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RESEARCH
HIGHLIGHTS



EVENTS AND
MEETINGS TO BE
ANNOUNCED



OTHER NEWS NONE
FOR THE MOMENT

NEWSLETTER

2015



Dear Colleagues and friends,

I have been asked by the CNRS to be in charge of the French part of the Indian-French Laboratory of Solid State Chemistry. IFLaSC in English or LaFICS in French is an Associated International Laboratory created in 2003 between the **Centre National de la Recherche Scientifique (CNRS)**, a French public scientific and technological institution, the **Université de Caen Basse Normandie (UCBN)**, the **Université de Strasbourg, Alsace** public scientific and professional institutions and The **Indian Institute of Science, Bangalore (IISc)**, an autonomous public institution funded by the government of India. Several laboratories and institutions linked to the CNRS, the UCBN and the IISc are involved in this LaFICS that are:

- the Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)
- the Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS)
- the Laboratoire de Cristallographie et Science des Matériaux de Caen (CRISMAT)
- the Ecole Nationale Supérieure d'Ingénieurs de Caen
- the Université de Strasbourg
- The Solid State and Structural Chemistry Unit, SSCU, in Bangalore
- Materials Research Center (MRC), IISc, in Bangalore
- The Indian Institute of Technology, Bombay, India (IIT/B), through its Department of Metallurgical Engineering & Materials Science (MEMS)



- The Indian Institute of Technology, Madras, India (IIT/M), through its Department of Chemistry

With this News Letter I wish to bring some more dynamism to this LIA and encourage Indians and French Researches to promote excellent and fruitful collaborative projects.

In this News Letter you will then find some insights concerning the activities performed in the framework of this LIA.

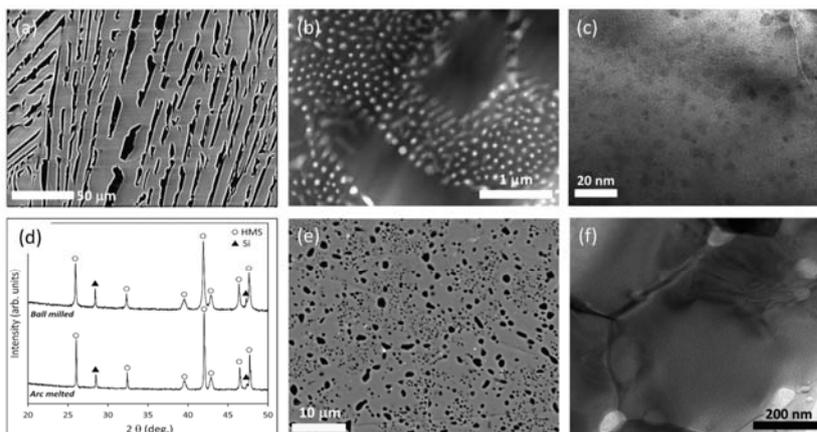
Enjoy your reading!

Marie Helene DELVILLE, PhD

Research highlights

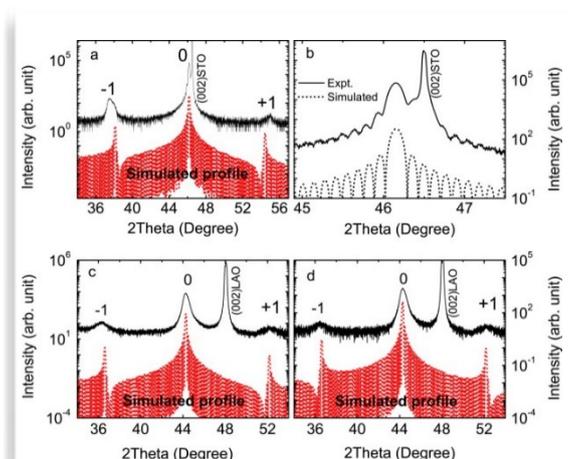
Ail, U.; Gorsse, S.; Perumal, S.; Prakasam, M.; Umarji, A.; Vives, S.; Bellanger, P.; Decourt, R., Thermal conductivity of beta-FeSi₂/Si endogenous composites formed by the eutectoid decomposition of alpha-Fe₂Si₅. *Journal of Materials Science* 2015, 50, 6713-6718..
ICMCB, France/IIS Bangalore, India

