SUPERCONDUCTING AND MAGNETIC PROPERTIES OF NEW LAYERED METAL PNICTIDES AND CHALCOGENIDES

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by

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Submitted

in fulfillment of the requirement of the Degree of Doctor of Philosophy

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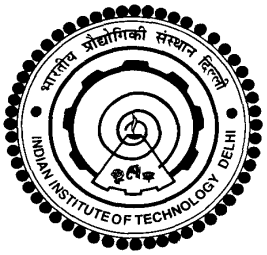

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CERTIFICATE

This is to certify that the thesis entitled, "Superconducting and magnetic properties of new layered metal pnictides and chalcogenides", being submitted by **Mr. Gohil S. Thakur**, 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. Gohil S. Thakur 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.

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INDIA

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Gohil S Thakur

Abstract

Mankind is always intrigued by new materials and unusual properties. Constant efforts are made to understand the unusual properties within the framework of existing theories. Superconductivity is one such property of matter that has fascinated the researchers for over a century. Significant research activity in the broad area of superconductivity has led to many exciting discoveries in the past like the superconductivity in metals, alloys, heavy–fermion superconductors, high T_c oxide superconductors and even superconductivity in magnetic materials. After the euphoria of high T_c oxide superconductors, Fe–based layered pnictide and rare–earth based chalcogenides have garnered special attention due to immense scope of further exploration. In this work we present our efforts to investigate new superconducting materials related to $LnOBiS_2$ and $AFBiS_2$ family. Apart from these novel layered magnetic materials of the type CuFePn (Pn = As and Sb) with Cu_2Sb structure were synthesized and studied. Magnetic structure of rare–earth based layered pnictide $LnCuAs_2$ (with $ZrCuSi_2$ type structure) has been studied using neutron diffraction technique. All the compounds studied crystallize in *P*4/*nmm* space group. There are several hundreds of known materials of these two classes with interesting properties like magnetism and superconductivity. Hence, there exists a huge possibility of manipulating electronic, magnetic and other properties by chemical substitution at various sites leading to tailor made materials.

Effects of isovalent chemical substitution on the superconducting and magnetic properties of $LnO_{0.5}F_{0.5}BiS_2$ have been investigated. Structural studies have been carried out in detail. Substitution of smaller Sm ion at La site in $LaO_{0.5}F_{0.5}BiS_2$ ($La_{1-y}Sm_yO_{0.5}F_{0.5}BiS_2$; y = 0.0 to

1.0) leads to an enhancement in T_c from 2.5 K for y = 0.0 to 4.6 K for y = 0.8. This enhancement in T_c is related to the structural distortion in Bi–S layers which is caused by increased chemical pressure. Single crystal of the new member of this class $SmO_{0.5}F_{0.5}BiS_2$ (y = 1.0) is surprisingly found to be non–superconducting. Y substitution on Ce sites ($Ce_{1-x}Y_xO_{0.5}F_{0.5}BiS_2$: x = 0.0–0.3) leads to a small enhancement in the T_c (from T_c = 2.4 K for x = 0 to T_c = 3 K for x = 0.2). This material also shows coexistence of superconductivity and ferromagnetism.

We have studied Se substituted $Sr_{0.5}Ce_{0.5}FBiS_{2-x}Se_x$ (x = 0, 0.5 and 1.0) and La substituted $Eu_{1-x}La_xFBiS_2$ (x = 0, 0.5 and 0.6). $Sr_{0.5}Ce_{0.5}FBiS_2$ exhibits coexistence of superconductivity and ferromagnetism (T_c = 2.5 K and T_C = 7.5 K). Se substitution at S sites induces bulk superconductivity with enhanced T_c upto 3.3 K. Sharp diamagnetic signal in susceptibility is observed which was not observed in sample with x = 0 (Se free). We observed unique *dual magnetic hysteresis loops* with superposition of ferromagnetic and superconducting loops indicating clear coexistence of superconductivity and magnetism in Se doped samples. This kind of hysteresis loop is a novel feature and has been observed for the first time in Bi–S_2 superconductors. A marked reduction in Ce moment (~ 0.1 μ_B) in the superconducting state suggests itinerant ferromagnetism. Enhancement of T_c from 0.3 K (in $EuFBiS_2$) to 2.5 K is observed in $Eu_{1-x}La_xBiS_2F$ (x = 0.5 and 0.6). Upon application of pressure (upto 2.5 GPa) on x = 0.5 composition, further enhancement in T_c (upto 10 K) is observed. We speculate that this material undergoes a structural phase transition under high pressure. This is the first case where such a great enhancement (~ 30 folds) in T_c has been observed.

Compositions of the type $FeTe_{0.5}Se_{0.5-x}O_x$ (x = 0, 0.01, 0.03, 0.04 and 0.06) and $Fe_{1-x}Mn_xTe_{0.5}Se_{0.5}$ (x = 0.01 and 0.02) were also studied in detail. Partial O–substitution at Se sites leads to decrease in T_c from 14.9 to 13.1 (for x = 0 to x = 0.06, respectively). Also the diamagnetic signal becomes broad on increasing oxygen content. This decrease in T_c is attributed to the disorder created at Se/Te sites by substitution of oxygen which disturbs the Se/Te arrangement. Mn–doping (at Fe sites) also leads to a similar decrease in T_c. This is due to the pair–breaking effect of Mn^{2+}–ions.

We have synthesized some new phases CuFePn (Pn = As and Sb) belonging to Cu_2Sb family which structurally resemble the superconducting LiFeAs. CuFeSb is found to be room temperature soft–ferromagnet with Curie temperature $T_C \sim 375$ K with Fe moment ~ $1.8\mu_B$ in the ordered state. On the other hand CuFeAs was found to be weak antiferromagnetic with $T_N \sim 9$ K and a very small Fe moment of ~ 0.1 μ_B. Magnetic properties of these phases are confirmed by variable temperature Mössbauer studies. The anion height plays an important in deciding the magnetic ground state of these Fe–pnictides.

Magnetic structures of layered arsenide $LnCuAs_2$ (Ln = Pr, Nd, Tb, Dy, Ho and Yb) have been determined. All these phases show antiferromagnetic ordering at low temperature (2–13 K). $PrCuAs_2$ and $NdCuAs_2$ were found to have a simple commensurate structure below T_N (6.4 and 3.5 K respectively) with propagation vector k = (0, 0, 0.5). While the Pr moments align along the crystallographic c–axis, Nd and Dy moments lie in the ab–plane. The difference in the moment alignment is attributed to the crystal field effects. $TbCuAs_2$ and $HoCuAs_2$ exhibit a complex *incommensurate* magnetic structure below T_N

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND SYMBOLS

Å	Angstrom
^{o}C	Centigrade
μm	Micrometer
Cm	centimeter
h	Hours
PXRD	Powder X-ray diffraction
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Analysis
RRR	Residual resistivity ratio
μ	Magnetic Moment
H	Magnetic Field
μ_B	Bohr–magneton
eV	Electron – Volt
K	Kelvin
°	Degree (angle)
λ	Wavelength
Ω	Ohm
T	Tesla
G	Gauss
Oe	Oersted
M	DC Magnetization

χ_M	Molar Magnetic susceptibility (dc)
χ_M^{-1}	Inverse Molar Magnetic susceptibility (dc)
ρ	Resistivity
γ	Sommerfeld coefficient
θ	Weiss constant and Bragg's diffraction angle
θ_D	Debye temperature
k	Propagation vector
GPa	Gega Pascals
V	Electric field gradient
δ	Isomer shift
Γ	Line width