



NWO Graduate Program in Advanced Materials

Growth and characterization of intercalated Transition Metal Dichalcogenides for Thermoelectric and Magnetic Properties

PhD. Proposal submitted to
Zernike Institute for Advanced Materials
Faculty of Mathematics and Natural Sciences
University of Groningen

By
Nilesh S. Awari
S2301288
Topmaster Nanoscience Program 2012-2014.

Project title

a. Title of Research Proposal

Growth and characterization of intercalated Transition Metal Dichalcogenides for Thermoelectric and Magnetic Properties

b. Name of the Applicant

Nilesh S. Awari

c. Name of the Promotor

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Solid State Materials for Electronics

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e. Abstract

The layered Transition Metal Dichalcogenides (TMD's) have been attractive materials for last few decades because of their rich variety of physical and chemical properties [1]. Tantalum sulfides (TaS_2) and selenides (TaSe_2) are part of this family which are metallic in nature and facilitate intercalation of many types of host atoms within the layers. Intercalation with Fe ions gives rise to exotic magnetic properties [2] and intercalation with alkali ions; such as Li and Na; has been predicted to show thermoelectric properties [1]. Also, studies on the magnetic properties of $\text{Fe}_{1/4}\text{TaS}_2$ have shown interesting results in the inelastic regime in terms of the anomalous Hall effect and magnetoresistance [3].

The possibility of hosting many different foreign metal ions in the van der Waals gap between the adjacent sheets, and thus changing their physical properties, makes these systems prototypical compounds for intercalation. The scientific study of these systems with different metallic ions as an intercalated guest opens the window towards many interesting and fundamental physical properties. The main goal of this proposal is to focus on the magnetic and thermoelectric properties of suitable intercalated TMDs.

Project Description

a. Research Proposal

Subject, current state of knowledge in the field and aim of the research

Transition metal dichalcogenides (TMDs) with stoichiometric composition MX_2 exhibit a wide range of physical properties. For example; HfS_2 is an insulator, (MoS_2 , PtS_2 , PtSe_2) are semiconductors, (WTe_2 , TeS_2) are semimetals and (TaS_2 , TaSe_2 , NbS_2) are metals [4]. All these systems share similar crystallographic structures, namely hexagonally coordinated layers which are van der Waals bonded along the c-axis. Studies on these systems have been refocused since the interesting physical properties of graphene and topological insulators (which have the similar hexagonal structures) were reported. The extremely anisotropic crystal structures of these layered materials provide a natural quasi-two-dimensional platform for the fundamental study of electronic transport and magnetism in low dimensions. Various members of this family also show superconductivity and the onset of charge density wave behavior at low temperatures [5,6]. The possibility of intercalating different guest ions between two TMD layers leads to significant changes in their physical properties. For example, the superconducting transition temperatures of various members of MS_2 compounds change when they are intercalated with Na or K [7]. The superconductivity and CDW phenomena can be tuned when TaS_2 is intercalated with Cu [8]. The structural and magnetic properties of T_xMX_2 depend strongly on the degree of intercalation x [6]. Lately it has been suggested that under certain intercalation conditions, thermoelectric properties also emerge [1]. Of all the above materials, Fe_xTaS_2 has been studied in most detail. This proposal will focus on both Fe_xTaS_2 and other members of the TMD family.

Magnetism in intercalated chalcogenides has recently received a lot of attention. Upon intercalation with magnetic transition metal ions such as iron and manganese, large coercivity ferromagnets are found. Fe_xTaS_2 shows ferromagnetic ordering below 160K for $x=1/4$ and below 35K for $x=1/3$ with the easy axis of magnetization along the crystallographic c axis. It has been suggested that the exchange mechanism responsible for the onset of ferromagnetism is the RKKY mechanism. In this regime, magnetic exchange is mediated by the conduction electrons of the host lattice. The $x=1/4$ compound exhibits the largest transition temperature since the interatomic separation of the magnetic intercalates best matches the RKKY wavevector. Indeed, upon increasing the intercalate concentration, antiferromagnetic behavior emerges when the interatomic separation begins to correspond to a change in sign of the RKKY interaction. $\text{Fe}_{1/4}\text{TaS}_2$ shows sharp switching of magnetization, anisotropic magnetoresistance, very large magneto-crystalline anisotropy and the anomalous Hall effect [10,3]. The magnetic domain structure of single crystal $\text{Fe}_{1/4}\text{TaS}_2$ was studied by imaging the magneto-optical (MO) Faraday Effect. Real-time MO

images revealed unusual dendritic domain structures and slow dynamics of domain formation and propagation [11].