This article shows the study of thermoelectric properties of semiconducting beta-FeSi₂ containing a homogeneous distribution of Si secondary phase. The synthesis was carried out using arc melting followed by the densification by uniaxial hot pressing. Endogenous beta-FeSi₂/Si composites were produced by the eutectoid decomposition of high-temperature alpha-Fe₂Si₅ phase. The aging heat treatments have been carried out at various temperatures below the equilibrium eutectoid temperature for various durations in order to tune the size of the eutectoid product. Thermal properties of the samples were studied in the temperature range of 100-350 °C. The microstructural investigations support the fact that the finest microstructure generated through the eutectoid decomposition of the alpha-Fe₂Si₅ metastable phase is responsible of the phonon scattering. The results suggest an opportunity to produce bulk iron silicide alloys with reduced thermal conductivity in order to enhance its thermoelectric performance.



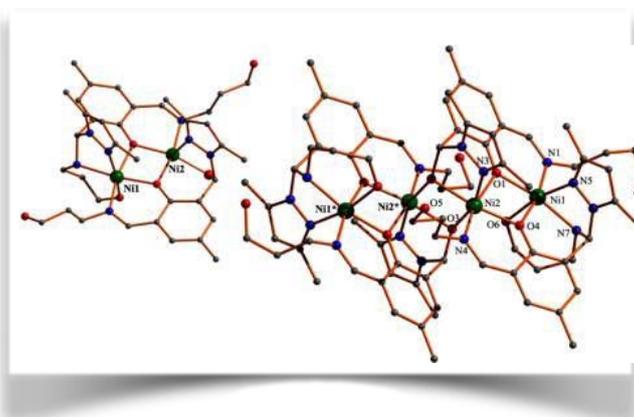
Behera, B. C.; Padhan, P.; Prellier, W., Influence of substrate in all-ferromagnetic superlattices. *Journal of Magnetism and Magnetic Materials* 2015, 388, 22-27.
CRISMAT, France/IIT Madras, India

In this paper the authors show that Raman scattering and magnetization of the superlattices consisting of ultrathin layer of two metal like ferromagnets $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and SrRuO_3 (SRO) grown on (001) oriented LaAlO_3 (LAO) and SrTiO_3 (STO) substrates, were studied. The Raman spectrum of LAO/[1-u.c. LSMO/2-u.c. SRO](x60) super lattice shows modes which are shifted towards higher frequencies relative to that of LAO/[2-u.c. SRO/1-u. c. LSMO](x60) superlattice. However, the Raman spectra of these superlattices indicate the presence or orthorhombic structures of LSMO and SRO for both stacking orders. The STO/[1-u.c. LSMO/2-u.c. SRO](x60) superlattices exhibit Curie temperature (T_C) at similar to 270 K and Neel temperature (T_N) at similar to 140 K. Surprisingly, T_C of superlattice on LAO grown simultaneously with STO reduces to similar to 209 K for in-plane magnetic held and to similar to 99 K for out-plane held. But for the reverse stacking grown on LAO the T_C increases to similar to 121 and similar to 218 K for in-plane and out-of-plane orientation of held, respectively. The superlattices grown On LAO do not show any signature of T_N . This result clearly indicates the influence of substrate induced stress and stacking order on exchange coupling between the LSMO and SRO in the superlattices, providing a useful tool towards tailoring the magnetic properties of heterostructures..



Ghosh, A. K.; Mahapatra, T. S.; Clerac, R.; Mathoniere, C.; Bertoasi, V.; Ray, D., Direct C-N Coupling in an in Situ Ligand Transformation and the Self-Assembly of a Tetrametallic Ni-4(II) Staircase. *Inorganic Chemistry* 2015, 54, 5136-5138.
IIT Kharagpur, India/ICMCB, France

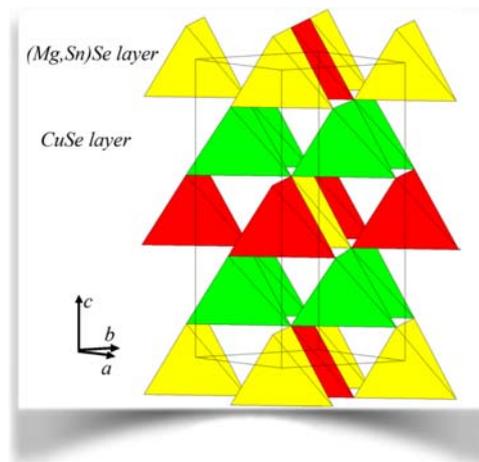
The authors here have studied the A [Ni-4(II)] staircase complex serendipitously prepared from the reaction of the binucleating Schiff base proligand 2,6-bis[[[(3-hydroxypropyl)imino]methyl]-4-methylphenol (H(3)L2) and 3,5-dimethylpyrazole (Me(2)pzH) with nickel(II) nitrate in a reaction at room temperature, initially aimed to yield a dinuclear complex. From a room temperature metal ion/ligand reaction, the proligand H₃L₂ in situ transformed to modified forms HL₃₂- and HL₄₂-, allowing the [Ni-4] formation. Variable-temperature magnetic behavior of a [Ni-4] complex reveals antiferromagnetic interactions with stabilization of a diamagnetic ground state ($S-T = 0$).



