observed optical absorption peak of Cu²⁺ is found to be maximum at 780 nm for 10 mol% of Nb₂O₅ content. Bonding parameters and % bonding symmetry are calculated from both optical and ESR data changing with increasing Nb₂O₅ content.

Keywords: Tellurite glasses, Electron spin resonance spectra, IR spectra, Raman spectra, Optical absorption spectra

1 Introduction

Niobium-tellurium oxide based glasses are promising materials for non-linear optical devices because of their low glass transition temperature (T_g), high thermal expansion coefficient, high refractive index, low phonon energy, high dielectric constant, good infrared transmission and large third order nonlinear susceptibility¹⁻³.

In tellurium glasses, main glass former is tellurium oxide (TeO₂), which has been regarded as a conditional glass former since it does not have the ability to transform to the glassy state without modifiers. Crystalline TeO₂ consists of TeO₄ trigonal bipyramidal structural units with a loan pair of electron attached to Te. Addition of modifying oxides, like Li₂O, Na₂O, K₂O, to TeO₂ glass, results in breakage of Te-O-Te linkage, thereby, resulting systematic conversation of TeO₄ to TeO₃ structural units.

Glasses containing Nb_2O_5 , due to their optical and electric properties4, also have technological importance for device applications. Alkali niobium tellurite glasses and glass ceramics have shown extremely interesting non-linear optical properties and these glasses are suitable for making optical wave guide devices. The structure of tellurite glasses is also of interest because their basic structural unit is an asymmetrical TeO₄ trigonal bipyramd with a lone pair of electrons in an equatorial position, and the content of network modifier changes the coordination number of the tellurium ion with respect to oxygen ions. This change leads to a TeO₃ trigonal pyramid which is considered to restrict the glass formation⁵.

Shioya *et al.*⁶ has studied the optical properties of transparent glass ceramics in $K_2O-Nb_2O_5-TeO_2$ glasses. Kim *et al.*⁷ reported the refractive index and relative permittivity of transparent glass ceramics in Na₂O-Nb₂O₅-TeO₂ system. Recently, Lin *et al.*⁵ developed the niobium based glasses for optical wave guide laser and amplifier.

In the present study, an attempt has been made to prepare and characterize the $10Na_2O-xNb_2O_5$ - (89-x) TeO₂-1CuO glass system using spectroscopic properties like ESR, infrared and optical absorption studies.

2 Experimental Procedure

Glasses with composition formula $10Na_2O-xNb_2O_5-(89-x)TeO_2-1CuO$ (x ranged from 0 to 20 mol%) were prepared and given in Table 1. Appropriate amount of Analar grade Na_2CO_3 , Nb_2O_5 and TeO₂ were taken in to the mortar and grounded thoroughly for homogeneous mixing. Then, 1 mol%

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CuO was added as a spin probe and melted in platinum crucible at 950°C for 40 min in electrical INDFUR furnace. Melts were stirred frequently for high homogeneity and were poured onto a steel plate maintained at 250°C and pressed quickly with another steel plate to a thickness of about 1 mm. Glass samples were transferred to annealing furnace annealed at 250°C for 4 h to avoid mechanical strains and cracking in the sample.

X-ray diffraction patterns for all glass sample were recorded using copper target ($K_{\alpha} = 1.54$ Å) on Philips Panaltic X' Pert at room temperature.

Density of all the samples is measured at room temperature using the Archimedes method with xylene as an immersing medium. The measured densities are reproducible to $\pm 0.01 \text{ g.cm}^{-3}$. The molar volume is calculated from the relation $V_m = \frac{M}{\rho}$, where

M, is the molar mass of glass; and ρ is density of the glass.

From the density data, oxygen packing density is calculated using the following formula:

Oxygen packing density = $\sum x_i n_i / V_m$

where, x_i is the molar fraction of an oxide R_mO_n ; and n_i is number of oxygen atoms of this oxide. The glass transition temperature (T_g) was measured using a temperature differential scanning calorimeter (TA Instruments DSC 2010). All samples were heated at the standard rate of 10°C min⁻¹ in aluminum pans.

