Effect of Cobalt Doping on $Bi_{1-x}Sb_x$ Nano Particles

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Abstract: Apart from thermoelectric applications, $Bi_{1-x}Sb_x$is also known to exhibit exotic topological phase in the range ($0.07<x<0.22$). In the present work, influence of magnetic doping such as Cobalt in Structural, morphological and magneto transport properties of topological insulator $Bi_{1-x}Sb_x$nano particles is investigated. Resistivity measurements showa change from metallic behaviourin un doped sample to insulatingbehaviourin the Cobalt doped samples at low applied magnetic field and low temperature. Also, for temperatures up to 5K, field dependent magneto resistance in un doped sample shows a prominent dip around zero field which is seen to be destroyed due to cobalt doping. These results are indicative of the destruction of WAL at low temperature on account of magnetic doping.

1. INTRODUCTION

$Bi_{1-x}Sb_x$alloys are well known as excellent thermoelectric materials and have already been studied in great detail for past few decades [1]. However, recent studies on topological phases in condensed matter have revealed $Bi_{1-x}Sb_x$as a "topological insulator" belonging to a nontrivial *Z*2 topological class for ($0.07<x<0.22$) [2]which has been confirmed by ARPES measurements. Also, atransition from metallic to insulator phase (MIT) has been reported in single crystals of $Bi_{1-x}Sb_x$[3]. However, the effect of nano structuring is not fully understood.

In case of typical topological insulators like Bi_2Se_3, etc. doping with magnetic 3d transition elements is reported to have caused a crossover from Weak Anti- Localization (WAL) to weak Localization(WL) due to the breaking of time reversal symmetry and opening of an energy gap in the Dirac-cone like surface states [4]. In this work, low temperature magneto-transport properties of un doped $Bi_{1-x}Sb_x$with x=0.06 composition, is discussed along with its magnetically doped counterpart having 29% cobalt substitution in Bi site.

2. SAMPLE PREPARATION AND CHARACTERIZATION

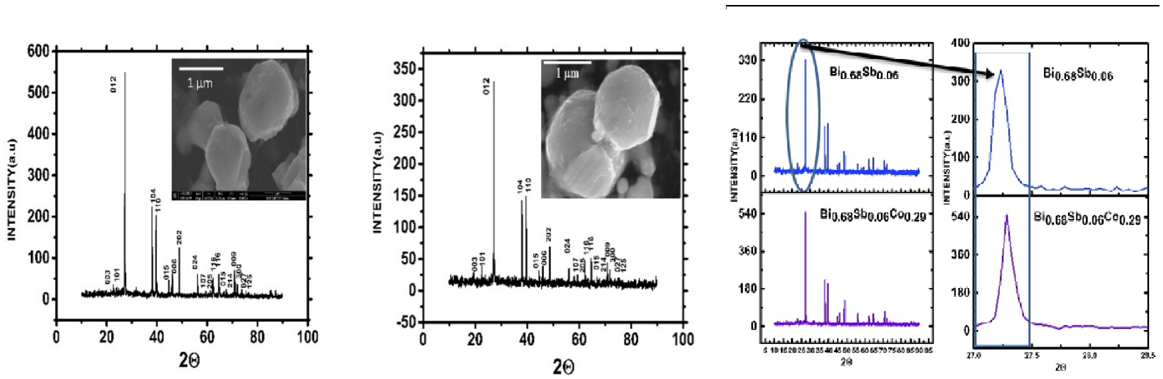
2.1 Synthesis of $Bi_{1-x}Sb_x$ Nanocrystals

$Bi_{1-x}Sb_x$nano crystals having different values of relative molar ratio of Bi and Sb ranging from (x= 0.00 to 1.00) were synthesized by microwave assisted solvo thermal method using a single-mode variable-power 300 Watts, CEM microwave oven, taking $BiCl_3$ and $SbCl_3$ as precursors and NaOH and Oleylamine(OAM) as reducing agents with ethylene glycol as the solvent. The mixture was at first, subjected to vigorous stirring as well as heating for 1 hour to remove oxygen and moisture respectively followed by an hour of microwave heating at $195^{O}C$ in closed chamber. The cleaning of the precipitate obtained was done using ethanol, acetone and DI water for a multiple number of times.For cobalt doping in $Bi_{1-x}Sb_x$, $CoCl_2.2H_2O$ was used along with $BiCl_3$ and $SbCl_3$as reactants.

