CHAPTER-VIII

SUMMARY

The powder XRD analysis of system-A shows that the unit cell type is found to be tetragonal. The average crystallite sizes are found to be 7-34 nm in A1-A4 and 14-28 nm in A5. The powder XRD patterns of system-B shows the incorporation of amorphous character with respect to the polycrystalline sample A5 (system-A). The powder XRD analysis of system-C shows that the unit cell type is found to be monoclinic. Average crystallite sizes are found to be 11-43 nm in C1- C3 and in the range 26 - 43 nm and 36 - 85 nm in C4 and C5, respectively. Average crystallite sizes increase in C5. The powder XRD analysis of system-D shows that the unit cell type is found to be monoclinic. The average crystallite sizes are found to be 17-24 nm in the samples D1- D4 and 8-14 nm in D5. The average crystallite sizes decrease in the sample D5. The EDX profiles show the presence of Cu, B and O in the system- A, Cu, B, O and Ag in the system- B, V, Bi and O in the system-C and V, Bi, Na and O in the system D. The DSC data does not show any significant phase transformation in the system - A and - B. The DTA / TGA curves show melting point of the samples (system-C and D) without any characteristic weight loss. The SEM micrographs of system-A, B C do not show characteristic surface structure. The SEM micrographs of the samples (system-D) show globular in surface structure. In system -A and -B the lower values of Cu$^+$ concentration as compared with those of Cu$^{2+}$ ions show that the reduced state Cu$^+$ exists as lattice defect. The chemical analysis of system-C and -D shows that the reduced state V$^{4+}$ ions exist as lattice defect in the samples. The IR results at 300 K of system- A and -B show the presence of trigonal [BO$_{3/2}$] and octahedral [CuO$_{6/2}$]$^{4+}$ units. The
IR spectral analysis of system-C and D shows the presence of [O=VO₄²⁻O₁/₂] and [BiO₆₂⁻]³⁻ octahedral unit. Hysteresis loop in the samples A1-A5 and B1-B5 at 300 K shows ferromagnetic behaviour. The magnetization studies in samples A1 and A4 in the range 0 to 65000 Oe shows the weak ferromagnetic nature. The magnetic susceptibility studies in the samples A1 and A4 in the range 5-350 K shows the ferromagnetic nature. The system C and D show paramagnetic behaviour due to low magnetic susceptibility values. The system A, B, C and D shows extremely low magnitude of the exchange integral. EPR studies of system A and B exhibit similar results. From the trend \( g_\parallel > g_\perp > g_e \) obtained from the EPR lineshape simulation of system A and B in the temperature range 5 - 300 K, it is concluded that Cu²⁺ (3d⁹) ions are situated in an axially distorted octahedral environment. The high value of \( \alpha^2 \) shows in-plane \( \sigma \)-bonding in the system A and B. In system A and B the lower values of \( \Delta_1/\delta^2 \) as compared with \( \Delta_2/\gamma^2 \) at 5, 77 and 300 K shows that out-of-plane \( \pi \)-bonding is higher as compared with the in-plane \( \pi \)-bonding. In system A and B the fairly low values of the Fermi contact term, \( \kappa \) show that mixing of the 4s orbital with 3dx²-y² orbital is insignificant. The EPR studies of system A and B show Jahn-Teller distortion by elongation. The observed EPR lineshapes in the temperature range 7- 300 K are unresolved in all samples (system C and D). The negative g-shift is obtained in both the system C and D due to positive values of spin-orbit coupling constant. Optical absorption spectral results of system A, B, C and D exhibit charge transfer and d-d bands. Optical absorption spectral results of system A and B show Jahn-Teller distortion.

We highlight the structure - property relations in the system-A, B, C and D on the basis of our EPR and optical absorption spectral results. The EPR studies provide valuable
information about the local structure and the geometry of the paramagnetic sites in the polycrystalline systems. Electron paramagnetic resonance (EPR) studies of Cu\(^{2+}\) ions in polycrystalline systems have received considerable attention. The EPR parameters are sensitive to the local symmetry, the character of the chemical bonds, as well as other structural factors. The EPR spectra of system A shows slight change in the range of temperature 5 - 300 K. Similarly EPR spectra of system B show slight change in the range of temperature 15 - 300 K. The spin-Hamiltonian parameters g- and A-values calculated from EPR lineshapes of system-A and B show that octahedron containing the paramagnetic sites is similar. The EPR and optical absorption spectral results of system-A and B show that the symmetry of paramagnetic site (Cu\(^{2+}\)) is D\(_{4h}\). The bonding parameters like in-plane σ-bonding, in-plane π-bonding and out-of-plane π-bonding calculated from simulated EPR lineshapes of system-A and B show similarity. These similar bonding parameters show that the environment of Cu\(^{2+}\) ions is a tetragonally distorted octahedron [O\(_{1/2}\)-CuO\(_{4/2}\)-O\(_{1/2}\)]. Due to similar symmetry, structure and the geometry of the Cu\(^{2+}\) sites, the system-A and B exhibit similar properties. Optical absorption spectral results also show similar symmetry, structure and the geometry of the Cu\(^{2+}\) sites in system-A and B. The system-A and B shows similar charge transfer and d-d bands due to their similar structure. The powder XRD patterns of system-A and B are different. The addition of Ag\(_2\)O in sample A5 of system A changes the XRD patterns of system B. The system-B shows amorphous character whereas the system-A shows polycrystalline character. The system-A and B exhibit similar properties due to similar structure and geometry of the Cu\(^{2+}\) sites. The system-C and D show different powder XRD patterns. The addition of Na\(_2\)O changes the XRD patterns of system
D. The \( g_{\text{iso}} \) values calculated from EPR lineshapes of system-C and D show that the site symmetry and geometry around VO\(^{2+}\)ion are same. The \( g_{\text{iso}} \) values calculated from EPR lineshapes of system-C and D show that the site symmetry and geometry around VO\(^{2+}\)ion are \( C_{4V} \). The system-C and D shows similar property due to similar distorted octahedral structure around VO\(^{2+}\)ion site. Optical absorption spectral results of system-C and D shows similar charge transfer and d-d bands due to similar symmetry and geometry around VO\(^{2+}\)ion. The system-C and D exhibit similar properties due to similar structure and geometry of vanadyl ion.

The above polycrystalline systems with mixed valence transition metal ions having thermally excited hopping small polaron are interesting ferromagnetic materials (system A and B) and paramagnetic materials (system C and D). Thus, if the structure-property relations in these materials are properly exploited these will have potential applications in materials engineering.