Infrared transmittance of all powder glass samples (glass and KBr mixed pellets) were recorded by Perkin-Elmer FT-IS spectrometer model 1605 in the

Table1—Composition of 10Na ₂ O- xNb ₂ O ₅ -(89-x)TeO ₂ -1CuO glass system				
Glass label	Composition			
NNT1	10Na2O-89TeO2-1CuO			
NNT2	10Na ₂ O-5Nb ₂ O ₅ -84TeO ₂ -1CuO			
NNT3	10Na ₂ O-10Nb ₂ O ₅ -79TeO ₂ -1CuO			
NNT4	10Na ₂ O-15Nb ₂ O ₅ -74TeO ₂ -1CuO			
NNT5	10Na ₂ O-20Nb ₂ O ₅ -69TeO ₂ -1CuO			

wave number range 400-4000 cm⁻¹ at room temperature. ESR spectra of powdered glass samples were recorded in X-band at room temperature by JEOL-JES FE 3X ESR spectrometer with 100 kHz field modulation.

Optical absorption spectra of all glasses were recorded on Shimazdu UV-3100 spectrometer in the wavelength range 200-1000 nm at room temperature using air as a reference medium. The 'Peak-pick' facility provided in the spectrometer was used to measure the peak position.

3 Results and Discussion

3.1 X-ray diffraction

The X-ray diffraction powder patterns for NNT glass series are shown in Fig. 1. No sharp peaks have been observed in the X-ray diffraction patterns of glass sample; however, they contain two broad curves, typical of structures without long range order. Hence, it is confirmed that present glass systems are amorphous in nature.

3.2 Basic glass properties

Physical properties of present glasses were evaluated and are presented in Table 2. It is clear from this table that density increases from 4.81 to 5.42 g.cm⁻³ when TeO₂ substituted by Nb₂O₅. This is due to Nb₂O₅ which has the molecular weight higher than TeO₂. Molar volume ($V_{\rm m}$) increases from



Table 2—Average molecular weights, densities (ρ), molar volumes (V_m), oxygen packing densities (OPD), glass transition temperatures (T_g), Onset crystallization temperatures (T_x) and glass stabilities for the 10Na₂O- xNb₂O₅-(89-x)TeO₂-1CuO glasses

Glass label	Avarage molecular weight (g/mol)	Density (ρ) (gm/cm ³)	Molar volume ($V_{\rm m}$) (cm ³ /mol)	$\begin{array}{c} \text{OPD}(\overline{O}) \\ \text{(g-at/l)} \end{array}$	Glass transition temp. (T_g) (°C)	Onset cryst. temp. (T_x) (°C)	Glass stability (⊿T) (°C)
NNT1	153.438	4.81	31.89	59.249	286	389	103
NNT2	158.748	5.04	31.49	64.768	113	415	302
NNT3	164.059	5.18	31.67	69.146	342	377	35
NNT4	169.369	5.31	31.89	73.362	379	474	125
NNT5	174.680	5.42	32.29	77.259	428	-	-

31.89 to 32.29 cm³ mol⁻¹ and oxygen packing density (OPD) increases from 59.24 to 77.25 mol L⁻¹ as Nb₂O₅ content increases from 5 to 25 mol%. This can be explained by taking into account that the substitution of TeO₂ mol by mol by Nb₂O₅ the number of oxygen atoms in the glass network increases according to the ratio 2/5.

3.3 Differential scanning calorimetry (DSC)

DSC thermograms of the glass system, $10Na_2O_xNb_2O_5$ -(89-*x*) TeO₂-1CuO, is shown in Fig. 2 The DSC curves for the glasses show a very broad endothermic hump corresponding to the glass transition temperature, T_g ; starting of crystallization (called onset



Fig. 2—DSC curves of 10Na₂O- *x*Nb₂O₅-(89-*x*)TeO₂-1CuO for NNT1, NNT3 and NNT5 glass systems

crystallization temperature) T_x ; and other endothermic event corresponding to the melting temperature $T_{\rm m}$. The T_g data of the glasses are given in Table 2. The glass transition temperature increases from 286 to 428° C with increase in the Nb₂O₅ content. The reason for increase in the T_g is that Nb-O-Te and Nb-O-Nb linkages are increasing, requiring higher temperature for relaxation⁸. Furthermore, oxygen packing density increases with Nb₂O₅ content. The tightness of packing in the oxide network decides the glass transition temperature. Thus, with increase of Nb₂O₅ content, tightness of the glass increase leading to the increase in glass transition temperature. The difference between the onset of crystallization temperature (T_x) and glass transition temperature, $\Delta T = (T_x - T_g)$, has frequently been quoted as a rough indicator of glass stability. It represents the temperature interval during which nucleation takes place. From Table 2, it is clear that glass stability increases as the Nb₂O₅ content increases in the present glass systems.