Furthermore, Fe_xTaS_2 has unquenched orbital angular momentums, resulting in a total magnetic moment with a significant orbital contribution as well as the spin contribution. Here the spin-orbit interaction plays an important role. Such systems are of interest for example in the form of thin films where the magnetization of the material is perpendicular to the film and can thus be used in perpendicular recording data on hard drives..

Also, the energy product $(\text{BH})_{\text{max}}$ for $\text{Fe}_{1/4}\text{TaS}_2$ is 20 times smaller than that of the well-known permanent magnets. The high threshold field of the Fe intercalated TMDs renders them as a stable, strong ferromagnets and potential candidates for low temperature applications [6].

Recently, thermoelectric properties of $\text{TaS}_2(\text{Se}_2)$ systems with Na and Li as intercalated guests have been predicted [1]. This study was based on the pseudo-potential method and semi-classical Boltzmann theory. This article reports that the thermoelectric properties of the system depend strongly on the kind of alkali metal used for intercalation, the structure of system (2H or 1T, to be discussed below) and temperature. According to the report, 2H-LiTaS₂ is the best candidate with a predicted figure of merit of 1.1. This prediction makes the study of this system scientifically and technologically relevant. The important quantity for thermoelectric materials is figure of merit defined as,

$$ZT = S^2\sigma T/\kappa,$$

where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity ($\kappa = \kappa_e + \kappa_l$). In order to maximize the ZT, one needs to either increase S and/or σ or decrease κ . However, σ is tied to κ by the Wiedermann-Franz relation,

$$\kappa_e = L_0\sigma T,$$

where L_0 is the Lorentz number and therefore the ratio σ/κ is essentially constant for a particular temperature. The best thermoelectric materials currently used in devices show ZT of approximately 1, which has been the upper limit for last few decades. However, there is no theoretical or thermodynamical reason for this value as an upper bound [12]. To optimize the ZT it is important to find parameter that can alter the mutual dependence of S, σ and κ_e , as all these parameters depend on concentration of charge carriers and in general, varying one changes the others. One of the ways to reduce the lattice thermal conductivity is by introducing heavy elements (high atomic mass will reduce the thermal conductivity of the lattice) and by introducing nanostructured objects which reduces κ but not S and σ . Some of the goals of current research in this field are to find materials that have higher efficiency or have the capability to operate over wider temperature range. Because of the layered nature of the crystal structure of TMDs, the thermal conductivity along the c axis is 2 orders of magnitude lower than in the plane of the hexagonal layer because phonons propagating perpendicular to the layers are scattered.

Magnetic 1 dimensional TMDs can be the better solution for thermoelectric properties, because in dimensional confinement the thermal conductivity is

lowered. The amount of intercalated magnetic dopants changes the interlayer spacing in nanostructured TMDs [16]. The first report on such a 1D structure of Mn_xTaS_2 shows that the magnetic properties are qualitatively similar to their macroscopic analogs. The greatest difference between bulk and nanostructured systems was seen at the temperatures at which transition occurred [16]. The magnetically doped (Mn) TaS_2 nanostructure also shows spin glass like behavior. A wide variety of magnetic dopants and TMDs await further exploration towards novel magnetic properties with dimensional confinement.

Structure of TMDs: Transition metal dichalcogenides have the stoichiometry MX_2 (M = metal atom such as Ta, Ni, V, Re, Nb, Mo, W etc. and X is a chalcogen, i.e. S, Se or Te) and generally consist of a hexagonal lattice of metal atoms (M) sandwiched between an upper and lower layer of chalcogen atoms (X). These materials come in many different polytypes [17]. Depending on the number of d-electrons, TMDs can be designated either 2H, with trigonal prismatic (D_{3h}) coordination of M (for d^1 and d^2 metals) or 1T with octahedral (C_{3v}) coordination of M (for d^0 , d^3 and some d^1 metals) [18].

