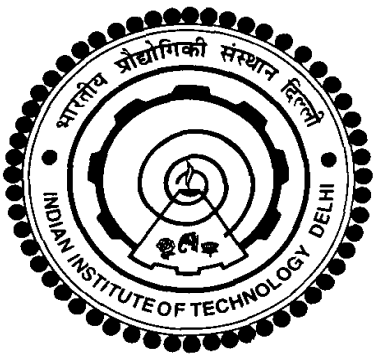
INVESTIGATION OF NEW SUPERCONDUCTING MATERIALS HAVING BiS_2 LAYERS

ZEBA



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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INVESTIGATION OF NEW SUPERCONDUCTING MATERIALS HAVING BiS_2 LAYERS

by

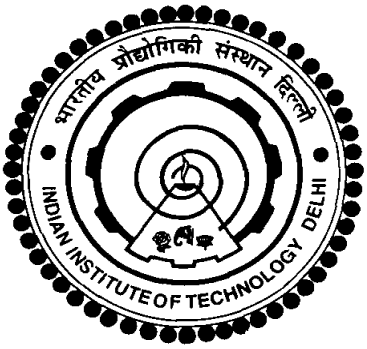
ZEBA

Department of Chemistry

Submitted

in fulfillment of the requirements of the Degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2017

DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"Investigation of new superconducting materials having BiS_2 layers "**, being submitted by **Ms. Zeba**, 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 her. Ms. Zeba 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.

Professor A. K. Ganguli

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Zeba

Abstract

Researchers have been fascinated towards the discovery of materials with interesting properties with broad range applications. Discovery of high T_c cuprate superconductors is considered as one of the biggest achievements of the last century. Manifestation of superconductivity in various different kinds of materials such as metallic elements, alloys, intermetallic compounds, organics, oxides, borides, pnictides, magnetic materials etc. demonstrates that the phenomenon could show up in most unfavorable materials like oxides and fluorides. Mostly the efforts have been made to improve the T_c but equally important aspects are to improve the critical current density, decrease the H_{c2} anisotropy and find a superconductor that is easy and cheap to synthesize and can be drawn to wires. After the exciting period of high T_c oxide and Fe–based layered pnictide superconductors, rare–earth based bismuth chalcogenides have gained vast attention. In this thesis we present our efforts to design and investigate new BiS_2–based superconducting and magnetic materials.

Substitution of divalent Sr at the Eu–sites in $Eu_3Bi_2S_4F_4$: $Eu_2SrBi_2S_4F_4$ and $EuSr_2Bi_2S_4F_4$, has led to the synthesis of new 3244–type phases. Effects of chemical substitution brought about by Sr on the superconducting and magnetic properties of $Eu_3Bi_2S_4F_4$ have been investigated. Their structural studies have been carried out in detail. $Eu_2SrBi_2S_4F_4$ is an intrinsic superconductor (T_c = 0.79 K). An interesting structural feature of $Eu_2SrBi_2S_4F_4$ and $EuSr_2Bi_2S_4F_4$ is that there are two Eu–sites: Eu(1) and Eu(2); Eu(1) has two Eu–atoms in nearly *divalent state a*nd Eu(2) has one Eu–atom in *strongly mixed valence.* Precise information about the mixed valence states of Eu has been investigated by ^{151}Eu Mössbauer spectroscopy, XPS studies and magnetic measurements.

We have studied Se–substituted $Eu_2SrBi_2S_{4-x}Se_xF_4$ and $EuSr_2Bi_2S_{4-x}Se_xF_4$ (x = 0.5, 1, 1.5 and 2). We have been able to induce superconductivity in $EuSr_2Bi_2S_4F_4$ by Se–substitution at the

S–site (isovalent substitution) with T_c = 2.9 K in $EuSr_2Bi_2S_2Se_2F_4$. The other compound $Eu_2SrBi_2S_4F_4$ shows a significant enhancement of T_c. In Se–substituted $Eu_2SrBi_2S_{4-x}Se_xF_4$, we find T_c = 2.6 K for x= 1.5 and T_c = 2.8 K for x = 2 whereas T_c = 0.79 K in the Se–free sample. Besides superconductivity, an important effect associated with Se–substitution is that it gives rise to remarkable changes of the Eu valence. For both the compounds ^{151}Eu Mössbauer and X–ray photoemission spectroscopic measurements show changes in the Eu valence on Se–substitution.

The next site substitution has been carried out by doping Pb at Bi–sites in $Eu_3Bi_2S_4F_4$. Compositions of the type $Eu_3Bi_{2-x}Pb_xS_4F_4$ (x = 0.25, 0.5, 0.75 and 1) have been synthesized and the shrink in lattice volume suggets incorporation of Pb in the lattice. All the compounds crystallize in the well known tetragonal 3244–type structure (space group: *I*4/*mmm*). Pb–substitution at Bi–sites is a case of aliovalent substitution. A striking feature due to Pb–substitution is Pb (x = 0.25) in the system suppresses superconductivity and becomes highly insulating. Magetic measurements suggest presence of mixed valent Eu as a function of Pb–substitution.