3.4 Infrared spectra

The infrared spectra of present glass series are shown in Fig. 3. The peak positions are presented in



Fig. 3—Infrared spectra of 10Na₂O- xNb₂O₅-(89-x)TeO₂-1CuO glass system

Table 3 and the band assignments of glass series is given in Table 4. For the present glass system, significant bands are observed in the wave number ranges of 450-479, 611-642, 750-779, 882-895 and $1648-1654 \text{ cm}^{-1}$. The observed bands at 450-479 cm⁻¹ have been assigned to Te-O-Te linkages⁹. As Nb₂O₅ content increases, a new band is observed at 779 cm⁻¹ region that is due to Nb-O combination of shorter distance of six Nb-O combinations belonging to an NbO₆ octahedron with non-bridging oxygen with much distortion¹⁰. The strong and broad absorption band observed in the region of 611-779 cm⁻¹ is attributed to vibration bands such as TeO₄ TeO₃ and NbO₆ octahedron. The intensity of a peak at 450 cm⁻¹ decreases with decrease in the TeO₂ content and the intensities of the peaks at 779 cm⁻¹ increase with increase in the Nb_2O_5 content. This clearly indicates that structural units changes gradually from asymmetrical TeO_4 trigonal bipyramid to TeO_3 trigonal pyramid^{11,12}. The band observed in region of 1648-1654 cm⁻¹ is due to OH bond, which arises due to air moisture of the glass sample.

3.5 Raman spectra

The Raman spectra of glass system are shown in Fig. 4 in the wave number range of 100-1200 cm⁻¹. The peak positions of Raman spectra of all the glass samples are presented in Table 5 and the band assignments of LNT glass series is given in Table 6. Raman absorption bands are observed at around 230-234, 455-466, 664-672, 750- 767 and 867-881 cm⁻¹ for the present system. The band at 230 cm⁻¹ is attributed to the vibration of Nb-O-Nb in NbO₆

Table 3—Peak positions from infrared spectra for 10Na ₂ O- <i>x</i> Nb ₂ O ₅ -(89- <i>x</i>) TeO ₂ -1CuO glasses					
Glass label	Peak positions (cm ⁻¹)				
Region of IR	Assignments				
bands (cm ⁻¹)					
455-467	Symmetric vibrations of Te _{eq} -O _{ax} -Te _{eq}				
485-497	Vibrations of Nb-O in NbO ₆ octahedra				
620-673	TeO ₄ trigonal bipyramids				
750-784	TeO ₃ trigonal pyramids				
882-898	Bending modes of Nb-O-Nb in NbO ₆ octahedra				

Table 4—IR band assignments of NNT glasses						
NNT1	456	634	765	-	1654	3483
NNT2	450	628	769	882	1648	-
NNT3	455	636	779	889	-	-
NNT4	479	642	775	893	-	-
NNT5	473	611	750	895	-	-

octahedra⁸. This band is not observed in the first glass sample because first glass samples are free from Nb₂O₅. As Nb₂O₅ increases, the intensity of the band at 230 cm⁻¹ increases indicating that Nb-O-Nb deformation modes are increasing with Nb₂O₅ content.

The band at around 455-466 cm⁻¹ is due to the symmetric stretching vibrations of $Te_{eq}-O_{ax}$ -Te linkage. Intensity of this band gradually increases with increase in Nb₂O₅ content, which can be assigned to increase in the Te-O-Te and Te-O-Nb bridging bonds, which would increase the network connectivity, in agreement with the T_g increase¹³.

