IR, EPR and magnetic susceptibility studies on xCuO-0.45B2O3-(0.55-x)As2O3 polycrystalline system

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The XRD studies on xCuO-0.45B2O3-(0.55-x)As2O3 polycrystalline system reveal that for 0.05 ≤ x ≤ 0.30 the average particle sizes are in the range 192-249 Å. The density values do not follow any regularity with mol% CuO. The chemical analysis results show the formation of Cu2+ by reduction of Cu3+ in the matrix. The room temperature IR studies indicate the presence of Cu—O bond, planar [BO3] and tetrahedral [OAsO2] units in the matrix. Presence of B—O—B linkage is also identified at lower mol% As2O3. DTAXTG result shows no characteristic structural phase transformation in the range room temperature to 900°C. The fairly low values of the small polaron radii indicate that the polaron is slightly localized on a particular site. The very low values of the magnetic susceptibility suggest weak paramagnetic behaviour of the specimens. The values of the exchange integrals of the small polaron are found to be fairly low. The values of the g- and A-matrices are found to be similar within the composition range studied, at 300 K and at 77 K, and also do not change significantly in the range 300-77 K. This result shows that the [O12-CuO412-O12] octahedra containing the paramagnetic site Cu2+ is not affected significantly with the change in composition as well as with temperature in the range 300-77 K. The EPR lineshape simulation of specimen S1 at 77 K reveal that the paramagnetic Cu2+ ion is in a tetragonally distorted octahedron of six oxygen atoms, [O12-CuO412-O12], having D4h symmetry. There is significant out-of-plane π-bonding present in the octahedron, as a result, the square planar [CuO412] unit of the octahedron is highly “squeezed”.

CuO-based glassy and polycrystalline systems are less studied as compared with V2O5- and MoO3-based systems. The basic difference between CuO and the above metal oxide systems is the electronic configuration of the transition metal (TM) ions. In the case of CuO-based systems1, copper exists as Cu2+ (3d10) and Cu3+ (3d9) where the electrical conductivity and the electron paramagnetic resonance (EPR) response of the systems is due to ‘hole’2, whereas, in the case of the above oxide systems3-4 the electrical conductivity is due to the thermally excited hopping of the small polaron5,6, which is basically the n-type conductivity. In the case of systems containing boron trioxide7-11, B2O3, and arsenic trioxide12-13, As2O3, because of the structural complications involving the different units forming the network, it is interesting to study the structure-property relations of such systems. In this paper, we discuss the results of our experimental studies on structure and structure–property relations of the binary and ternary CuO-B2O3-As2O3 polycrystalline systems based on the infrared (IR) spectroscopy, EPR spectroscopy and magnetic susceptibility measurements.

