

Synopsis

The thesis entitled "**Structural Characterization of Complex Oxides and Sulfates Towards the Design of Photocatalytic and Sodium Ion Conducting Materials**" consists of ve chapters. **Chapter 1** gives a brief introductory note which outlines the various synthesis procedures, characterization techniques and a description of properties like photocatalysis and ionic conductivity.

Chapter 2 discusses the solution combustion synthesis of $\text{Bi}_2\text{Zr}_2\text{O}_7$ using urea, tartaric Acid and glycine as fuels. Only the samples prepared using urea and tartaric acid result in pure compounds and are further characterized by X-ray diffraction studies depicting a disordered uorite type structures. Careful Rietveld refinements bring out subtle structural differences in these two samples as well, a feature which is demonstrated for the first time among samples prepared from two different fuels. Difference Fourier maps confirms the structures, and the catalytic behaviour is shown to correlate to these subtle changes in oxygen occupancy. The band gap determined from UV-Vis spectroscopic results conform to the structural differences of the compound. Photocatalytic degradation of cation dyes suggest that the compound prepared using urea shows better photocatalytic activity and is comparable to the commercial Degussa P-25.

Chapter 3 describes the effect of Bi doping on photocatalytic activity of CeO_2 (band gap is in the UV range) is evaluated with $\text{Bi}_x\text{Ce}_{1-x}\text{O}_2$ ($x = 0.2, 0.4, 0.6$) using solution combustion method using glycine as fuel. These compounds have a band gap in the visible range and the structures are established by Rietveld refinements clearly establishing that the oxygen vacancies increase with increasing bismuth substitution. Featureless difference Fourier maps confirm the structures and photodegradation experiments on a cationic and an anionic dye clearly establishing that the photocatalytic activity increases with increase in bismuth content leading to increased oxygen vacancies.

Chapter 4 describes synthesis, crystal structure, phase transition and ionic conductivity in a family of vanthoite mineral $\text{Na}_6\text{Mn}(\text{SO}_4)_4$. Single crystal of $\text{Na}_6\text{Mn}(\text{SO}_4)_4$ are grown from aqueous solution by slow evaporation method at 80°C , crystal grown are analyzed by single crystal X-ray diffraction which depict monoclinic system with space group $\text{P}2_1/\text{c}$ at room temperature. Ionic conductivity measurements are carried out by using impedance spectroscopy, and conductivity value is found to be $2.01 \times 10^{-5} \text{ Scm}^{-1}$ at 490°C and $7.4 \times 10^{-3} \text{ Scm}^{-1}$ at 505°C . Two order magnitude change in conductivity value on a temperature window of 15°C confirms a first order nature of phase transition. Further, conductivity of the mineral reached of $3.9 \times 10^{-2} \text{ Scm}^{-1}$ at 600°C which establishes the superionic nature of the mineral. In addition, the nature of phase transition was examined by using thermal analysis such as DSC, DTA and variable temperature powder X-ray diffraction technique. The PXRD after the phase transition at 550°C was also indexed, profile fitted with orthorhombic space group.

Chapter 5 presents the crystal growth and in situ structural studies of di and tetra hydrate of vanthoite mineral $\text{Na}_6\text{M}(\text{SO}_4)_4$ ($\text{M} = \text{Ni}$ and Co). As discussed in Chapter 4, these crystals are grown in aqueous solution by slow evaporation method at 80°C in an oven. Interestingly, di and tetra hydrate of $\text{Na}_6\text{M}(\text{SO}_4)_4$ ($\text{M} = \text{Ni}$ and Co) are grown concomitantly. Single crystal X-ray diffraction measurements reveal the structure to be triclinic with space group $P\bar{1}$. Further di-hydrates of $\text{Na}_6\text{M}(\text{SO}_4)_4$ ($\text{M} = \text{Ni}$ and Co) are isostructural, and the tetrahydrates also follow the same trend. Thermal Gravimetric analyses and in situ powder diffraction studies were carried out to characterize the step-wise dehydration process in these materials.