NEW IRON-CONTAINING OXYPNICTIDE SUPERCONDUCTORS: SYNTHESIS AND PROPERTIES

by

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Submitted in accordance with the requirement for the Degree of

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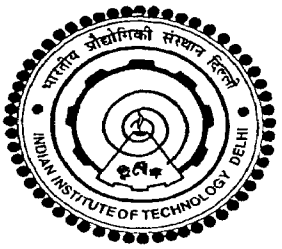

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CERTIFICATE

This is to certify that the thesis entitled, **"NEW IRON-CONTAINING OXYPNICTIDE SUPERCONDUCTORS: SYNTHESIS AND PROPERTIES"**, being submitted by Mr. Jai Prakash, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Jai Prakash has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

Date : 24th May 2011

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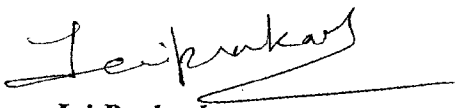

Jai Prakash

ABSTRACT

Research in advanced materials in past thirty years has led to the discovery of several new materials with interesting properties which has scope for wide ranging applications. Among them the discovery of oxide superconductors in 1986 is considered to be one of the greatest discoveries of the twentieth century. Apart from oxide superconductors, fullerenes, quasicrystals, giant magneto-resistive materials (GMR), materials showing fractional quantum Hall effect, multiferroics, negative thermal expansion materials and nano-crystalline materials are some of the major discoveries which have excited chemists, physicists, material scientists and device engineers. Superconductivity has been of interest from its inception and was of tremendous interest especially in the period of 1950 to 1970. After a brief lull the discovery of oxide superconductors in 1986 led to an explosive growth in the subject of superconducting materials between 1986 to 1995. Intermittently new superconductors have been found which have not been so popular due to low transition temperatures (T_c) in these superconductors like Li_xNbO_2, Na_xCoO_2 .H_2O and several others which have T_c less than 10 K. However the researchers in the area of superconductivity continue to look for new materials to reach the ultimate goal of room temperature superconductivity. Recently the subject has come alive with the discovery of superconductivity at 26 K in rare-earth based oxypnictide superconductors with fluorine-doping. This thesis is devoted to the search for new oxypnictide superconductors in an attempt to understand the properties of these new oxypnictide superconductors with respect to the BCS type superconductors and copper oxide based high T_c superconductors and to find new materials with higher transition temperature (T_c) and critical field (H_c).

In Chapter 1, a brief overview of research in the area of the recently discovered Fe-based pnictide and chalcogenide superconductors is presented. Synthetic methodologies for obtaining these compounds have also been outlined. The structural aspects have been related

to the well-known structures of ZrCuSiAs and $ThCr_2Si_2$. The influence of chemical substitution on structure and electronic properties of Fe-based pnictides have been discussed and commonalities among various families of Fe-containing superconductors have been brought out. The motivation behind the present study has been outlined.

Chapter 2 discusses the synthesis, characterization and superconducting properties of fluoride doped Ln(O/F)FeAs (Ln= La and Ce) superconductors. All the compounds crystallize in well known tetragonal ZrCuSiAs type structure (space group: *P4/nmm*). Fluoride substitution at the oxygen site in LnOFeAs (Ln = La\ and Ce) results in decrease in both the lattice parameters (**a** and **c**) due to smaller ionic size of F^- ion as compared to O^{2-} ion. Temperature dependent resistivity studies of parent LnOFeAs show anomaly at ~150-160 K depending on the rare earth. Fluoride substitution at oxygen site in LnOFeAs (Ln = La, Ce and Sm) leads to suppression of resistive anomaly with the evolution of superconductivity. Rare earth fluorides (LnF_3) were used as a fluorine source for these above mentioned compounds. Superconducting transition temperature (T_c) was found to be ~28, ~39 and ~43 K for $LaO_{0.9}F_{0.2}FeAs$, $CeO_{0.9}F_{0.1}FeAs$ and $CeO_{0.8}F_{0.2}FeAs$ superconductors, respectively. $CeO_{0.8}F_{0.2}FeAs$ superconductor show higher T_c (T_c = 43 K) as compared to La analog due to increase in chemical pressure (brought by smaller ionic size of Ce^{3+} ion as compared to La^{3+} ion). An upper critical field ($H_{c2}(0)$) of 102 T was estimated for $LaO_{0.9}F_{0.2}FeAs$ superconductor which is highest among the LaO/FFeAs superconductors. We have also synthesized these F-doped superconductors by an alternative route using alkali metal fluorides (NaF and KF) as fluorine source which are less air sensitive and less expensive as compared to rare-earth fluorides (LnF_3). KF doped $La_{1-x}K_xO_{1-x}F_xFeAs$ also show superconductivity at 26.2 and 26.4 K for 'x' = 0.15 and 'x' = 0.2 composition, respectively. KF doped superconductors show enhancement in $H_{c2}(0)$ as compared to F-doped LaO/FFeAs superconductors. NaF doping in $La_{1-x}Na_xO_{1-x}F_xFeAs$ also results in evolution of