Materials and Methods

The samples were prepared using reagent grade chemicals. Appropriate amounts of CuO, H3BO3 and As2O3 were mixed well, heated in a furnace at 773 K for 5 hr, and then quenched in air. The polycrystalline phases of the samples were ascertained using an X-ray diffractometer (Model MINIFLEX CN 2005) working at 30 kV/10 mA using CuKα radiation (λ ~ 1.5405 Å) in the range 5° to 85° in 2θ. The chemical analyses of the samples were done to ascertain the Cu2+ and Cu3+ ions concentrations using standard procedures14. A FTIR-8700 spectrometer was used to record the room temperature IR spectra using KBr pellet technique in the range 400-4000 cm−1. The magnetic susceptibility measurements at room temperature were done by Faraday technique using a locally built magnetometer at the Department of Chemistry, I. I. T. Kanpur. All measurements were made at fixed magnetic field of 10 kG. X-band EPR spectral measurements at 300 K and 77 K were recorded on a JEOL JES-TE 100 spectrometer system with 100 kHz magnetic field modulation. Quartz sample tubes were used for recording the EPR lineshapes of the powder.
Table 1—Compositions, range of average crystallite sizes, densities, concentrations and reduced ratio of the Cu\(^{1+}\) and Cu\(^{2+}\) ions in the samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>x</th>
<th>Range of average crystallite size (Å)</th>
<th>Density</th>
<th>No. of Cu(^{1+}) ion (per gm)</th>
<th>No. of Cu(^{2+}) ion (per gm)</th>
<th>Reduced ratio, (c=\frac{(\text{Cu}^{1+})}{(\text{Cu}^{1+}+\text{Cu}^{2+})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.05</td>
<td>242.027-194.067</td>
<td>2.36</td>
<td>(3.01 \times 10^{20})</td>
<td>(7.53 \times 10^{21})</td>
<td>0.039</td>
</tr>
<tr>
<td>A2</td>
<td>0.10</td>
<td>245.385-225.380</td>
<td>2.70</td>
<td>(4.52 \times 10^{20})</td>
<td>(9.03 \times 10^{21})</td>
<td>0.048</td>
</tr>
<tr>
<td>A3</td>
<td>0.15</td>
<td>242.027-192.448</td>
<td>2.11</td>
<td>(7.53 \times 10^{20})</td>
<td>(8.58 \times 10^{21})</td>
<td>0.081</td>
</tr>
<tr>
<td>A4</td>
<td>0.20</td>
<td>249.042-197.076</td>
<td>2.58</td>
<td>(8.26 \times 10^{20})</td>
<td>(7.98 \times 10^{21})</td>
<td>0.094</td>
</tr>
<tr>
<td>A5</td>
<td>0.25</td>
<td>249.042-197.076</td>
<td>3.10</td>
<td>(9.03 \times 10^{20})</td>
<td>(6.76 \times 10^{21})</td>
<td>0.118</td>
</tr>
<tr>
<td>A6</td>
<td>0.30</td>
<td>240.164-197.076</td>
<td>2.82</td>
<td>(9.79 \times 10^{20})</td>
<td>(5.12 \times 10^{21})</td>
<td>0.161</td>
</tr>
</tbody>
</table>

In order to determine the derivative peak-to-peak linewidth variation as a function of composition the lineshapes were recorded with sufficiently low microwave power to avoid saturation. The magnetic field calibrations were done with respect to the resonance line of the DPPH \((g_{\text{DPPH}}=2.00354)\). The compositions of the samples studied are shown in Table 1.

Results and Discussion

In Fig. 1 the XRD patterns of the samples are presented. The major diffraction peaks in the samples occur at the same diffraction angles. The positions of the diffraction peaks show that same phase is present in all the samples. The range of the average crystallite sizes in the samples calculated using Scherrer’s equation are shown in Table 1 along with the densities and the results of chemical analyses. The fairly high values of the average crystallite sizes show that even with the well-known glass formers such as \(B_2O_3\) and \(AS_2O_3\), crystallites of appreciable dimensions can be achieved by the above preparation procedure. The densities are measured by liquid displacement method. The values of the densities show no regularity with the composition in the samples. The results of the chemical analyses show the presence of Cu\(^{1+}\) and Cu\(^{2+}\) ions in the matrix. The formation of Cu\(^{1+}\) ions by reduction of Cu\(^{2+}\) ions in the CuO-containing matrix is discussed in the literature. However, we visualize that such reduction in our system could occur during the elimination of water and formation of boron trioxide by decomposition of boric acid, \(H_2BO_3\). Another plausible reason for such reduction is due to the oxidation of As\(^{3+}\) to As\(^{5+}\) in such systems during the heating process. However, the concentrations of the Cu\(^{1+}\) ions are found to be one order of magnitude lower than those of the Cu\(^{2+}\) ion concentration. This shows that Cu\(^{1+}\) ions exist as defects in the matrix. The Cu\(^{2+}\)(3d\(^{9}\)) ion has an unpaired electron which is essentially a small polaron as mentioned earlier. The values of the reduced ratio, \(c\), also do not show any regular variation with compositions in the samples. Using the appropriate relations as discussed elsewhere, the values of the small polaron radius, \(r_p\), and the average TM ion separation, \(R\), were calculated and presented in Table 2 along with the room temperature magnetic susceptibility and the exchange integral values of the small polaron in the matrix. The values of \(r_p\) and \(R\) are found to be similar to those of copper phosphate glasses as reported by Duran et al. The relatively small values of \(r_p\) suggests that the
Table 2—Small polaron radius, \( r_p \), average TM ion separation, \( R \), magnetic susceptibility, \( \chi \), and the small polaron exchange integral, \( j \) in the ternary polycrystalline CuO-B_{2}O_{3}-As_{2}O_{3} system