2.2 Characterization

The structural and morphologicalcharacterization of nanocrystals were by performed using XRD and FESEM respectively. The crystal structures were determined from powder X-ray Diffraction XRD, done using Bruker D8 Advance X-ray diffractometer (CuK-α) and morphology has been characterized using a FEI made "Nova Nano SEM

450" field-emission scanning electron microscopy (FESEM) and Nanoscope E Atomic Force Microscopy (AFM). DRS (diffuse reflectance spectroscopy) was performed using Parkinson made UV-visible spectrophotometer to obtain the band-gap of the materials. XRD images showed single phase formation of both $Bi_{0.94}Sb_{0.06}$ and $Bi_{0.68}Sb_{0.06}Co_{0.29}$ withrhombohedral R-3mH structure fig1(a) and fig1(b). A shift of the main peak towards higher value of theta (shown in figure 1c) is indicative of inclusion of cobalt in the $Bi_{1-x}Sb_x$ lattice as cobalt having smaller atomic size is expected to reduce the lattice parameter.Also FESEM images of both undoped $Bi_{0.94}Sb_{0.06}$ (fig1.a inset) as well as Co doped $Bi_{0.68}Sb_{0.06}Co_{0.29}$ (fig1.b inset) crystals showed hexagonal shaped crystals having size of approximately 1μm while EDX measurements showed Sb inclusion percentage (x=0.06) in the nano crystals for $Bi_{0.94}Sb_{0.06}$ and Co concentration in doped sample is found to be 0.29. The nanocrystal size and shape as well as morphology is seen to remain the same with Co doping. Hence, the effect of particle size in physical properties of the un doped and Co doped samples can be safely ruled out.



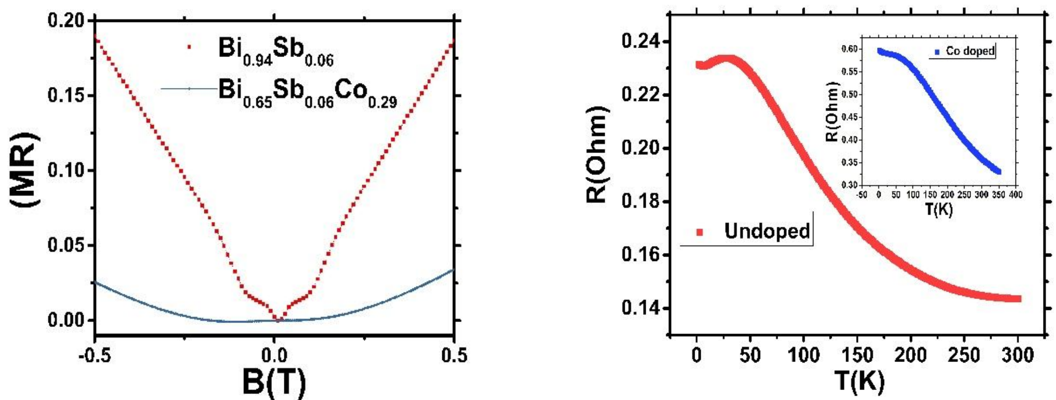
a) b) c)

Figure 1. FESEM images of (a) XRD pattern and SEM image (inset)of nanocrystalline$Bi_{0.94}Sb_{0.06}$ and (b) XRD pattern and SEM image (inset) of $Bi_{0.68}Sb_{0.06}Co_{0.29}$ (b) comparison of XRD pattern and main peak shift of $Bi_{0.94}Sb_{0.06}$and $Bi_{0.68}Sb_{0.06}Co_{0.29}$