Kumar, V. P.; Guilmeau, E.; Raveau, B.; Caignaert, V.; Varadaraju, U. V., A new wide band gap thermoelectric quaternary selenide $\text{Cu}_2\text{MgSnSe}_4$. *Journal of Applied Physics* 2015, 118.

IITM India/CRISMAT, France

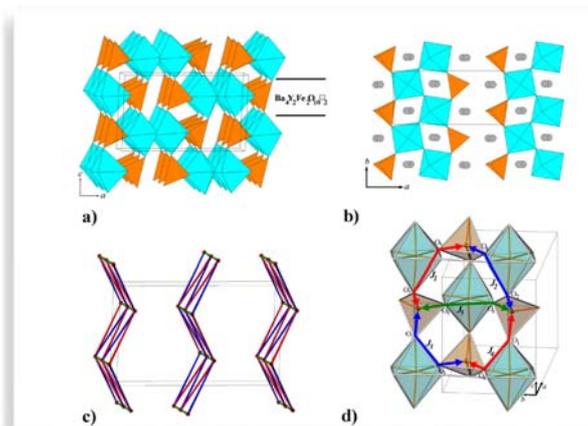
This paper deals with $\text{Cu}_2\text{MgSnSe}_4$ based compounds composed of high earth abundant elements which have been identified to exhibit good thermoelectric performance in the mid-temperature range. The pristine phase shows a band gap of 1.7 eV, which is slightly higher than similar ternary and quaternary copper based stannite compounds. $\text{Cu}_2\text{MgSnSe}_4$ crystallizes in the tetragonal I (4) over bar $2m$ space group. Substitution of In at Sn site tends to decrease the tetragonal distortion toward the cubic symmetry. The electrical and thermal transport properties of Cu and In-doped $\text{Cu}_2\text{MgSnSe}_4$ in the temperature range of 300 K-700K are studied. The substitution of In^{3+} for Sn^{4+} and Cu^{2+} for Mg^{2+} induces charge carriers as holes, which in turn lead to improvement in thermoelectric efficiency. The role of mass fluctuations and structural disorder in the evolution of the thermal conductivity of the doped selenides is discussed. A maximum ZT of 0.42 is attained for $\text{Cu}_2\text{MgSn}_{0.925}\text{In}_{0.075}\text{Se}_4$ around 700 K, and this value is comparable to that of $\text{Cu}_2\text{ZnSnSe}_4$.



Kundu, A. K.; Hardy, V.; Caignaert, V.; Raveau, B., Interplay between 3d-3d and 3d-4f interactions at the origin of the magnetic ordering in the $\text{Ba}_2\text{LnFeO}_5$ oxides. *Journal of Physics-Condensed Matter* 2015, 27..

IIT Jabalpur, India/CRISMAT, France

A new family of oxides in which 3d-3d and 3d-4f interactions are of comparable strength has been synthesized and characterized both from structural and physical viewpoints. These compounds of formulation $\text{Ba}_2\text{LnFeO}_5$ ($\text{Ln} = \text{Sm, Eu, Gd, Dy, Ho, Er, Yb}$) are isotypic to the perovskite derivative Ba_2YFeO_5 . They exhibit an original structure consisting of isolated FeO_4 tetrahedra linked via LnO_6 (or YO_6) octahedra. Magnetic and calorimetric measurements show that all these compounds exhibit a unique, antiferromagnetic transition involving both the 3d and 4f ions. The antiferromagnetic properties of the $\text{Ln} = \text{Y}$ phase (non-magnetic Y^{3+}) and of the $\text{Ln} = \text{Eu}$ (non-magnetic ground state multiplet of Eu^{3+}) are ascribed to super-super exchange Fe-O-O-Fe interactions, leading to the lowest T_N (5.5 K for Y and 4.6 K for Eu). The introduction of a magnetic lanthanide, i.e. $\text{Ln} = \text{Sm, Gd, Dy, Ho, Er, Yb}$, in the octahedral sites, leads to larger T_N values (up to 9.8 K for $\text{Ln} = \text{Yb}$). It is found that several mechanisms must be taken into account to explain the complex evolution of the magnetic properties along the $\text{Ba}_2\text{LnFeO}_5$ series. In particular, the super-exchange Ln-O-Fe, as well as the on-site Ln(3+) magnetocrystalline anisotropy, are suggested to play crucial roles. This $\text{Ba}_2\text{LnFeO}_5$ series offers a rare opportunity