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Small polaron radius, ( r_p ) (Å)</th>
<th>Average TM ion separation, ( R ) (Å)</th>
<th>Magnetic susceptibility ( \chi ) (emu/g G)</th>
<th>Exchange integral ( j ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2.030</td>
<td>7.460</td>
<td>5.938\times 10^{-6}</td>
<td>0.02</td>
</tr>
<tr>
<td>A2</td>
<td>1.904</td>
<td>6.517</td>
<td>1.551\times 10^{-6}</td>
<td>0.23</td>
</tr>
<tr>
<td>A3</td>
<td>1.914</td>
<td>5.496</td>
<td>1.194\times 10^{-6}</td>
<td>0.36</td>
</tr>
<tr>
<td>A4</td>
<td>1.951</td>
<td>5.325</td>
<td>1.109\times 10^{-6}</td>
<td>0.31</td>
</tr>
<tr>
<td>A5</td>
<td>2.043</td>
<td>5.172</td>
<td>1.891\times 10^{-6}</td>
<td>0.14</td>
</tr>
<tr>
<td>A6</td>
<td>2.206</td>
<td>5.036</td>
<td>2.272\times 10^{-6}</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The small polaron is strongly localized on a Cu\(^{2+}\) site in the lattice. The values of the polaron radii do not show any regular variation with mol\% CuO in the samples. However, interestingly we observe regular decrease in the value of \( R \) from 7.460 Å in A1 to 5.036 Å in A6 with gradual 5 mol\% increase in CuO-content from A1 to A6. This is due to the increase in the total number of copper atoms in the specimens.

In Fig. 2 the room temperature IR spectra of the samples recorded in the range 400-4000 cm\(^{-1}\) are given. In copper phosphate glasses, it is known from literature\(^1\) that copper exists as Cu\(^{1+}\) and Cu\(^{2+}\) ions, and the environment of Cu\(^{2+}\) is tetragonally distorted octahedron\(^{18}\), [O\(_{12}\)CuO\(_{12}\)O\(_{12}\)]. However, the B\(_{2}O_{3}\)-containing systems show more complex geometries of the structural network\(^{7-11}\). Apart from the trigonal [BO\(_{3}\)] units, the six-membered boroxol rings help in the formation of triborate and pentaborate groups (joined in pairs which are equivalent to two tetraborate groups) and also diborate groups\(^{18}\). And, in the case of As\(_{2}O_{3}\)-containing systems, the structural units present in the matrix are tetrahedral [OAsO\(_{3}\)] groups\(^{12,13}\). So, in order to interpret the results of our IR spectral studies we visualize a structural model of our matrix comprising the above structural units.

The shoulder around 484 cm\(^{-1}\) in the samples is due to symmetric bending\(^{19}\) of [OAsO\(_{3}\)] groups. The very intense peak in the range 602-613 cm\(^{-1}\) in the specimens is ascribed to the Cu-O stretching mode\(^{20}\) in the network. The weak peak in the range 791-804 cm\(^{-1}\) in all the samples is due to the symmetric stretching\(^{21}\) of the out-of-plane \( \pi \)-bonding of the trigonal [BO\(_{3}\)] unit, while the very weak peak in the range 922-926 cm\(^{-1}\) in the specimens is due to the symmetric stretching\(^{22}\) of the trigonal [BO\(_{3}\)] unit. The very weak peak at 991 cm\(^{-1}\) in A1, which is reduced to very weak shoulder in the case of other samples is due to As–O stretching mode\(^{23}\) of the tetrahedral [OAsO\(_{3}\)] unit. For a large number of borates\(^{18}\) it was shown that the stretching vibration of the B-O bonds in [BO\(_{3}\)] unit occurs in the region 1100-1300 cm\(^{-1}\). Thus the sharp peak in the range 1197-1202 cm\(^{-1}\) in the case of all the samples is due to B-O bonds of the trigonal [BO\(_{3}\)] unit. The shoulder around 1360 cm\(^{-1}\) which is prominent in A5 and A6, however, present in all the samples is due to the presence of trigonal [BO\(_{3}\)] units in the matrix\(^{24,25}\). We observe a very intense peak in the case of all the samples, centered around 1470-1456 cm\(^{-1}\). This peak is attributed to the antisymmetric vibration of the B-O-B groups in the matrix\(^{18,24,26}\). It is important to mention here that in the
matrix B-O-B bridge occurs due to the interconnection of [BO$_3$] units. Normally, in IR spectroscopic results the bands above 1600 cm$^{-1}$ are due to the moisture in the KBr pellet. However, the weak shoulders around 1742-1715 cm$^{-1}$ in the samples A2-A6, may be attributed to the B-O stretching mode of the matrix.