The bands observed at 664-672 cm⁻¹ are due to the stretching band of tellurium and axial oxygen (Te- O_{ax}) in TeO₄ trigonal bipyramids (tbp) and bands



Fig. 4—Raman spectra of 10Na₂O-*x*Nb₂O₅-(89-*x*)TeO₂-1CuO glass system

Table 5—Peak positions of Raman spectra for (89-x) TeO 1CuO glasses	$10Na_2O-xNb_2O_5-$
$(67-\lambda)$ 1002- 1000 glasses	1

Glass label		Peak positions (cm ⁻¹)					
NNT1	-	466	664	767	-		
NNT2	-	463	672	756	881		
NNT3	230	460	672	756	881		
NNT4	234	458	669	750	867		
NNT5	230	455	667	764	873		

Table 6—Raman	band	assignments	for	NNT	glasses
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Region of Raman bands (cm ⁻¹)	Assignments
230	Vibrations of Nb-O-Nb in NbO ₆ octahedra
448-455	Symmetric vibrations of Teeq-Oax-Teeq
659-668	TeO ₄ trigonal bipyramids
746-775	TeO ₃ trigonal pyramids
870-877	Bending modes of Nb-O-Nb in NbO ₆ octahedra

at around 750- 767 cm⁻¹ are assigned to Te-O stretching mode in TeO₃ trigonal pyramids $(tp)^{14}$. At low concentrations of Nb₂O₅, the glass structure mainly consists of TeO₄ trigonal bipyramids making up a continuous network. When the Nb₂O₅ content increases, the band intensity at 672 cm⁻¹ decreases while intensity at 764 cm⁻¹ increases. This change clearly indicates that the tellurium network is converting from TeO₄ (tbp) units to TeO₃ (tp) units via an intermediate coordination called TeO₃₊₁, where one Te-O_{ax} distance is elongated while the opposite is shortened. This conversion of TeO₄ (tbp) units to TeO₃ (tp) units to TeO₃ (tp) units is also evidenced from IR spectra.

A band resolved at around 873 cm⁻¹ in all glass samples except NNT1 is due to the bending modes of Nb-O-Nb bonds found in octahedral structure of NbO₆ and symmetrical stretching vibrations of Nb-O bonds found in NbO₆ octahedra. The slight increase in intensity of this band with the increase in the Nb₂O₅ content from 5 to 20 mol% indicates that the number of NbO₆ octahedra is increasing in the glass structure^{8,15}. These Raman results obtained for the present glasses are in good agreement with IR information.

3.6 ESR spectra

The electron resonance spectra are due to the Cu²⁺ ions entering the glass matrix as a paramagnetic prob. Usually spectrum shows the four partially resolved hyperfine structure (hfs) due to the interaction of the unpaired electron with the nucleus of a copper ion whose spin quantum number is I=3/2. In the spectra, three hfs are observed well but fourth one is not observed, and is overlapped on perpendicular features of the spectrum. However, perpendicular hyperfine are not resolved leading to an intense band in the high field region. The spectrum closely resembles that of Cu²⁺ ion in most oxide glasses. The ESR spectra for the samples NNT1, NNT3 and NNT5 are shown in Fig. 5. The ESR spectra were analyzed using Spin Hamiltonian:



Fig. 5—ESR spectra of Cu $^{2+}$ in Na₂O-*x*Nb₂O₅-(89-*x*) TeO₂:1CuO glass system

$$\begin{split} H &= g_{\parallel}\,\beta H_z S_z \!+ g_{\perp}\beta\,\left(H_x\,S_x + H_y S_y\right) + \,A_{\parallel}S_z I_z + A_{\perp}\,\left(S_x\,I_x \right. \\ &+ S_y\,I_y). \end{split}$$

where, *z* is the symmetry axis of the individual copper centers; β is the Bohr mageton; *S* and *I* are the electron and nuclear spin operators; $H_{x, \perp} H_y$ and H_z are the static magnetic field components, g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the g tensor; and A_{\parallel} & A_{\perp} are parallel and perpendicular components of the hyperfine tensor A; and the nuclear quadrupole interaction has been neglected. The values of A_{\parallel} & A_{\perp} are calculated using the following equations¹⁶:

$$H_{\parallel}(-3/2) - H_{\parallel}(+3/2) = 3A_{\parallel}$$

$$H_{\perp}(-3/2) - H_{\perp}(+3/2) = 3A_{\perp}$$

From the Spin Hamiltonian parameters (Table 7), it is found that $g_{\parallel} > g_{\perp}$, i.e., Cu^{2+} is in an octahedral coordination with tetrahedral distortion. The ground state of Cu^{2+} is d_{x2-y2} .