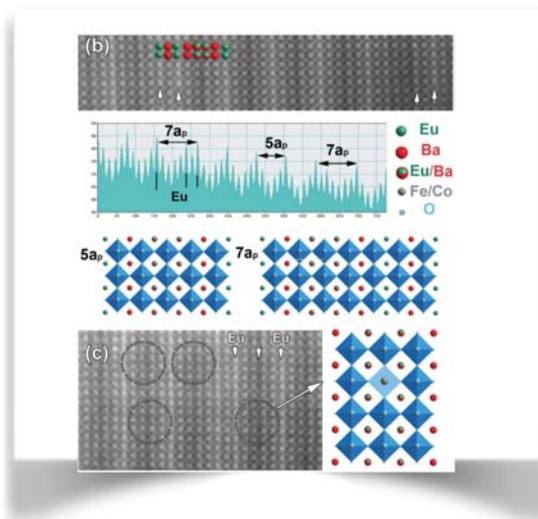


to investigate experimentally a situation where the 3d-3d and 3d-4f interactions co-operate on an equal footing to trigger a unique long-range magnetic ordering in insulating oxides.

Magesh, J.; Murugavel, P.; Krishnamurthy, J.; Adyam, V.; Prellier, W., A study of magnetic ordering in multiferroic hexagonal Ho_{1-x}Dy_xMnO₃. Journal of Applied Physics 2015, 117.

CRISMAT, France/IITK, India/IITM, India

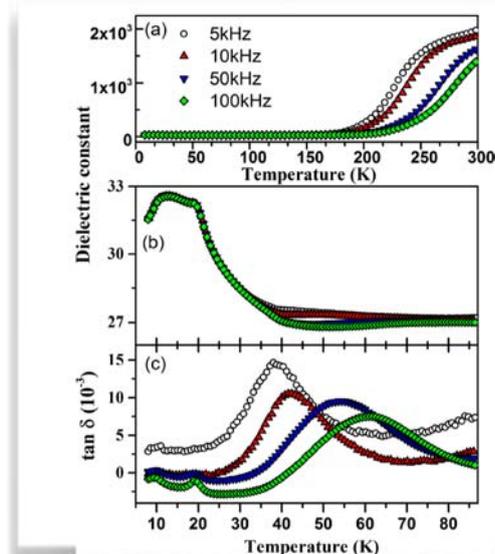
Quintuple perovskites Ln₂Ba₃Fe_{5-x}Co_xO_{15-δ}, with Ln = Sm, Eu have been synthesized for x values varying from 0 to 2. The HRTEM and HAADF investigations show that these oxides are ordered at the nanoscale with a tetragonal "ap × ap × 5ap" lattice, corresponding to an ordered fivefold stacking of the Ba and Ln layers. These structures are in fact chem. twinned, so that only cubic or pseudo-cubic symmetry is detected by XRD investigation. The detailed magnetic study shows the existence of short range antiferromagnetic ordering, canted in nature at from 5 to 330 K. This particular behavior is interpreted on the basis of local antiferromagnetic M-O-M (M = Fe/Co) interactions within the nanodomains that are limited by pinning of the Co/Fe spins at the boundaries. The authors studied compns. are Sm₂Ba₃Fe₃Co₂O_{14.07}, Eu₂Ba₃Fe₃Co₂O_{13.72}, Sm₂Ba₃Fe_{3.5}Co_{1.5}O_{14.16} and Eu₂Ba₃Fe_{3.5}Co_{1.5}O_{13.81}.