The results of chemical analyses (Table 1) showed that the polycrystalline matrix contains Cu$^{2+}$ site which is very important for the magnetic measurements. The fairly low values of the observed magnetic susceptibility of the specimens (Table 2) indicate weak paramagnetism in these materials. From the values of the magnetic susceptibilities the values of the exchange integrals of the specimens are calculated. The values of the exchange integrals are found to increase from A1(x=0.05) to A3(x=0.15) with increasing mol% CuO, and then decreases up to A6(x=0.30). This is due to the fact that as mol% CuO increases in the matrix, more numbers of polyhedra containing the Cu ions are formed in the matrix. As a result, due to the available proximity of the Cu ions, the exchange becomes more feasible, thereby the magnitudes of the exchange integrals increase. However, with the constraint of constant B$_2$O$_3$ content in the matrix, further increase in the mol% CuO, the bipolaron hopping from As$^{3+}$ to As$^{5+}$ acts as fluctuation barrier to small polaron hopping. This results in the gradual decrease in the magnitudes of exchange integrals from A3(x=0.15) to A6(x=0.30).

Figures 3 and 4 show the observed EPR lineshapes of the specimens recorded at 300 and 77 K, respectively. The nature of the lineshapes show very interesting feature. The lineshape at 300 K show distortion of the baselines for all the specimens, while such distortion is very less at 77 K. This is due to the fact that in the matrix the electrons on the oxygen atoms undergo magnetic exchange through metal centers. This is temperature dependent, and occurs very fast at 300 K due to high thermal excitation energy. However, at 77 K due to less excitation energy exchange does not occur significantly. Thus the lineshapes at 77 K do not exhibit distortion significantly. Furthermore, it is known from literature that in the glasses containing mixed-valence TM ions the small polaron hops from a lower valent state to a higher valent state due to thermal excitation. If the rate of hopping is fast enough, then the anisotropic feature of the lineshape of the paramagnetic site gets smeared out. Thus, in the present case of CuO-based polycrystalline system, the faster rate of small polaron hopping from Cu$^{2+}$ to Cu$^{1+}$ site, partially smeared out the hyperfine structures of Cu$^{2+}$ lineshape at 300 K. However, at 77 K the small polaron hopping rate is low, and gets localized at a

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**Fig. 3**—EPR lineshapes of the specimens in the polycrystalline CuO-B$_2$O$_3$-As$_2$O$_3$ system recorded at 300 K.

**Fig. 4**—EPR lineshapes of the specimens in the polycrystalline CuO-B$_2$O$_3$-As$_2$O$_3$ system recorded at 300 K.
Table 3—Observed values of the g- and A-matrices and derivative peak-to-peak linewidth, \( \Delta H \), of the specimens of CuO-B\(_2\)O\(_3\)-As\(_2\)O\(_3\) polycrystalline systems at 300 and 77 K

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>g-matrix</th>
<th>A-matrix ( \times 10^4 \text{ cm}^{-1} )</th>
<th>Derivative peak-to-peak linewidth, ( \Delta H ) (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300K 77K</td>
<td>300K 77K</td>
<td>300K 77K</td>
</tr>
<tr>
<td>A1</td>
<td>2.185 2.191</td>
<td>103 116</td>
<td>41 41</td>
</tr>
<tr>
<td>A2</td>
<td>2.192 2.188</td>
<td>103 133</td>
<td>41 41</td>
</tr>
<tr>
<td>A3</td>
<td>2.181 2.181</td>
<td>103 133</td>
<td>41 41</td>
</tr>
<tr>
<td>A4</td>
<td>2.191 2.179</td>
<td>103 116</td>
<td>54 55</td>
</tr>
<tr>
<td>A5</td>
<td>2.150 2.188</td>
<td>108 112</td>
<td>55 55</td>
</tr>
<tr>
<td>A6</td>
<td>2.167 2.181</td>
<td>103 107</td>
<td>41 54</td>
</tr>
</tbody>
</table>

