

Dedicated

to


My Parrents and Family

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Forwarded


21/12/15

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Undertaking from the Candidate

I, *Abhishek Kumar*, research scholar under the supervision of *Prof. Sandip Chatterjee*, Department of Physics, IIT (BHU) Varanasi give undertaking that the thesis entitled “*Structural and Magnetic Properties of Multiferroic TbMnO₃ and Quasi-One Dimensional Quantum Spin System LiCuVO₄*” submitted by me for the degree of *Doctor of Philosophy* is a record of first-hand research work carried out by me during the period of study.

I avail myself to responsibility such as an act will be taken on the behalf of me, mistakes, errors of facts, and misinterpretation are of course entirely my own.

Date : 21/12/2015

Place : Varanasi


(Abhishek Kumar)


CANDIDATE'S DECLARATION

I, **Abhishek Kumar**, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **Prof. Sandip Chatterje**, Department of Physics, IIT (BHU) Varanasi for a period of approximately 4 years and 10 month from (March, 2011 to Dec., 2015) at Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma.

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and the body of the thesis. I further certify that I have not willfully lifted up some other's works, para, text, data, result, etc. reported in the journals, books, magazines, reports, dissertations, thesis, etc., or available at websites and included them in this Ph.D. thesis and cited as my own work.

Date: 21/12/2015

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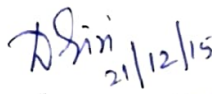

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CERTIFICATE FROM THE SUPERVISOR

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.


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PH.D. PRE-SUBMISSION SEMINAR CERTIFICATE

This is to certify that **Mr. Abhishek Kumar**, a bonafide research scholar of Department of Physics, Indian Institute of Technology (Banaras Hindu University) Varanasi has successfully presented/completed the pre-submission seminar on the thesis entitled "**Structural and Magnetic Properties of Multiferroic $TbMnO_3$ and Quasi-one Dimensional Quantum Spin System $LiCuVO_4$** " dated 06.08.2015, which is an essential part of his Ph.D. programme.

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Title of the Thesis: Structural and Magnetic Properties of Multiferroic TbMnO_3 and Quasi-one Dimensional Quantum Spin System LiCuVO_4

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(Abhishek Kumar)

In everyday life of human being, they need many devices e.g. mobile, computer, pen drive, transistor etc. All the devices cannot be carried every time at any place. So, miniaturization of devices with multifunction come into the life e.g. smartphone which are used for multipurpose. It is possible only by developing multifunctional materials. To develop smaller and faster multifunctional devices, it is crucial to have materials which possesses two or more functional properties strongly coupled to each other in one material.

Multiferroics are one class of multifunctional materials having two or more long range ferroic ordering simultaneously in one single phase. In multiferroic material, there may exist a coupling between two ferroic ordering (e.g. ferroelectric and ferromagnetic). If the material exhibits a coupling between ferroelectric and magnetism then it is called “magnetoelectric coupling”. This magnetoelectric coupling effect is a novel properties of material which is mostly used in the development of non-volatile futuristic four logic state memory devices and many other devices also. Multiferroic materials with strong magnetoelectric coupling (appearance of magnetization \mathbf{M} in an electric field \mathbf{E} , or appearance of electric polarization \mathbf{P} by the application of magnetic field \mathbf{H}) can enable 4- state logic devices. The microscopic origin of magnetism is basically the same in all magnetic materials: it is the presence of localized electrons, mostly in the partially filled d or f shells of transition-metal or rare-earth ions, which have a corresponding localized spin, or magnetic moment. Exchange interactions between the localized moments govern magnetic order. On the other hand, the situation with ferroelectrics is quite different. There are several different microscopic sources of ferroelectricity, and accordingly one can have different types of multiferroics.

Transition metal Perovskites such as manganites, cobaltites and cuprates have attracted great interest due to their remarkable properties such as metal-insulator transition (manganites and cobaltites), colossal magnetoresistance and magnetoelectric coupling (manganites) and high T_c superconductivity and one dimensional quantum spin system as quantum magnet (cuprates). Strong magnetoelectric coupling has been observed mostly in perovskites multiferroic materials and some cuprates also. In manganites and cuprates, hole doping is the best way to enhance or improve the magnetic properties and induce ferromagnetism and also magnetoelectric coupling which is

applicable in the development of many devices such as magnetic recording media, memory devices, magnetic sensors etc.

In my thesis, synthesis and study of some single phase Multiferroics and one dimensional cuprates has been carried out.

Summary of each chapter is given below:

Chapter 1: In this chapter we have discussed regarding the multiferroicity and a brief review on historical background in the development of the field of magnetoelectric coupling and multiferroics. The origin of ferroelectricity and types of multiferroics have been discussed in detail. Application of magnetoelectric coupling in the development of devices e.g. magnetic recording media, memory devices, sensors etc. also discussed.