Magesh, J.; Murugavel, P.; Mangalam, R. V. K.; Singh, K.; Simon, C.; Prellier, W., Ferroelectric ordering and magnetoelectric effect of pristine and Ho-doped orthorhombic DyMnO₃ by dielectric studies. Journal of Applied Physics 2015, 118.

IIT Madras, India/CRISMAT, France

In this paper, the magnetoelectric coupling and ferroelectric ordering of the orthorhombic Dy_{1-x}Ho_xMnO₃ (x = 0 and 0.1) are studied from the magnetodielectric response of the polycrystalline samples. The dielectric study on the DyMnO₃ reveals ferroelectric transition at 18K along with an addition transition at 12K. We suggest that the transition at 12K could have originated from the polarization flop rather than being the rare earth magnetic ordering. The magnetodielectric study reveals a magnetoelectric coupling strength of 10%, which is stronger by two orders of magnitude in comparison to the hexagonal manganites. Surprisingly, the Ho³⁺ substitution in DyMnO₃ suppresses the magnetoelectric coupling strength via the suppression of the spiral magnetic ordering. In addition, it also reduces the antiferromagnetic ordering and ferroelectric ordering temperatures. Overall,

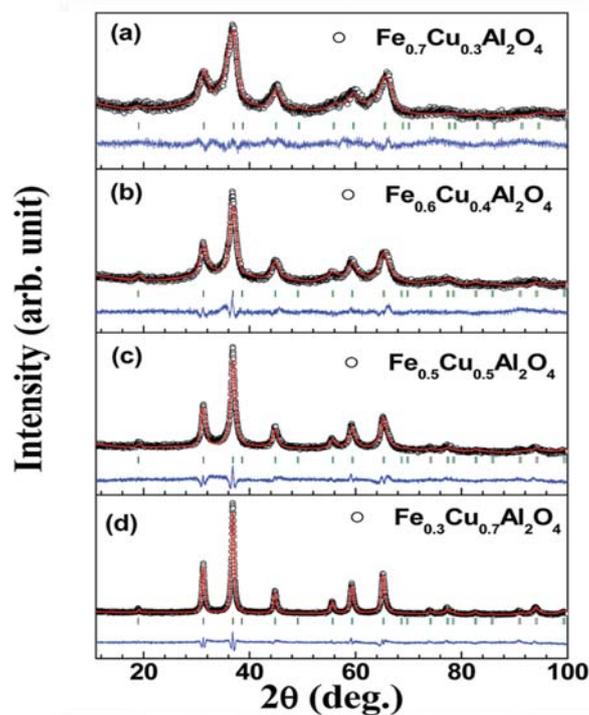


the studies show that the rare earth plays an important role in the magnetoelectric coupling strength through the modulation of spiral magnetic structure. .

Maiti, S.; Kundu, A. K.; Lebedev, O. I.; Bera, P.; Anandan, C.; Gayen, A.; Seikh, M. M., Synthesis and magnetic properties of nano-dimensional $\text{Fe}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ ($0.3 \leq x \leq 0.8$). *Rsc Advances* 2015, 5, 83809-83817..

IIT Jadavpur India / CRISMAT, France/ NAL Bangalore India, AK Kundu was previously in Bangalore and went on collaborating with CRISMAT.

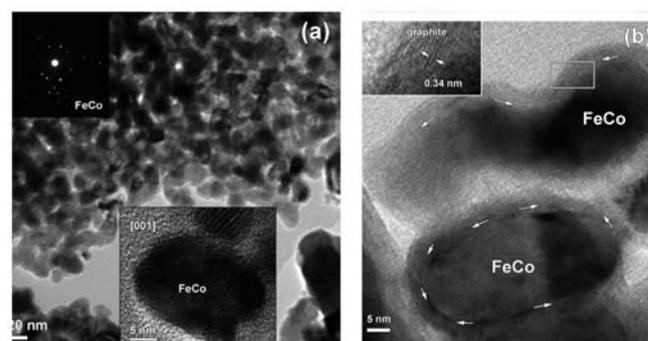
In this paper, the authors reported, the sol-gel synthesized, microstructural analysis, surface and magnetic properties of solid solutions of $\text{Fe}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$. The single phase of the samples for x values varied between 0.3 and 0.8 at 700 degrees C has been obtained. The powder X-ray diffraction, electron diffraction and HRTEM analysis reveal that the particle size systematically increases with the increase in x value. The XPS studies have confirmed the presence of Cu^{2+} species with a $(\text{Fe} + \text{Cu})/\text{Al}$ surface atomic ratio close to the bulk stoichiometric value. Unlike the common magnetic spinels with B-site magnetic cations, $\text{Fe}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ shows only A-site magnetism in a diamond-type lattice. The samples with smaller particle size, namely the samples for $x = 0.3$ and 0.4 exhibit small magnetization. The origin of such magnetism is attributed to the inversion in the spinel structure and the defect induced magnetism. Except for the $x = 0.7$ sample, all other samples show spin glass behavior