superconductivity with maximum T_c at ~31 K for 'x' = 0.15 composition which is highest T_c achieved in F –doped LaOFeAs (Ln = Ce and Sm) synthesized at ambient pressure. We have also synthesized F-doped LnOFeAs superconductors by an alternative route using NH_4F as a fluorine source at relatively lower temperature (1050 °C). These F-doped superconductors synthesized by using NH_4F as fluorine source show similar superconducting transition temperature (T_c) as compared to F-doped LaOFeAs (Ln = Ce and Sm) superconductors synthesized using LnF_3 as fluorine source.

In Chapter 3 we present the synthesis and properties of transition metal substituted oxypnictides of the type $LnOFe_{1-x}Co_xAs$ (Ln = Ce and Pr), $CeOFe_{1-x}M_xAs$ (M = Cr, Mn, Ni, Cu and Zn) and $CeO_{0.9}F_{0.1}Fe_{1-x}Co_xAs$. All the compounds crystallize in the well known tetragonal ZrCuSiAs type structure (space gp: *P4/nmm*). Substitution of cobalt ions at the iron site in $CeOFe_{1-x}Co_xAs$ results in shortening of **a** and **c**-lattice parameters which could be attributed to the smaller ionic size of Co^{2+} ion as compared to Fe^{2+} ion in four coordination. Similar shrinking of **c**-lattice parameter was also observed for Co- substituted $PrOFe_{1-x}Co_xAs$ compounds while **a** –lattice parameter remains nearly constant with cobalt doping. Mössbauer measurement of $PrOFe_{1-x}Co_xAs$ ('x' =0 and 0.1) shows the presence of iron in +2 oxidation state. Also the large decrease in isomer shift of parent PrOFeAs on cooling (below 100 K) indicates the structural transition. The undoped LnOFeAs (Ln = Ce and Pr) compounds shows anomaly in the resistivity measurement at ~160 and ~150 K for CeOFeAs and PrOFeAs , respectively due to structural transition from tetragonal (space group: *P4/nmm*) to orthorhombic structure (space group: *Cmma*). Substitution of small amount of cobalt ions (5%) at the iron site in $LnOFe_{1-x}Co_xAs$ (Ln = Ce and Pr) suppresses the structural transition and antiferromagnetism with the evolution of superconductivity. The maximum superconducting transition temperature (T_c) was found for 'x' = 0.1 composition in $LnOFe_{1-x}Co_xAs$ (Ln = Ce and Pr). $CeOFe_{0.9}Co_{0.1}As$ shows onset of superconductivity at 11.3 K which

enhances to 14.3 K on replacing Ce with smaller Pr in $PrOFe_{0.9}Co_{0.1}As$. This increase in T_c could be attributed to the smaller lattice parameters (volume of tetragonal unit cell) of $PrOFe_{0.9}Co_{0.1}As$ compared to Ce analog. Increase in Co-substitution beyond 10 % results in suppression of superconducting transition temperature (T_c) in $LnOFe_{1-x}Co_xAs$ (Ln = Ce and Pr). Ni and Zn substituted $LnOFe_{1-x}M_xAs$ (M = Ni and Zn) compounds show decrease in both the lattice parameters (**a** and **c**) due to smaller ionic size of Ni^{2+} and Zn^{2+} as compared to Fe^{2+} ion in four coordination. Substitution of Cr and Mn at the iron site in CeOFeAs results in slight increase in both the lattice parameters (**a** and **c**). Substitution of nickel at the iron site in CeOFeAs results in suppression of resistivity anomaly and metallic behaviour was observed upto 4 K below which sudden drop in resistivity was observed. On the other hand substitution of diamagnetic zinc ions at the iron site in CeOFeAs (semimetallic) results in semiconducting behaviour. Similarly semiconducting behaviour was also observed on substitution of Cr and Mn at iron site in CeOFeAs. Cu- substituted $CeOFe_{0.9}Cu_{0.1}As$ shows metal to insulator transition. For $CeO_{0.9}F_{0.1}Fe_{1-x}Co_xAs$, the lattice parameters (**a** and **c**) were found to be smaller as compared to parent CeOFeAs due to simultaneous substitution of smaller F^- ions (as compared to O^{2-} ion) and smaller Co^{2+} ion (as compared to Fe^{2+}). Suppression of superconducting transition temperature (T_c) was observed on substitution of cobalt ions in $CeO_{0.9}F_{0.1}FeAs$ (T_c = ~38 K) up to 'x' = 0.1 and metallic behaviour was observed for 'x' $\geq$ 0.15 compositions.