We have investigated the effect of external pressure on magnetization measurements of $BiO_{0.75}F_{0.25}BiS_2$. It crystallizes in tetragonal $CeOBiS_2$–type structure (S. G.: *P*4/*nmm*). Our studies suggest improved superconducting properties in polycrystalline samples of $BiO_{0.75}F_{0.25}FBiS_2$. T_c in our sample is 5.3 K, at ambient pressure, which is a marginal but definite enhancement over T_c reported earlier (T_c = 5.1 K). Both H_{c2} and H_{c1} from the *M–H* curve decrease under external pressure P ($0 \leq P \leq 1$ GPa). We observe a decrease in critical current density commensurate with decreasing transition temperature on applying pressure.

We have synthesized a new crystallographically ordered quaternary Heusler alloy, MnNiCuSb. The crystal structure of the alloy has been determined by Rietveld refinement of

the powder X–ray diffraction data. This alloy crystallizes in the LiMgPdSb–type structure with $F\bar{4}3m$ space group. MnNiCuSb is a ferromagnet with a high T_C ~ 690K and magnetic moment of 3.85μ_B/f.u. We have also studied two other off–stoichiometric compositions; one Cu rich and other Ni rich ($MnNi_{0.9}Cu_{1.1}Sb$ and $MnNi_{1.1}Cu_{0.9}Sb$) which are also ferromagnets. It must be stressed that MnNiCuSb is one of the very few known quaternary Heusler alloys without Fe, with 1: 1: 1: 1 composition.

सार

विस्तृत रेंज अनुप्रयोगों के गुण के साथ दिलचस्प सामग्री की खोज के लिए शोधकर्ताओं मोहित है। उच्च T_c cuprate सुपरकंडक्टर्स की खोज पिछली शताब्दी की सबसे बड़ी उपलब्धियों में से एक माना जाता है। विभिन्न प्रकार के सामग्रियों में अतिसंवेदनशीलता जैसे कि धातु तत्व, मिश्र, इंटरमिलेटिक यौगिकों, ऑर्गेनिक्स, आक्साइड, बोराइड्स, निक्टाईड्स, चुंबकीय सामग्री आदि की अभिव्यक्ति दर्शाता है कि इस घटना को ऑक्साइड और फ्लोराइड जैसी सबसे प्रतिकूल सामग्री में दिखाया जा सकता है। अधिकतर T_c को सुधारने के लिए प्रयास किए गए हैं लेकिन समान रूप से महत्वपूर्ण हैं critical current density में सुधार, H_{c2} एनिसोट्रॉपी कम करने और एक इस तरह सुपरकंडक्टर की खोज जो संश्लेषित करने के लिए आसान और सस्ता है और तारों के लिए तैयार किया जा सकता है। उच्च T_c ऑक्साइड की रोमांचक अवधि के बाद Fe आधारित स्तरित निक्टाईड सुपरकंडक्टर्स, rare earth आधारित बिस्मथ chalcogenides विशाल ध्यान प्राप्त किया है। इस शोध में हम अपने प्रयासों को प्रस्तुत करते हैं नए BiS_2 आधारित सुपरकोन्डक्टिंग और चुंबकीय सामग्री को डिजाइन और जांचना।

$Eu_3Bi_2S_4F_4$ में Eu-साइट्स पर डिवैलेंट Sr के प्रतिस्थापन: $Eu_3Bi_2S_4F_4$, $Eu_2SrBi_2S_4F_4$ तथा $EuSr_2Bi_2S_4F_4$ नए 3244-प्रकार के सामग्री की खोज के कारण है। रासायनिक प्रतिस्थापन के प्रभाव के बारे में लाया $Eu_3Bi_2S_4F_4$ के सुपरकोंडक्टिंग और चुंबकीय गुणों पर Sr द्वारा जांच की गई है। उनके संरचनात्मक अध्ययन को विस्तार से किया गया है। $Eu_2SrBi_2S_4F_4$ एक आंतरिक है सुपरकंडक्टर (T_c = 0.79 K)। $Eu_2SrBi_2S_4F_4$ की एक दिलचस्प संरचनात्मक सुविधा और $EuSr_2Bi_2S_4F_4$ यह है कि दो Eu साइटें हैं: Eu(1) और Eu(2); Eu(1) में दो Eu-परमाणु होते हैं लगभग divalent state और Eu(2) में एक Eu-परमाणु है जो strongly mixed valence state में है। Eu के mixed valence state के बारे में जानकारी ^{151}Eu