Moreover, in this part of introduction, we have also discussed about Quantum spin system, one dimensional quantum magnetism and interchain & intrachain exchange interaction in cuprates. The role of low dimensional system in the explanation of many ground state properties or quantum phenomena has been discussed in details. Magnetic properties of one dimensional cuprate chain governed by nearest neighbor (NN) and next nearest neighbor (NNN) spin interaction already discussed in details. Low dimensional system attracted much more attention because it is solved exactly by applying many theoretical models and gives pure quantum solution.

Chapter 2: In this chapter, we have discussed about sample synthesis process and experimental tools (namely; X-ray Diffractometer, Superconducting quantum interference device (SQUID), Neutron diffractometer, XPS (X-ray photoemission spectra), Swift Heavy Ion beam irradiation and Raman Spectroscopy), we have used for characterization and measurement of our samples.

Chapter 3: In this chapter, we have discussed about the synthesis of Zn, Mn, Co doped LiCuVO_4 via solid state reaction method. After synthesis, we have characterized our samples with XRD, magnetic measurement, Neutron diffraction, XPS (X-ray Photoemission Spectroscopy) and studies structural and magnetic properties. It has been observed that LiCuVO_4 which is antiferromagnetic in pure form shows ferromagnetic ordering after doping of Mn in Cu- site of spinel LiCuVO_4 , on the other hand Zn and Co doped increases antiferromagnetic correlations.

In support of our assumption that Mn is going in to octahedral Cu site and ensure the charge redistribution with Mn doping, we have studied Neutron diffraction and XPS pattern of our Mn and other doped samples. XPS study shows that, some Cu^{+2} converted into Cu^{+3} (nonmagnetic) and to maintain charge neutrality the conversion of some Mn^{+2} into Mn^{+3} occurs. Neutron diffraction study shows no long range ferromagnetic ordering and also significant modification in Cu-O bond length is observed. This confirms our assumptions. The exchange interaction modified with Mn-doping induces ferromagnetism. This might be the reason of origin of inducing ferromagnetism.

Chapter 4: In this chapter, we have studied swift heavy ion beam irradiation effects of LiCuVO_4 and $\text{LiCu}_{0.95}\text{Mn}_{0.05}\text{O}_4$. Structural and Magnetic properties of LiCuVO_4 , Mn-doped and irradiated $\text{LiCu}_{0.95}\text{Mn}_{0.05}\text{O}_4$ have been studied. A short range magnetic ordering has been observed in Mn ($x=0.05$) doped spinel LiCuVO_4 system but it is not stable on further doping of Mn. Ion beam irradiation also reduces ferromagnetic ordering due to defects creation. Structural modification due to defects created by ion beam irradiation and doping have been studied by Reitveld refinement of XRD pattern and Raman spectra. X-ray diffraction results indicate that the pristine materials relax on irradiation. The irradiated materials' XRD peaks become broader than those of the pristine, which increases further with fluence values. Broadening of peak is due to the formation of the smaller grain size with the irradiation. No significant change is observed in the Raman modes of the system with doping of Mn in LiCuVO_4 . For $x=0.05$ the peak width decreases slightly (indicative of increase of strain) and as Mn content increases (viz. for $x=0.1$) the peak broadens indicating the release of strain with increase of Mn content which is consistent with the XRD result.

Chapter 5: In this chapter, we have studied structural and magnetic properties of Y and Ni doped TbMnO_3 in Tb and Mn site respectively. Both Y and Ni doping decrease the Neel temperature, T_N . Y doping reduces effectively both the $J_{\text{Tb-Tb}}$ and $J_{\text{Mn-Mn}}$ exchange interactions, whereas Ni doping on the Mn site decreases only the $J_{\text{Mn-Mn}}$ exchange interaction. In the Raman study of Y-doped and undoped TbMnO_3 samples eight features are observed where as in Ni-doped TbMnO_3 few modes disappear due to MnO_6 bending and in-plane O_2 stretching. This might be due to the lattice disorder which is induced by Ni doping.

Chapter 6: In this chapter, we have studied the existence of Exchange bias and Griffith phase in TbMnO_3 and also in Ce-doped in TbMnO_3 -site by studying the magnetization as a function of temperature and field under different cooling field. It has been observed from the analysis of Curie-Weiss (CW) fitting that they show the downshift from standard CW line (Griffith Phase) and also exhibits shift of origin of hysteresis loop (Exchange Bias) in undoped sample. In undoped sample oxygen vacancy is observed from EDX measurement which converts some Mn^{+2} to Mn^{+3} and exchange interaction between $\text{Mn}^{+2}/\text{Mn}^{+3}$ (double exchange mechanism) comes into the play and induces ferromagnetism. In $\text{Tb}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0.025, 0.05$) exchange bias and Griffith phase also observed because Ce-doping in Tb-site also converts some Mn^{+2} to Mn^{+3} .

Chapter 7: In this chapter, we have discussed summary and conclusion of the thesis.