particular Cu\(^{2+}\) site. As a result, the axially symmetric lineshape is observed at 77 K. Thus the above studies on the nature of the EPR lineshapes at 300 and 77 K shows that magnetic exchange of electrons occur between oxygens through an intervening atom, which in fact affects the baseline. This exchange is temperature dependent and the hyperfine structures of the lineshapes depend on the thermally excited hopping rate of the small polaron from Cu\(^{2+}\) to a Cu\(^{1+}\) site in the matrix.

From Figs 3 and 4 the g- and A-matrices and the derivative EPR peak-to-peak linewidths, \( \Delta H \), were calculated and presented in Table 3. Data in Table 3 show that the values of the g-matrices are higher compared with the free electron g-value of 2.0023. This positive g-shift is ascribed to the negative sign of the spin-orbit coupling constant, \( \lambda \), of the paramagnetic site, Cu\(^{2+}\), in this case. The data further show that there is no regular variation in the values of the g-matrices at 300 and 77 K with the mol% CuO in the specimens. No regular change in the values of g-matrices between 300 and 77 K has also been observed. Furthermore, the magnitudes of the g-matrices do not vary significantly within the composition range in A1-A6, at 300 and 77 K and also within the temperature range of 300-77 K. Similar result is also observed in the case of A-matrices for the samples A1-A6. These results show that there is no significant change in the local structures of the samples in terms of the bonding around the coordination polyhedron containing the paramagnetic site with change in composition, and also in the temperature range of 300-77 K. The nearly similar values of the peak-to-peak linewidth, \( \Delta H \), in the samples at 300 and 77 K shows that the hopping rate of the small polaron is similar within the temperature range of 300-77 K.

In Fig. 5 we present the computer simulated EPR lineshape of A1 along with the experimental lineshape recorded at 77 K. The lineshape has poorly resolved 4-parallel lines and unresolved perpendicular lines, characteristic of Cu\(^{2+}\) (\( I = 3/2 \)) axially symmetric lineshape. Using an axially symmetric spin-Hamiltonian as under:

\[
\mathcal{H} = g_\| S_z H_z + g_\perp (\beta_e S_z H_z + \beta_e S_y H_y) + A_\parallel S_z I_z + A_\perp (S_z I_z + S_y I_y)
\]  

Fig. 5—(a) Experimental, (b) Computer simulated lineshapes of specimen A1 (x = 0.05) of CuO-B\(_2\)O\(_3\)-As\(_2\)O\(_3\) system at 77 K.
We simulated the EPR lineshape at 77 K using Bruker's EPR lineshape simulation program SIMFONIA and present the obtained spin-Hamiltonian parameters as under:

\[ g_\parallel = 2.337, A_\parallel = 120.0 \times 10^{-4} \text{ cm}^{-1}, g_\perp = 2.034, \text{ and } A_\perp = 9.3 \times 10^{-4} \text{ cm}^{-1}. \]

The trends in the values of \( g_\parallel > g_\perp \) indicates that the environment of the Cu\(^{2+}\) is tetragonally distorted octahedron of six oxygens with D\(_{4h}\) symmetry the spin-Hamiltonian parameters are related as under:\(^3\)

\[ g_\parallel = g_c + 8\alpha^2 \delta^2 / \Delta_1, \]

\[ g_\perp = g_c + 2\alpha^2 \gamma^2 / \Delta_2, \]

\[ \Delta_1 = -(K + P[-(4/7)\alpha^2 + (g_\parallel - g_c) + (3/7)(g_\perp - g_c)]), \]

\[ \Delta_2 = -(K + P[(2/7)\alpha^2 + (11/14)(g_\perp - g_c)]). \]

The specific terms used in the above relations have the following connotations:

\( \lambda: \) spin-orbit coupling constant of Cu\(^{2+}\) (3d\(^9\)) ion,

\( K: \) measure of isotropic part of the hyperfine interaction term of \(^{63}\)Cu or \(^{65}\)Cu nucleus,