Mössbauer Spectroscopy, XPS अध्ययन और चुंबकीय माप द्वारा जांच की गई है। हमने Se-प्रतिस्थापित $Eu_2SrBi_2S_{4-x}Se_xF_4$ और $EuSr_2Bi_2S_{4-x}Se_xF_4$ (x= 0.5, 1, 1.5 और 2)। हम $EuSr_2Bi_2S_4F_4$ के S-साइट में Se-प्रतिस्थापन (सहवर्ती प्रतिस्थापन) द्वारा सुपरकॉडक्टिविटी को उत्पन्न करने में सक्षम रहे $EuSr_2Bi_2S_2Se_2F_4$ में T_c= 2.9 K के साथ। अन्य यौगिक $Eu_2SrBi_2S_4F_4$ T_c के एक महत्वपूर्ण वृद्धि को दर्शाता है। Se-प्रतिस्थापित $Eu_2SrBi_2S_{4-x}Se_xF_4$ मे हमे x= 1.5 के लिए T_c= 2.6 K और x= 2 के लिए T_c= 2.8 K जबकि Se मुक्त यौगिक मे T_c= 0.79 K के नमूना मिलते हैं। सुपरकोन्डक्टीविटी के अलावा, Se-प्रतिस्थापन से जुड़े एक महत्वपूर्ण प्रभाव यह है कि इससे Eu के valence में उल्लेखनीय परिवर्तन हो सकते हैं। दोनों यौगिकों के लिए ^{151}Eu Mössbauer और X-ray Photoemission Spectroscopy मापन Se-प्रतिस्थापन करने पर Eu में valence परिवर्तन दिखाते हैं।

अगली site प्रतिस्थापन $Eu_3Bi_2S_4F_4$ में Bi-साइट पर Pb डोपिंग द्वारा किया गया है। विभिन्न $Eu_3Bi_{2-x}Pb_xS_4F_4$ (x= 0.25, 0.5, 0.75 और 1) की संरचनाओं को संश्लेषित किया गया है और lattice volume में सिकोड़ें, lattice में Pb के निगमन को शामिल करते हैं। सभी यौगिकों प्रसिद्ध Tetragonal 3244-प्रकार संरचना (space group: I4/mmm) में स्फटिक करें। Bi साइट पर Pb प्रतिस्थापन aliovalent प्रतिस्थापन का एक मामला है। Pb प्रतिस्थापन प्रणाली में Pb (x= 0.25) सुपरकंडक्टिविटी को दबाके और विसंवाहक हो जाता है। मैगेटिक मापन ने Pb- प्रतिस्थापित संरचनाओं मे Eu की मिश्रित वेलेंट की उपस्थिति का सुझाव दिया है।

हमने चुंबकीयरण माप पर बाहरी दबाव के प्रभाव की जांच की है $BiO_{0.75}F_{0.25}BiS_2$। यह tetragonal $CeOBiS_2$-प्रकार संरचना (space group.: P4/nmm) में संगठित है। हमारी अध्ययनों में polycrystalline $BiO_{0.75}F_{0.25}FBiS_2$ नमूनों में उन्नत सुपरकंडक्टिंग गुणों का सुझाव है। हमारे नमूना में T_c 5.3 K, परिवेश के दबाव में है, जो एक T_c में सीमांत लेकिन

पहले की (T_c= 5.1 K) निश्चित वृद्धि है। M-H से दोनों H_{c2} और H_{c1} बाहरी दबाव P (0 ≤ P ≤1 GPa) के तहत कमी देखे गए। बाहरी दबाव लागू करने पर critical current density में कमी तथा critical temperature में कमी देखे गए है।

हमने एक नया क्रिस्टलोग्राफी क्रमबद्ध चतुर्धातिकीय Heusler मिश्र धातु का संश्लेषित किया है, MnNiCuSb। मिश्र धातु के क्रिस्टल संरचना का मूल्यांकन Rietveld द्वारा शोधन किया गया है पाउडर एक्स-रे विवर्तन डेटा यह मिश्र धातु LiMgPdSb-प्रकार की संरचना में क्रिस्टलीकृत होती है F-43m space group के साथ MNNiCuSb एक उच्च T_C~ 690 K और 3.85 μ_B/f.u. चुंबकीय मूल्य के साथ एक फेरोमग्नेट है। हमने दो अन्य स्टेचियोमेट्रिक रचनाओं का भी अध्ययन किया है; एक Cu rich और अन्य Ni rich ($MnNi_{0.9}Cu_{1.1}Sb$ और $MnNi_{1.1}Cu_{0.9}Sb$) जो भी फेरोमग्नेट हैं। यह जोर दिया जाना चाहिए कि MNNiCuSb बहुत कम ज्ञात बिना Fe के चतुर्धातुक Heusler मिश्रों में से एक है, 1: 1: 1: 1 संरचना के साथ।

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