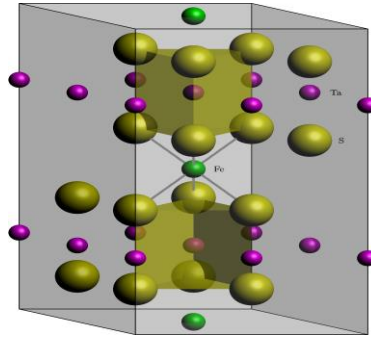


Fig.1: 2H crystal structure of $Fe_{1/4}TaS_2$

b. Main Goal(s) and Research Questions(s)

The goals of this project are two folds-

1. A systematic study of the growth and characterization of TaS_2 , $TaSe_2$ and other TMD single crystals with alkali intercalation for thermoelectric properties. Attempts will be made to enhance the thermoelectric properties. Attempts will also be made to grow low-dimensional TMD nanostructures with lowered lattice thermal conductivity and possible quantum confinement effects on the thermoelectric properties.
2. We will attempt to enhance the magnetic properties of TaS_2 and $TaSe_2$ crystals with systematic intercalation of different magnetic guest (such as Fe, Mn, Cr). Also a systematic study of different magnetic dopants in low dimensional

TMDs will be done to gain insight into different correlations between magnetic behavior and dimensional confinement.

c. Approach and Methods

The first step to achieve our stated goals is to find suitable methods for growing single crystals of TMDs. The growth of single crystals of TMDs with intercalation can likely be achieved by the iodine vapor transport method [6]. The elements are taken in stoichiometric ratio in a powder form and sealed in evacuated silica tubes together with iodine powder. This tube is placed in horizontal two-zone furnace and a temperature gradient is maintained along the tube over period of a few days. Single crystals will grow in the cold end of the tube. The concentration of intercalates can be varied in a continuous manner, as described in reference [19]. Several series of crystals with different TM intercalants and stoichiometries will be grown and studied systematically. Once the crystals are grown, energy dispersive X-ray analysis and single crystal/powder X-ray diffraction techniques will be employed to determine the composition and structure of the materials. For nanostructured TMDs, powder X-ray diffraction will be supplemented by transmission electron microscopy to probe the crystal structures and morphology. Once the crystal structures and/or morphology of the grown compounds have been determined, the magnetization can be studied using a superconducting quantum interference device (SQUID) magnetometer. The magnetic structures of the most interesting materials, if not already known, will be probed using neutron scattering; beamtime will be applied for at large-scale facilities. Neutron diffraction will also be essential to locate the positions of light alkali metals, especially Li, in intercalated thermoelectric MX_2 . Electrical resistance as a function of temperature can be measured using four probe techniques. A systematic approach to increase the Curie temperature of these materials will be important as far as the search for better magnetic materials with higher Curie temperature and maintaining a high coercivity is concerned.

Fe_xTaS_2 is an interesting material in which study ultrafast dynamics of orbital and spin moments can be done. Because this system has 3d transition metal valence orbitals with large magnetic moment and smaller spin-orbit coupling (namely Fe) and 5d valence levels of transition metals (namely Ta) with a large spin-orbit coupling but smaller magnetic moment. Such measurements will be performed in collaboration with the group of Dr. R. Tobey.

The synthesis of magnetic 1D dichalcogenide nanostructures can be done following almost the same procedure that will be employed for bulk single crystals, except that slower ramp rate for the heating must be used [16]. The synthesis route given in reference [16], will need to be optimized for different magnetic dopants and TMDs to explore the possible use of magnetic nanostructured of TMDs for novel magnetic and thermoelectric properties.

