Preface

In recent years the Vanadium oxide spinels have attracted much attention because of the orbital degeneracy, and the interplay of spin, orbital and lattice degrees of freedom. This interplay arises not only from conventional spin-orbit coupling but also from the fact that the occupation of the specific orbitals with geometrical anisotropy prefers specific types of magnetic interaction in specific direction. In spinel Vanadate the magnetic V^{3+} ions with t_{2g} orbital degeneracy are located at vertices of a network of corner sharing tetrahedral that is magnetically frustrating.

Moreover, the AV_2O_4 spinels are a family of Mott insulators. Essentially, Mott insulators are paradigmatic examples of strongly correlated materials. The strong-coupling limit, $U >> t$ (U is the inter-atomic Coulomb energy and t is the spin dependent expectation value for the charge transfer between sites), corresponds to materials in which valence electrons are strongly localized in their atomic orbitals (Mott-Hubbard insulator). The opposite weak-coupling limit, $U << t$, corresponds to correlated metals whose electrons are completely delocalized (Paramagnetic metal). This implies that a Mott transition is induced at a critical value Uc/t. These AV_2O_4 spinels fulfill the criterion of varying the t/U ratio because of the metal-metal distance can be changed by applying the chemical pressure i.e., by changing the size of the A^{2+} cation.

The present thesis is focused on the Structural, Magnetic and Transport properties of MnV_2O_4, FeV_2O_4 and ZnV_2O_4 at room temperature as well as at low temperature. In order to give a systematic discussion, I have organized my thesis into 6 chapters.

Chapter 1: In this chapter we will be introducing the spinel vanadate system in terms of the physical properties of the materials and also discussing the theoretical background used to explain the data. We will discuss Crystal Field theory, followed by a discussion on the d-electron system and the spinel vanadate physics such as the magnetic properties and the exchange energy in this system. Furthermore, the electrical transport models used to explain the electrical properties of these materials such as the Arrhenius model and Variable Range Hopping (VRH) model will be discussed.

Chapter 2: In this chapter we will discuss the experimental techniques of the Structural and Magnetic measurements and the electrical transport measurement at low temperature.

Chapter 3: We have investigated the transport, magnetic and structural properties of MnV_2O_4 by doping Zn on the Mn site and Cr on the V site. It has been observed that with Zn doping both the Curie temperature (T_C) and structural transition temperature (T_S) are decreased while the gap between them increased rapidly. On the other hand, with Cr-doping on the V site the T_C remains almost constant but T_S is reduced rapidly.

Chapter 4: In this chapter X-ray absorption near edge spectra (XANES) and magnetization of Zn doped MnV_2O_4 have been measured and from the magnetic measurement the critical exponents and magnetocaloric effect have been estimated. The XANES study indicates that Zn doping does not change the valence states in Mn and V. It has been shown that the obtained values of critical exponents β, γ and δ do not belong to universal class and the values are in between the 3D Heisenberg model and the mean field interaction model. The magnetization data follow the scaling equation and collapse into two branches indicating that the calculated critical exponents and critical temperature are unambiguous and intrinsic to the system. All the samples show large magneto-caloric effect. The second peak in magneto-caloric curve of $Mn_{0.95}Zn_{0.05}V_2O_4$ is due to the strong coupling between orbital and spin degrees of freedom. But 10% Zn doping reduces the residual spins on the V-V pairs resulting the decrease of coupling between orbital and spin degrees of freedom.

Chapter 5: In this chapter, we have studied the chemical pressure effect on the structural, transport, magnetic and electronic properties of ZnV_2O_4 by doping Mn and Co onto the Zn sites of ZnV_2O_4. With Mn doping the V–V distance is increased and with Co doping it is decreased. The resistivity and thermoelectric power data indicate that, with decrease of V–V distance, the system moves towards quantum phase transition. The transport data also indicate that the conduction is due to small polaron hopping. The chemical pressure shows a non-monotonous behaviour of charge gap and activation energy.

On the other hand, when Ti is doped on the V-site of ZnV_2O_4, the metal–metal distance is decreased and, at the same time, T_N is also increased.

Chapter 6: The structural, magnetic, electrical and transport properties of FeV_2O_4, by doping Li and Cr ions respectively in A and B sites, have been studied in this chapter. Dilution of A-site by Li doping decreases the V-V distances which in effect increase the A-V coupling. This increased coupling enhances the ferri-magnetic ordering temperature and reduces the ferroelectric transition temperature. Furthermore, since Li is non-magnetic the A-V coupling is also decreased. The increase in A-V coupling dominates over the decrease in A-V coupling with Li doping. On the other hand, Cr doping increases the ferri-magnetic ordering temperature but does not alter the ferroelectric transition temperature which is due to the fact that the polarization origin to the presence of almost non-substituted regions.