3. RESULTS AND DISCUSSION

Longitudinal resistivity measurements in presence of applied magnetic field were performed on undoped as well as magnetically doped samples of $Bi_{0.94}Sb_{0.06}$.Both the un doped as well as Co doped sample exhibit positive MR as shown in figure 2a. The resistivity (R) versus magnetic field (B) plot (fig.2.a) corresponding to undoped $Bi_{0.94}Sb_{0.06}$ shows suppressed Weak Anti-Localization (WAL) at a temperature (4K). WAL was noticed for T ranging from 2K to 5K, and disappears from 6K onwards showing a parabola like B field dependence (not shown here). On doping with magnetic 3D transition element Co, total suppression of WAL (fig.1.b, blue curve) is seen (as compared to the parent, red curve) which can be attributed to the breaking of Time Reversal Symmetry(TRS) and hence spin momentum locking, [5]Due to spin momentum locking, the spin of an electron sweeping out closed paths (which cause the electron to return to its original path with opposite direction) develops a π Berry phase, which causes destructive interference between the incident and scattered paths.Hence, back scattering of electrons becomes impossible andconsequently such closed paths cannot exist. This lack of back scattering causes impedance-less electron flow in absence of external magnetic fields and magnetic impurities. This phenomenon is called Weak Anti Localization (WAL)[5]. However, in the presence of magnetic fields, TRS and hence spin momentum locking is broken and the incident and scattering paths develop opposite phases from the fields, causing the coherent destructive interference effect to die out [5]. This manifests as an increase in resistance in presence of applied fields as well as magnetic impurities.The positive linear like MR behavior in undoped samples can be attributed to Topological Surface States(TSS)[6], the parabola like +ve MR in Co doped sample can be attributed to Lorentz force acting on charge carriers[7]. This transition from linear to parabola like MR is an indication for the destruction of TRS[5] on account of doping with magnetic impurities.

The R versus T plot of the un doped sample at 2T is shown in fig 2.b. A Metal to Insulator transition is observed around 27 K which is missing in the cobalt doped counterpart as shown in the inset of fig 2.b. A transition from metallic behavior (supposedly exhibited by TSS) for undoped (red curve of fig2.b) to insulating behavior (exhibited by bulk states) for the Co doped (blue curve of fig2.b) samples at low T and low fields (2T) is observed.Metallic like resistivity behaviour (fig 2b) as well as WAL(fig 2a) are both disappearing with cobalt doping. Metallic behaviour is expected in the WAL regime as WAL signifies increased conduction of charge carriers which is less probable in the insulating regime. Also WAL and the presence of TSS (supposedly showing metallic behavior) are linked by the preservation of TRS [5]. Disappearance of both WAL and metallic behaviour at low temperature can be attributed tothe destruction of TRS as a result of cobalt doping. However, the transition from WAL to WL which has been showed by [4] for chromium doped Bi_2Se_3 could not be observed in spite of a significant amount of Co doping (even up to 29 %). The reasons for this unexpected behaviour are under investigation.



a) b)

Figure 2. a)Magneto resistance MR vs B plot of $Bi_{0.94}Sb_{0.06}$(red curve) and $Bi_{0.68}Sb_{0.06}Co_{0.29}$ (blue curve) b)Resistance R vs temperature T plot of $Bi_{0.94}Sb_{0.06}$(red curve) and $Bi_{0.68}Sb_{0.06}Co_{0.29}$ (blue curve)

4. CONCLUSION

In this paper, the effect of magnetic doping (cobalt) in structural, morphological and magneto transport properties of topological insulator $Bi_{1-x}Sb_x$nanoparticles is investigated. For temperatures up to 5K, field dependent magneto resistance in un doped sample shows a prominent dip around zero field which is seen to be destroyed due to cobalt doping. This can be attributed to the destruction of WAL on account of breaking of TRS manifested by the disappearance of the WAL dip in Co doped sample. Also, change from metallic to insulating behaviour from undoped to the Co doped samples at low B and T (conditions in which WAL is seen) also supports this observation. However, no transition from WAL to WL is observed in spite of a significant amount of Co doping. The only effect of Co doping is the change from WAL behaviour to classical parabolic like behaviour.

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REFERENCES

1. Tang et al. Journal of Materials Chemistry C 2.24 (2014): 4710-4726.
2. F.Nakamura et al,Phys.Rev.B**84**, 235308 (2011).
3. A.Taskin et al, Phys.Rev.B**80**, 085303,2009
4. M. Liu et al.Phys.Rev.Lett., 108, 036805 (2012)
5. Brahlek et al, Solid State Communication, **215-216**(2015),54-62
6. A.A.Abrikosov, Phys.Rev.B**58**, 5,1998
7. A. Biswas et al, Journal Appl Phys,**116**, 213704 (2014)