AN EXPERIMENTAL STUDY ON $Bi_{2-X}Sb_XTe_3$ CRYSTALS AND THIN FILMS

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by

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DECLARATION BY THE CANDIDATE

I hereby declare that the research work presented in this thesis entitled "AN EXPERIMENTAL STUDY ON $Bi_{2-X}Sb_XTe_3$ CRYSTALS AND THIN FILMS" is my own work and was carried out under the guidance of Dr. P. H. Soni, Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara. All the ideas and references have been duly acknowledged. I have put in research work for requisite number of terms as required by the University.

I further declare that to the best of my knowledge, the thesis does not contain any part or any work, which has been submitted for the award of any degree either in this University or in other University/Institute without proper citation.

Date: Manish M. Patel

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List of Publications

1. Vicker's Microgardness of $Bi_{2-x}SbxTe_3$ (x=0 to 0.2) Single crystals

   M. M. Patel, P. H. Soni and C. F. Desai

   Crystalline and Non- Crystalline Solids, Narosa, 1(2014)22.

2. Optical Band gap of $Bi_{2-x}SbxTe_3$ (x=0 to 0.2) Thin films

   M. M. Patel, P. H. Soni and C. F. Desai

   J. of Material Science (Communicated)

3. Growth and characterization of $Bi_{2-x}SbxTe_3$ (x=0 to 0.2) single crystals

   M. M. Patel, P. H. Soni and C. F. Desai

   J. of Cryst. Growth (Communicated)

SUMMARY

Apart from the intensive research still going on on the primitive elemental semiconductors Ge and Si, at present much more attention is being paid to compound semiconductors, viz., binary, ternary and quaternary ones. Among the binary compounds, the group II-IV, IV-VI, III-V and V_2-VI_3, semiconducting compounds have been receiving considerable attention due to their important photoconducting, photovoltaic, electrooptic and general electronic properties. Their pseudobinary and ternary compounds have also found their due significance. For the study of basic semiconducting properties, it is of primary importance that these properties be measured on bulk single crystals. The single crystals themselves are also most frequently required directly or indirectly for device fabrication. The performance of the devices principly depends on the bulk crystalline characteristics. Of the crucial importance among the characteristics are purity, perfection and homogeneity. Because of this, the field of crystal growth carries no less significance than the crystals themselves. In most of the applications the semiconductors are used in the form of single crystals or thin films or both at a time. These materials have been subject of study by quite a number of workers. Most of these studies are concerned with thin films and their opto-electronic characterization. The work reported in the present thesis includes crystal growth, optical band gap and hardness of crystals, as well as optical band gap of thin films. The materials included in the study are Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$.The thesis is presented in two parts.

Part-1 of the thesis consists of two chapters. Chapter 1 gives a general introduction to the basic background for the present work and importance of the thermoelectric materials and their applications. A brief survey of earlier work reported on growth, and micro hardness of the crystals (Bi_2Te_3 in particular) is given. It also includes reports on optical and electronic properties of these materials.

Chapter 2 deals with the experimental techniques used during the courses of the present work. The techniques include the crystal growth, thin film preparation, optical microscopy, hardness indentation and optical band gap measurements.

Part 2 of the thesis consists of three chapters. Chapter 3 deals with the results of growth of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ single crystals. The crystals were grown by Bridgman-Stockbarger method. Various methods of crystal growth in general and of crystal growth from melt in particular have been discussed. Fairly large good quality crystals of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ could be obtained by the Bridgman-Stockbarger technique at the ampoule lowering rate of 3.5mm/hr and temperature gradient around 45˚C/cm. The Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ single crystals have also been grown by Zone melting method and the growth features on the free surface of the crystal have been studied and the observation on growth features indicates the layer mechanism to be effective in the growth of crystal. There are cellular growth features mechanism due to constitutional supercoolling to effective in the growth of the crystal and stoichiometric deviation of the material due to preferential evaporation of tellurium and also classify the growth of crystals are on (111) plane. In the case of Bridgman growth, increase in growth velocity is observed to decrease the crystal perfection. EDAX analysis shows that the growth of crystals are stoichiometric and homogenous. The X-ray diffractrometry study indicates the substitution effect of Sb at the bismuth sites in Bi_2Te_3. The band gap of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ crystals are about 0.16, 0.18, 0.19 and 0.22 eV (all direct) , respectively. There are no observable indirect transitions in the crystals.

Chapter 4 deals with hardness studies on Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ crystals. The variation of hardness with applied load has been studied in detail. Particularly, the observed complex low load dependence of hardness has been explored in light of above investigations. The results indicate that the hardness peaks obtained in the low load range may be explained in terms deformation induced coherent regions. The Hardness values of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ single crystals have been obtained to be 448, 499, 532 and 630, respectively. Microhardness is load dependent quantity and the variation is quite prominent in the low load ranges and only for sufficient high applied loads it becomes virtually independent of load. The hardness peaks observed in H_v versus load (P) plots may be explained in terms of deformation induced coherent regions. Due to work hardening, the crystal hardness increases. The Mayer index is not truly constant but may be different in different load ranges.

Chapter 5 discusses the results on optical band gap of thin films of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$. These also include the effect of film thickness on optical band gap. The results are discussed invoking the size effect operative in the thickness range used.The band gap of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$ and $Bi_{1.9}Sb_{0.1}Te_3$ thin films are on an average 0.17 eV, 0.19 eV, 0.20 eV (direct), respectively, for film thickness around 1800 Å. At smaller thickness the band gaps are larger than the bulk values. The film thickness dependence of the band gap of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$ and $Bi_{1.9}Sb_{0.1}Te_3$ indicate the optical transition to be governed by quantum size effect within the thickness range studied.

CONTENTS

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PART-I

PART-II