Chapter 4 discusses the synthesis and properties of new oxypnictides of the type $La_{1-x}Th_xOFeAs$, $La_{1-x}Y_xO_{0.9}F_{0.1}FeAs$, $Ce_{1-x}Y_xO_{1-y}F_yFeAs$ and $La_{1-x}Yb_xO_{0.8}F_{0.2}FeAs$. All the compounds crystallize in the well known tetragonal ZrCuSiAs type structure (space group: *P4/nmm*). Thorium substituted $La_{1-x}Th_xOFeAs$ compounds show decrease in **a** and **c**-lattice parameters due to smaller ionic size of Th^{4+} ion as compared to La^{3+} ion. Energy dispersive X-ray analysis (EDAX) shows the presence of Th along with La, O, Fe and As for 'x' = 0.2

composition. Resistivity measurement for 'x' = 0.1 composition shows semimetallic behaviour with an anomaly at ~ 150 K similar to the undoped LaOFeAs. For 'x' = 0.2 composition superconductivity was observed at ~31 K which is higher as compared to F-doped La(O/F)FeAs superconductor (Max T_c = 28 K) at ambient pressure. Isovalent substitution of yttrium ions at rare-earth site in $Ce_{1-x}Y_xO_{1-y}F_yFeAs$ ('y' = 0, 0.1 and 0.2) and $La_{1-x}Y_xO_{0.9}F_{0.1}FeAs$ leads to reduction of lattice parameters (**a** and **c**) which could be attributed to smaller ionic size of Y^{3+} ions as compared to Ce^{3+} and La^{3+} ion which mimics the application of pressure(chemical pressure). EDX studies show the presence of Y along with Ce, O, F, Fe and As in $Ce_{0.6}Y_{0.4}O_{0.9}F_{0.1}FeAs$. $Ce_{1-x}Y_xOFeAs$ compounds show semimetallic behaviour with an anomaly in the resistivity measurement similar to undoped CeOFeAs. $Ce_{1-x}Y_xO_{0.9}F_{0.1}FeAs$ compounds were found to be superconducting and enhancement in superconducting transition temperature (T_c) was observed with increase in yttrium substitution with maximum T_c of ~49 K (for 'x' = 0.5 composition). Similar enhancement in T_c was also observed on substitution of smaller yttrium ions at the cerium site in 20% F-doped $Ce_{1-x}Y_xO_{0.8}F_{0.2}FeAs$ superconductors and maximum T_c was observed at ~49 K for 'x' = 0.4 composition. Similar enhancement in T_c with increase in chemical pressure was observed for yttrium substituted $La_{1-x}Y_xO_{0.9}F_{0.1}FeAs$. Yb-substituted $La_{1-x}Yb_xO_{0.8}F_{0.2}FeAs$ compounds show decrease in both **a** and **c**-lattice parameters (chemical pressure) which results in enhancement of T_c from 26 K (for La(O/F)FeAs) to 31 K (for x = 0.1). However further increase in Yb substitution (x > 0.1) suppresses the T_c in these Yb-doped superconductors.