There are considerable variations in g_{\parallel} and A_{\parallel} values but there is no variations in g_{\perp} and A_{\perp} values except NNT2. The g_{\parallel} values decrease as Nb₂O₅ content increases and reaches maximum at x = 10mol% and then increase on further increase of Nb₂O₅ content. This is due to the fact that distortion around Cu²⁺ ion is changing with increasing content of Nb₂O₅. This shows present glass system is strongly concentration dependent. The ESR parameters of Cu²⁺ ion in present glass is compared with other oxide glasses and are in good agreement with earlier reported values of spin Hamiltonian parameters and are of similar in nature¹⁷⁻²². The distortion around the Cu²⁺ ion is changing with increasing concentration of Nb₂O₅, especially at 10 mol% of Nb₂O₅, there is drastical changes in the glass network²³.

3.7 Optical absorption spectra

Divalent copper has a $3d^9$ electronic configuration; the 3d level splits to 2E_g and ${}^2T_{2g}$ in a ligand field of cubic symmetry. However, as the ground state for

Table 7—Spin Hamiltonian parameters of 10Na ₂ O- <i>x</i> Nb ₂ O ₅ - (89- <i>x</i>)TeO ₂ -1CuO glasses						
Glass label	$g_{\parallel}(\pm 0.002)$	g _⊥ (±0.002)	$A_{\parallel} (10^{-4} cm^{-1})$	$A_{\perp}(10^{-4} \text{cm}^{-1})$		
NNT1	2.357	2.067	116±2	26±2		
NNT2	2.358	2.082	116±2	81±2		
NNT3	2.348	2.068	124±2	34±2		
NNT4	2.357	2.067	116±2	33±2		
NNT5	2.357	2.068	116±2	34±2		

divalent Cu in an octahedral ligand field is ${}^{2}E_{g}$, tetragonal splitting due to Jhan-Teller distortion will occur and must be considered when analyzing the spectra. In a tetragonal field, ${}^{2}E_{g}$ level splits to ${}^{2}B_{1g}$ and ${}^{2}A_{1g}$; and ${}^{2}T_{2g}$ level splits to ${}^{2}B_{2g}$ and ${}^{2}E_{g}$ as shown in Fig. 6. Therefore, one broad absorption band observed in present glass samples around 780 nm is due to the ${}^{2}E_{g}(D) \rightarrow {}^{2}T_{2g}(D)$ transition.

The optical absorption spectra of Cu^{2+} ion in $10Na_2O$ - xNb_2O_5 -(89-x)TeO₂-1CuO glass system for sample NNT1, NNT3 and NNT5 are shown in Fig. 6. A single broad peak around 780 nm clearly indicates the presence of Cu^{2+} in this glasses²⁴⁻²⁵. This absorption peak can be assigned to ${}^{2}E_{g}(D) \rightarrow {}^{2}T_{2g}(D)$ transition of Cu^{2+} . With increasing Nb₂O₅, absorption maximum shifts to higher wavelength up to 10 mol% then shifts towards the lower wavelength on further increasing the Nb₂O₅.

The observation of the maximum (Table 8) in optical absorption peak wavelength in the present system can be explained on the basis of structural change in the glasses with variation of composition Nb₂O₅. The bonding parameters are calculated using ESR and optical data by the following equations^{16,26}:



Fig. 6—Optical absorption spectra of $\mathrm{Cu}^{2\scriptscriptstyle+}$ in NNT1, NNT3 and NNT5 glasses