Nautiyal, P.; Seikh, M. M.; Lebedev, O. I.; Kundu, A. K., Sol-gel synthesis of Fe-Co nanoparticles and magnetization study. *Journal of Magnetism and Magnetic Materials* 2015, 377, 402-405

IIT Jadavpur India / CRISMAT, France/ NAL Bangalore India, AK Kundu was previously in Bangalore and went on collaborating with CRISMAT

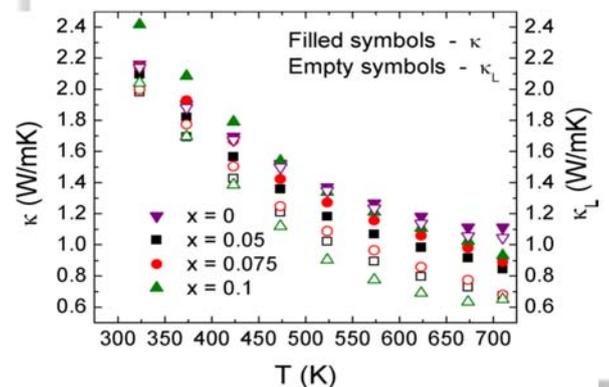
The authors here report the synthesis of carbon encapsulated Fe-Co nanoparticles using conventional sol-gel route and its magnetization studies. The x-ray diffraction indicates the formation of the single phase body centered cubic alloy Fe-Co phase with cell parameter $a_0 = 2.857$ angstrom. Nanoparticles are highly crystalline and exhibit low index faceting as determined from high-resolution transmission electron



microscopy (HRTEM) investigation. The observed orthogonal lattice planes with lattice distance of 2.86 angstrom are attributed to (100) and (010). HRTEM image confirms the cube like Fe-Co nanoparticles with core-shell structure of carbon encapsulation, composed of carbon and graphite materials. The magnetometry results of the carbon encapsulated alloy Fe-Co nanoparticles with core-shell structure designate as a ferromagnetically ordered soft magnet with coercive field of 890 Oe (at 5 K). The coercive field and magnetization value depend on the size of nanoparticles as well as the diamagnetic contribution of carbon encapsulation.

Pavan Kumar, V.; Guilmeau, E.; Raveau, B.; Caignaert, V.; Varadaraju, U. V., A new wide band gap thermoelectric quaternary selenide $\text{Cu}_2\text{MgSnSe}_4$. Journal of Applied Physics 2015, 118, 155101. CRISMAT, France/IIT Madras, India.

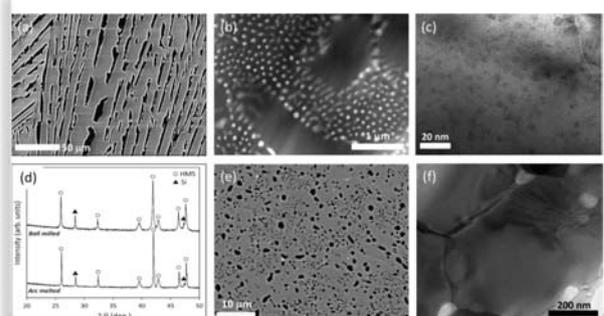
$\text{Cu}_2\text{MgSnSe}_4$ based compounds composed of high earth abundant elements have been identified to exhibit good thermoelectric performance in the mid-temperature range. The pristine phase shows a band gap of 1.7 eV, which is slightly higher than similar ternary and quaternary copper based stannite compounds. $\text{Cu}_2\text{MgSnSe}_4$ crystallizes in the tetragonal $I4\bar{2}m$ space group. Substitution of In at Sn site tends to decrease the tetragonal distortion toward the cubic symmetry. The electrical and thermal transport properties of Cu and In-doped $\text{Cu}_2\text{MgSnSe}_4$ in the temperature range of 300 K–700 K are studied. The substitution of In^{3+} for Sn^{4+} and Cu^{2+} for Mg^{2+} induces charge carriers as holes, which in turn lead to improvement in thermoelectric efficiency. The role of mass fluctuations and structural disorder in the evolution of the thermal conductivity of the doped selenides is discussed. A maximum ZT of 0.42 is attained for $\text{Cu}_2\text{MgSn}_{0.925}\text{In}_{0.075}\text{Se}_4$ around 700 K, and this value is comparable to that of $\text{Cu}_2\text{ZnSnSe}_4$.