\( \Delta_1: \) transition energy from E(b\(_{2g}\)) to E(b\(_{1g}\)), i.e. the octahedral splitting energy,

\( \Delta_2: \) transition energy from E(b\(_{2g}\)) to E(e\(_g\)), i.e. the tetragonal distortion energy,

\( \alpha^2: \) extent of in-plane \( \sigma \)-bonding,

\( \gamma^2: \) extent of in-plane \( \pi \)-bonding,

\( \delta^2: \) extent of out-of-plane \( \pi \)-bonding,

\[ P = 2\beta_N g_N <r^3>^3 \text{ (the free-ion dipolar term),} \]

where

\( \gamma: \) gyromagnetic ratio of \(^{63}\)Cu or \(^{65}\)Cu nucleus,

\( \beta_N: \) Bohr magneton,

\( \beta_N: \) Nuclear magneton,

\( r: \) distance of the unpaired electron from the Cu nucleus.

Using the values of \( P \) as 0.036 cm\(^{-1}\) as reported in the literature\(^3\) for Cu\(^{2+}\) for similar environment, we calculate the values of \( K \) and \( \alpha^2 \) and present these as follows: \( K = 0.0093 \text{ cm}^{-1} \) and \( \alpha^2 = 0.743 \). From the value of \( K \) we calculate the extent of the Mo 5s orbital contribution, Fermi contact term, \( \kappa \) as 0.26. The fairly low value of \( \kappa \) shows that the contribution of Mo 5s orbital in the \( \sigma \)-bond formation in the octahedron is very less. The appreciable value of \( \alpha^2 \) shows that the in-plane \( \sigma \)-bonding between the central Cu atom with the oxygen atoms is fairly strong in the \([\text{O}_{12z}-\text{CuO}_{4z}-\text{O}_{12z}]\) octahedral unit.

Using the values of \( K \) and \( \alpha^2 \), the values of the un-reduced crystal field energy parameters \( (\Delta_1/\delta^2) \) and \( (\Delta_2/\gamma^2) \) are evaluated and shown below:

\[ \Delta_1/\delta^2 = 14746 \text{ cm}^{-1}, \text{ and } \Delta_2/\gamma^2 = 38388 \text{ cm}^{-1}. \]

Due to the unavailability of sufficient data the above values could not be reduced further. The very low value of \( \Delta_1/\delta^2 \) indicates that in the \([\text{O}_{12z}-\text{CuO}_{4z}-\text{O}_{12z}]\) octahedral unit there is significant out-of-plane \( \pi \)-bonding. This indicates that the square planar unit \([\text{CuO}_{4z}]\) of the octahedron is highly "squeezed" towards the central Cu atom. Since \( \gamma \) is a measure of the in-plane \( \pi \)-bonding, the significantly high value of \( \Delta_2/\gamma^2 \) indicates that the in-plane \( \pi \)-bonding in the octahedral unit is very less. The above result shows that one of the \( p_x \) or \( p_y \) orbital of the oxygen atom oriented for forming the in-plane \( \pi \)-bonding contains single electron, thereby the out-of-plane \( \pi \)-bonding is significant in the \([\text{O}_{12z}-\text{CuO}_{4z}-\text{O}_{12z}]\) octahedral unit.

The above studies shows that the average crystal-lute sizes in the polycrystalline specimens are in the range 192 - 249 Å. The chemical analyses results show the presence of Cu\(^{1+}\) and Cu\(^{2+}\) ions in the matrix. The room temperature IR studies indicated the presence of Cu-O bond, trigonal \([\text{BO}_{4z}]\) and tetrahedral \([\text{OAsO}_{4z}]\) units in the matrix. The fairly low values of the small polaron radii indicate that the polaron is partially localized at a particular site. The similar values of the g- and A-matrices within the composition range studied at 300 K and 77 K and also in the temperature range 300-77 K shows that the bonding in the octahedra containing the paramagnetic is similar. The EPR lineshape simulation of Al\(_1\)(x=0.05) at 77 K shows that the environment of the paramagnetic site Cu\(^{2+}\) is a tetragonally distorted octahedron \([\text{O}_{12z}-\text{CuO}_{4z}-\text{O}_{12z}]\) having less in-plane \( \pi \)-bonding but significant out-of-plane \( \pi \)-bonding.

**References**

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