Table 8—Absorption peaks of Cu ²⁺ , bonding parameters and bonding symmetry of Cu ²⁺ doped in 10Na ₂ O- <i>x</i> Nb ₂ O ₅ - (89- <i>x</i>)TeO ₂ -1CuO glass system							
Glass label	Cu ²⁺ peak (nm)	α^2	β^2	${\beta_1}^2$	τ_{π} (%)	$\tau_{\sigma}(\%)$	
NNT1	775	0.7505	1.0246	0.9207	15.84	54.35	
NNT2	776	0.7581	1.0145	0.9137	17.25	52.71	
NNT3	780	0.7633	1.0076	0.8755	24.89	51.82	
NNT4	778	0.7510	1.0241	0.9174	16.51	54.26	
NNT5	775	0.7514	1.0235	0.9205	15.89	54.17	

$$g_{\parallel} = 2.0023 [1-4 \lambda \alpha^2 \beta_1^2 / \Delta E_{xy}]$$

$$g_{\perp} = 2.0023 [1-\lambda \alpha^2 \beta^2 / \Delta E_{xz, yz}]$$

where, λ is spin orbit coupling parameter is equal to -828 cm⁻¹ for Cu²⁺ and $\beta^2 \cong 1$ for octahedral environment; ΔE_{xy} and $\Delta E_{xz, yz}$, are the heights of the d_{xy} and $d_{xz, yz}$ molecular orbital levels above the ground state d_{x2-y2} , respectively and these values are estimated from optical absorption spectra²⁷. In optical absorption spectra, the position of observed absorption maximum of Cu²⁺ indicates the values of ΔE_{xy} . The in-plane σ -bonding parameter, α^2 , is calculated using following equation:

$$\alpha^2 = -A_{\parallel}/P + (g_{\parallel}-2) + 3/7(g_{\perp}-2) + 0.04$$

The normalized covalency of Cu^{2+} - O in-plane bonding of σ or π symmetry is calculated by following equations:

$$\Gamma_{\sigma} = 200(1-S)(1-\alpha^2) / (1-2S) (\%)$$

and $\Gamma_{\pi} = 200(1 - \beta_1^2)$ (%)

where, *S* is the overlap (S+_{oxygen} = 0.076).

As shown in Table 8, the bonding parameters are changing with the percent of Nb₂O₅. The bonding coefficients α^2 , β_1^2 and β^2 characterize the in-plane σ bonding, in-plane π bonding and out-of plane π bonding of the copper (II) complex, respectively. Their values lie between 0.5 and 1.0, the limits of pure covalent and pure ionic bonding. From Table 4, it is clear that the present system has ionic in nature. It is observed that normalized covalency of Cu²⁺- O in-plane bonding of σ symmetry (Γ_{σ}) increases up to 10 mol% of Nb₂O₅; then, decreases on further increasing of Nb₂O₅ content; whereas normalized covalency of Cu²⁺- O in-plane bonding of π symmetry (Γ_{π}) decreases up to10 mol% of Nb₂O₅; and then, increases.

4 Conclusions

The DSC, IR, Raman, ESR and optical absorption studies have been carried out on Cu^{2+} doped in $10Na_2O-xNb_2O_5-(89-x)TeO_2-1CuO$ glass system. The glass transition temperature and glass stability increase with the increase in Nb₂O₅ content. From Raman and IR results, it is clear that present glass is composed of structural units of TeO₄ trigonal bipyramid, TeO₃ trigonal pyramid and NbO₆ octahedra; and TeO₄ units convert to TeO₃ units as Nb₂O₅ content increases. ESR results indicate that $g_{\parallel} > g_{\perp}$ indicating that Cu²⁺ is present in octahedral

coordination with tetrahedral distortion. The ground state of Cu²⁺ion is d_{x2-y2} . The structural changes takes place as the concentration Nb₂O₅ varies. The g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} values change with Nb₂O₅ composition. From the optical absorption studies, it is clear that the optical absorption around 780 nm can be assigned to ${}^{2}E_{g}$ (D) $\rightarrow {}^{2}T_{2g}$ (D) transition of Cu²⁺. The absorption peak wavelength reaches a maximum at x = 10 mol% of Nb₂O₅. The bonding parameters calculated from both optical and ESR data are found to change with Nb₂O₅ concentration. Thus, it can be concluded that structural changes take place in the present system with the varying Nb₂O₅ content.

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