Thermoelectric Properties Measurement:

Measuring the Seebeck coefficient and electrical resistivity (in magnetic fields up to 9 T and in the temperature range 2K-350K for both measurements), and thermal conductivity below room temperature will be performed using a Physical Properties Measurement System (PPMS) in the Solid State Materials for Electronics lab. High temperature measurements are currently done via external collaborations but SSME are applying for funds to obtain the equipment. Magnetization can be measured in the SQUID magnetometer (2K-800K, max. field 7T). The electrical conductivity of non-intercalated metallic TMDs is quite high ($n \sim 10^{21} \text{cm}^{-3}$) making them unlikely to be good thermoelectrics because the Seebeck coefficient will likely be small. Intercalating TMDs with alkali metals likely lowers the carrier concentration, thus increasing the Seebeck coefficient; this aspect will be investigated in detail. Doping some thermoelectric materials with magnetic elements has been shown increase the thermo-power [13]. The possibility that magnetic intercalation in TMDs could result in better thermoelectric materials will be studied systematically in this project. It is possible that codoping with alkali metals and magnetic transition metals will be beneficial. A positive effect of magnetic field on the thermoelectric figure of merit has also been found for several thermoelectric materials [14]. Magnetic field can change the electrical conductivity (magnetoresistance), thermal conductivity (Maggi-Reghi-Leduc effect) and thermo-power (Nernst-Ettingshausen effects). Although changes in the thermal and electrical changes tend to be small, the variation in thermo-power can be appreciable, depending on sample geometry, giving one more way to optimize thermoelectric properties [15]. The synthesis of 1D magnetic dichalcogenides nanostructures [16], might be a suitable route to optimize the thermoelectric properties further through quantum confinement effects [20, 21].

References:

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Cost Estimate:

- **Personal Costs:**
Funding is requested for one ‘*Onderzoeker in Opleiding*’ position to be filled by the applicant.
- **Running Costs:**
Towards covering expenses for chemicals, other reagents and consumables, general maintenance of equipment and travel to conferences, summer schools.
- **Equipment:**
All the equipment required for this project is already present in the laboratories of the research groups within the Zernike Institute (mainly within Solid State Materials for Electronics) and associated research groups. Therefore, no additional budgetary allocation is requested for equipment.
- **Other Support:**
This project will be supported by the Zernike Institute and Rijkuniversiteit Groningen; they will contribute the senior scientists, technicians and provide other infrastructure through the GSS for the OIO.
- **Budget Summary:**

	2014	2015	2016	2017	2018	Total
PhD Students	1/4	1	1	1	3/4	4
Senior scientists	-	-	-	-	-	
Technicians	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel costs (k€)	12.75	51	51	51	38.25	204.000
Running budget (k€)	2.5	10	10	10	7.5	35.000
Equipment						
Total						239.000

Statement about Starting Date, Project Duration and Planning of Intermediate Steps:

The project will begin in September 2014 and last for a period of 4 years. Below is a summary of the intended plan for the project, but deviations from this plan might occur depending on findings that open further opportunities to discover newer and more exciting physics from these systems.

Time	Activity
1 st Year	<ul style="list-style-type: none">• Growth methods for TMD single crystals with different intercalation guests and optimization of growth parameters• Characterization techniques for grown single crystals
2 nd Year	<ul style="list-style-type: none">• Optimisation of growth parameters for high quality single crystals• Optimization of synthesis process for nanostructured magnetic TMDs• Neutron scattering experiments to probe magnetic structures, as well as crystal structures of Li-containing thermoelectric TMDs
3 rd Year	<ul style="list-style-type: none">• Further characterization of thermoelectric properties• Detailed studies on magnetic properties of nanostructured TMDs
4 th Year	<ul style="list-style-type: none">• finalising research• Thesis writing

Curriculum-Vitae:

NILESH S. AWARI

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PERSONAL INFORMATION	
	Date of Birth: 28-09-1987 (Age: 26 years) Nationality: Indian Current Address: Esdoornlaan 800, 9741 MK Groningen, The Netherlands
RESEARCH EXPERIENCE	
SEP 2013- UNTILL PESENT	Master Thesis at Zernike Institute for Advanced Materials, University of Groningen Supervisors: Prof. Dr. ir. Bart J. van Wees and F.K. Dejene. Working on spin precision measurements on 3-terminal metallic devices.
MAY 2010- JULY 2012	Junior Research Fellow at Tata Institute of Fundamenatl Research Supervisor: Dr. S. S. Prabhu. The optical properties of different materials were studied in the THz region using an electro-optic setup. All my publications thus far, listed below, came through this project.
APRIL 2009- JUNE 2009	Visiting Research Student at Tata Institute of Fundamental Research Supervisor: Dr. A. Thamizhvael. Single crystal of $CeAl_2$ were grown and studied for electrical and magnetic properties.
EDUCATION	
SEPTEMBER 2012- UNTILL PRESENT	Top Master Nanoscience, Zernike Institute for Advanced Materials. University of Groningen
AUGUST 2008- JUNE 2010	Master of Science in Physics with solid state physics. University of Mumbai, Mumbai, Maharashtra, India Graduation Projects: <ol style="list-style-type: none">1. Temperature dependence of carrier life-time in a p-n junction diode.