Perumal, S.; Gorsse, S.; Ail, U.; Prakasarn, M.; Vives, S.; Decourt, R.; Umarji, A. M., Low thermal conductivity of endogenous manganese silicide/Si composites for thermoelectricity. Materials Letters 2015, 155, 41-43.

ICMCB, France/ IIS Bangalore, India

Higher manganese silicide (HMS) based alloys with eutectic composition (Si-33.3 at% Mn) were prepared by arc-melting, melt-spinning and ball milling in order to evaluate the effect of microstructure on the thermal conductivity. Powder X-ray diffraction, SEM, EPMA and TEM analysis confirmed the presence of Si as a secondary phase distributed in the HMS matrix phase. Thermal properties of the samples were studied in the temperature range of 300–800 K.



The microstructure refinement resulting from ball milling leads to a decrease of the thermal conductivity from 4.4 W/mK to 1.9 W/mK, whereas meltspinning is inefficient to this respect. The results show an opportunity to produce bulk higher manganese silicide alloys with reduced thermal conductivity in order to enhance its thermoelectric performance.

Raveau, B.; Caignaert, V.; Kundu, A. K., Double Cationic-Anionic Ordering in Ba-Based Oxygen-Deficient Perovskites. *Z. Anorg. Allg. Chem.* 2015, 641, 990-997.

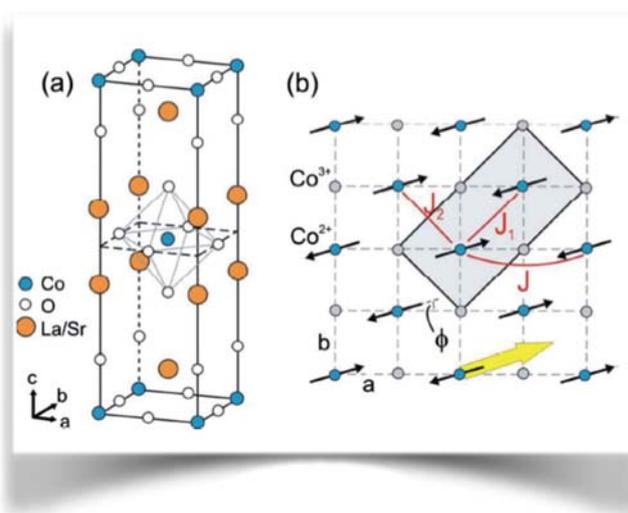
CRISMAT, France / IIT Jadavpur India AK Kundu was previously in Bangalore came to CRISMAT and went on collaborating with CRISMAT

Complex cationic-anionic ordering in barium-based oxygen deficient perovskites is reviewed. Considering the parent ABO_3 structure, the ordering between barium and a rare earth cation in the A site generates three classes of oxides, called double, triple and nanoscale ordered quintuple perovskites. From the ordering between a transition element (Fe, Co) and a larger cation on the B site two structural families are obtained, containing calcium and yttrium respectively. These oxides offer a vast playground for the investigation of magnetic and transport properties.

Raveau, B.; Seikh, M. M., Charge Ordering in Cobalt Oxides: Impact on Structure, Magnetic and Transport Properties. *Zeitschrift Fur Anorganische Und Allgemeine Chemie* 2015, 641, 1385-1394.

CRISMAT, France / West Bengal, India. Long term collaboration Prof Seigh was in Bangalore and did a post doc at CRISMAT.

This review shows the great impact of charge ordering upon the magnetic and transport properties of mixed valent Co^{4+}/Co^{3+} and Co^{3+}/Co^{2+} cobalt oxides. The relationships between charge ordering and physical properties are described for three structural families: the ordered oxygen deficient perovskites and the Ruddlesden and Popper (RP) derivative $La_{1.5}Sr_{0.5}CoO_4$, the layered $NaxCoO_2$ series and the 114 $CaBaCo_4O_7$ oxide.



As part of our common activities, Please find attached the numbers of collaborative papers since 2009 and in 2015 for both sides!