In Chapter 5 we have discussed the synthesis and properties of new P and Sb- doped oxypnictides of the type $LnO_{1-x}F_xFeAs_{1-y}Sb_y$ (Ln = La and Ce), $PrOFeAs_{1-x}P_x$, $PrOFe_{0.9}Co_{0.1}As_{1-x}P_x$ and $CeO_{0.9}F_{0.1}FeAs_{1-x}P_x$. Increase in the lattice parameters (**a** and **c**) was observed with increase in antimony substitution at the arsenic site in $Ce(O/F)FeAs_{1-x}Sb_x$

as expected due to the larger ionic size of antimony as compared to arsenic. On the other hand, the **a** and **c**-lattice parameters decrease on substitution of arsenic with phosphorous in $PrOFeAs_{1-x}P_x$, $PrOFe_{0.9}Co_{0.1}As_{1-x}P_x$ and $CeO_{0.9}F_{0.1}FeAs_{1-x}P_x$ which is also expected due smaller ionic size of 'P' as compared to 'As'. Resistivity measurements show anomaly in resistivity for $CeOFeAs_{1-x}Sb_x$ ('x' = 0.1, 0.2 and 0.3) similar to undoped CeOFeAs which indicates structural transition from tetragonal (space group: *P4/nmm*) to orthorhombic structure (space group: *Cmma*). The anomaly temperature decreases on substitution of Sb in $CeOFeAs_{1-x}Sb_x$. $CeO_{0.9}F_{0.1}FeAs_{1-x}Sb_x$ ('x' = 0, 0.05, 0.1 and 0.15) were found to be superconducting with maximum T_c of 43.17 K for 'x' = 0.1 which is higher than the antimony free $CeO_{0.9}F_{0.1}FeAs$ superconductor (T_c = 38 K). On the other hand, Sb doping in optimal fluoride doped $CeO_{0.8}F_{0.2}FeAs_{1-x}Sb_x$ ('x' = 0.1, 0.2, 0.3 and 0.4) leads to suppression of superconductivity. Resistivity studies show P-doping (increase in chemical pressure) in $PrOFe_{0.9}Co_{0.1}As_{1-x}P_x$ results in suppression of superconducting transition temperature (T_c). In $PrOFeAs_{1-x}P_x$ semimetallic behaviour was observed (as known for undoped PrOFeAs) till 'x'≤ 0.3. On further increasing the phosphorous content ('x' = 0.5), superconductivity was observed with $T_c \sim 9$ K. Resistivity and magnetic measurements show enhancement in T_c on phosphorous substitution in $CeO_{0.9}F_{0.1}FeAs_{1-x}P_x$ which could be attributed to the increase in chemical pressure.

Chapter 6 deals with the synthesis and properties of oxypnictides of the type $La_{1-\delta}OFeAs$, $LnO_{1-\delta}FeAs$ (Ln = La and Ce), $LaO_{1-x}F_xMnSb$, LnOMnSb (Ln = Ce and Pr) and $La_{1-x}Mg_xOFeAs$. Powder X-ray diffraction studies show that all the compounds crystallize in the well known tetragonal ZrCuSiAs type structure (space group: *P4/nmm*). Decrease in the lattice parameters (**a** and **c**) and unit cell volume was observed for lanthanum and oxygen deficient compounds ($La_{1-\delta}OFeAs$ and $LaO_{1-\delta}FeAs$). The substitution of fluorine at oxygen site in LaOMnSb also results in shortening of lattice parameters (**a** and **c**) which is expected

as the ionic size of F^- is smaller than the O^{2-} in tetrahedral coordination. CeOMnSb and PrOMnSb have smaller lattice parameters (**a** and **c**) as compared to La analog which is expected considering the ionic size of rare earth metals. Substitution of La^{3+} by smaller Mg^{2+} in $La_{1-x}Mg_xOFeAs$ also results in shortening of lattice parameters (**a** and **c**) which leads to increase in chemical pressure. Resistivity measurements show anomaly in resistivity for $La_{1-\delta}OFeAs$ and $LaO_{1-\delta}FeAs$ similar to undoped LnOFeAs (Ln = La and Ce) which indicates structural transition from tetragonal (space group: *P*4/*nmm*) to monoclinic structure (space group: *P*112/*n*). Resistivity studies for $LaO_{1-x}F_xMnSb$ show metallic behaviour and room temperature resistivity increases on substitution of fluorine. Metal to insulator transition was observed for CeOMnSb while PrOMnSb shows metallic behaviour. Mg doped $La_{1-x}Mg_xOFeAs$ were also found to be semimetallic and show anomaly in the resistivity similar to parent LaOFeAs.

Chapter 7 summarizes the important conclusions and scope of future research in these oxypnictide superconductors.

TABLE OF CONTENTS