AUGUST 2005- MARCH 2008	<p>2. Design & construction of dielectric measurement setup for solids.</p> <p>Bachelor of Science in Physics with Electronics Instrumentation. University of Mumbai, D. G. Ruparel College, Mumbai, Maharashtra, India. Minor subjects: Mathematics & Chemistry</p>
RESEARCH PUBLICATIONS	
<ol style="list-style-type: none"> 1. Charge density waves condensate as measure of charge order and disorder in $\text{Eu}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.50, 0.58$) manganites Parul Pandey, <u>Nilesh Awari</u>, Rakesh Rana, Abhishek Singh, S. S. Prabhu, Appl. Phys. Lett. 100, 062408, (2012) 2. Charge-density-waves condensate in charge-ordered manganites: impact of ferromagnetic order and spin glass disorder Rakesh Rana, <u>Nilesh Awari</u>, Parul Pandey, Abhishek Singh, S S Prabhu and D S Rana, J. Phys. Condens. Matter 25,106004(2012) 3. Multilayer broadband absorbing structure for Terahertz region Ashish Dubey, A. Jain, C. G. Jayalakshmi, T. C. Shami, <u>Nilesh Awari</u>, and S. S. Prabhu, Microwave and Optical Technology Letters 55, 2, (2013) 	
CONFERENCES & WORKSHOPS ATTENDED	
<ol style="list-style-type: none"> 1. One day workshop on “Cryogenics and Physics at Low Temperature” organized by Homi Bhabha Birth Centenary Commemorative Committee, Tata Institute of Fundamental Research (TIFR) & Low Temperature Facility of TIFR on July 9, 2009at TIFR, Mumbai. 2. National conference on “Physics of Semiconductors devices & Smart Materials (NC-PSDSM-2007)” organized by Karmaveer Bhaurao Patil College, Vashi, Navi Mumbai (Sponsored by DST & UGC, New Delhi); during December 21-22, 2007. 3. Participated in “Spectroscopic Data Analysis Workshop” organized jointly by Indian Association of Physics Teachers (IAPT) & D. G. Ruparel College, Mumbai; during February 12-13, 2010. 	
EXPERIMENTAL SKILLS	
<p>Ultra-short pulsed lasers (10fs), pump-probe experiments for THz spectroscopy</p> <p>Closed cycle cryosystems, bolometer and vacuum system.</p> <p>Clean room techniques for device fabrication. Optical/e-beam lithography. Metal evaporation.</p> <p>Experience in chemical vapor transport system for growth of chalcopyrite materials. X-ray diffraction, SQUID magnetometry.</p>	



Declaration of hospitality and financial support for research costs

Appendix to the Proposal for a PhD research position
in the NWO Graduate Programme Advanced Materials, deadline 2 Feb. 2014

Name of the applicant: Nilesh S. Awari

Title of the proposal: Growth and Characterization of intercalated
Transition Metal Dichalcogenides for
Thermoelectric and Magnetic Properties

By signing this document the staff member declares that she/he is willing to host and supervise the PhD research project that is mentioned above. In addition, the staff member declares that she/he has and makes available the materials, infrastructure and the funding that is needed for covering the research costs (the costs in addition to the salary of the PhD student some funding for travel and training), as described in the proposal.


The signing staff members must be affiliated with the Zernike Institute for Advanced Materials (including the associate members).

Signatures

Applicant (the student applying for the PhD grant)

Date: 31/01/2014 Name: Nilesh S. Awari Signature: 

Daily PhD supervisor (only needed if applicable, in case of supervision by an assistant professor or UD/UHD without ius promovendi)

Date: 31/1/2014 Name: GRAEME R. BLAKE Signature: 

1st Promotor (staff member with ius promovendi)

Date: Name: Signature: