Summary of the thesis work

The thesis is based on methodology of defect incorporation in novel oxide systems, characterization of defects by suitable techniques and interpretation of the results altogether. The study concentrates mainly on a representative high temperature superconductor $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ and a re-discovered semiconducting system, $\text{ZnO}$. Extension of the work has been carried out on two manganite systems ($\text{La}_{1.4}\text{Pb}_3\text{MnO}_3$ and $\text{La}_{0.5}\text{Pb}_0.3\text{Mn}_{1.4}\text{Cr}_0.6\text{O}_3$) and also a close analogue of $\text{ZnO}$, namely, $\text{CdO}$. An effort to create defects by different means including accelerator irradiations, heat treatments, chemical substitutions and reduction in grain size, looking for novel effects and developing qualitative understanding on the defect-property correlation in such the systems. All the materials chosen are oxides and have application or application potential in different industries. Low temperature resistivity and photoluminescence, room temperature positron annihilation spectroscopy, X-ray diffraction and ultraviolet-visible optical absorption have been utilized to characterize qualitative and quantitative aspects of defects in these oxides. The most general finding is that the final state of the perturbed system after incorporation of defects not only depends on the incorporated defects but strongly also on the initial defective nature of the system itself. Results of two or more characterization techniques employed at a time on the same material, the similarities and differences, have been discussed to understand underlying physics of probe-matter interaction. Theoretical explanations of the experimental results, whenever possible, have been put forward keeping an eye to generalize the results obtained for making use of the generated knowledge on other oxide materials. While discussing the results of this experimental investigation, attempts have been made to figure out similarities and differences with the existing literature so that a coherent scenario is evolved. A brief summary of the work done is as follows.
Chapter 1, "Introduction" briefly summarizes the existing experimental results and theories on these four types of oxides and sketches the importance of the present thesis work. A short description on the methodology of defect incorporation and defect characterization in ceramic oxides has also been given.

Chapter 2, "Experimental outline and data analysis" deals with the experiments carried out in this work with related data handing procedure.

Chapter 3, "Understanding Defects in Bi-2212 high temperature superconducting oxides" is based on the preparation of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ high temperature superconducting oxides (Bi-2212-HTSC) and their characterization by XRD, low temperature resistivity and room temperature positron spectroscopy. The initial defective state of the samples (i.e., grown in defects) have been varied by different cooling scheme (slow cooling or quenching) from the final sintering temperature. The effect of irradiation, under identical irradiation conditions, is seen to be dramatically different for slowly cooled and quenched samples. For comparison, irradiation effects on Bi-2212 single crystal have also been studied. Not only off-line measurements, resistivity measurements have been carried out during ion beam (here, Li$^{3+}$) exposure on the sample (in-situ measurements). It has been found that the sample resistivity depends strongly on the irradiation history (how much damage already incorporated) of the sample. Nature of carrier conduction in the normal state of Bi-2212 has been investigated. It shows that well known variable range hopping model is very much applicable to describe normal state properties of a high temperature superconductor. Conduction mechanism close to superconducting transition temperature and its possible change due to irradiation induced defects has also been investigated. Finally, positron annihilation spectroscopy has been employed to probe the heat-treatment or irradiation induced defects in Bi-2212.
Chapter 4, “Understanding Defects in perovskite manganite system” describes the substitution driven change of positron annihilation lifetime in two manganite systems, namely La$_{1-x}$Pb$_x$MnO$_3$ ($x = 0.05, 0.1, 0.3, 0.5$ and $0.7$) and La$_{0.5}$Pb$_{0.5}$Mn$_{1-y}$Cr$_y$O$_3$ ($y = 0.075, 0.15, 0.3, 0.35$ and $0.45$). It has been found that polaronic defects act as main defect centers in the paramagnetic-insulating regime of the manganites. With the help of earlier works, present data indicates the La-vacancy-oxygen-vacancy complex type defects in the manganite samples.

Chapter 5, “Understanding Defects in zinc oxide (ZnO)” is based on the identification of donor related defects in zinc oxide. It has been found that after H$^+$ irradiation on ZnO single crystal, a new donor defect with energy level close to the conduction band is created (shallow donor). Analysis of the low temperature photoluminescence spectrum shows that the donor is “hydrogen at a vacant oxygen site” type defects. The investigation on donor in ZnO has been extended to polycrystalline ZnO systems annealed at high temperatures (800 °C). In annealed ZnO, another shallow donor exists (which is not related to hydrogen) but the identification of which is not trivial. The possible correlation of oxygen vacancies with this unidentified donor in high temperature annealed ZnO has also been investigated. Combining positron annihilation spectroscopy and low temperature photoluminescence, unambiguous identification of zinc vacancies in as-grown or low temperature (300 °C) annealed ZnO have been done. Finally, a short section on similar annealing effects on another IIA-VIB semiconductor, CdO has been added for comparison. Analysis shows that oxygen vacancies are probably shallow donors in CdO. To mention, it has already been proven that isolated oxygen vacancies are deep, not shallow, donors in ZnO.

Chapter 6, “Conclusion” summarizes the conclusive part of the thesis work as well as new understanding and insights to trigger innovative ideas and experiments for the future.