PREFACE

Thermodynamic investigations of binary and multicomponent metallic systems are carried out with various objectives in view. In the first place, the processes used for the extraction and refining of metals in the field of chemical metallurgy and alloy development in physical metallurgy involve multicomponent metallic solutions. For the thermodynamic analysis of these processes it is necessary to know the thermodynamic properties of the solution with high accuracy. Second, the phase diagrams are very important for the materials engineers as far as the choice of materials for the particular application is concerned. It is necessary to determine the position of solidus and liquidus curve in the phase diagram with very good accuracy which is to be done by the careful thermodynamic analysis of the relevant system. Third, only electrical properties or magnetic properties or X – ray investigation cannot provide all the information about the constitution of the metallic system. Thus authentic thermodynamic data along with above investigations are essential to obtain the deeper insight into the constitution of the multicomponent metallic systems. Due to the toxic nature of lead, its use is restricted in many applications. Several research are currently carried out to develop lead free solder alloys. The most prominent lead free solder alloys are likely to be tin based multicomponent alloys. Predictions of the thermodynamic behavior of higher-order multicomponent alloys from thermodynamic data of binary and ternary systems have been proven very crucial as it is extremely challenging to investigate the thermodynamic properties of higher-order systems. Therefore, it is necessary to assess the thermodynamic data of various binary and ternary systems that are important to lead-free solder applications. The literature lacks thermodynamic information for some lead-free systems. Sn-Bi-Sb and Sn-Ga-In are good options as a solder ternary system free of lead.

The Thesis has been divided into six chapters.

In **Chapter-1**, we discussed the various properties of conventional Pb-Sn solders and why they are commonly used to date. We also explored soldering as a technique with historical roots datingback to 4000 BC in Mesopotamia. Furthermore, we delved into the other metals or elements utilized in these Sn-based solder alloys and the associated issues with lead-based solder alloys. Additionally, this section covers the sources of lead and introduces the principles and types of calorimeters. We also address the challenges involved in transitioning from lead-tin alloys to Pb- free solder alloys. Finally, we examine the general criteria for selecting solder alloys and underscore the importance of thermodynamic studies of lead-free solder alloys.

In **Chapter-2**, the experimental procedure and methodology are described. The purity, source, and physical state of metals used for the investigations are presented in tabular form. The methods for calculating various thermodynamic properties using the drop technique are briefly discussed. The procedures and techniques for measuring the enthalpy of mixing using the MHTC96 LINE EVO drop calorimeter are discussed, including the calibration of the calorimeter. Methods for calculating mixing from the peak are discussed, accompanied by suitable equations. Various geometrical models are also discussed, along with the RK Muggianu polynomial model.

In **Chapter-3**, Measurement of thermodynamic properties of boundary binaries Ga-Sn, Ga-In and In-Sn systems has been discussed. It has been carried out at temperature ranging from (673-773) K with the variation of dropping elements Sn, In and Sn in Ga-Sn, Ga-In and In-Sn system respectively. Calibration of the calorimeter was done by dropping four pieces of α-Al_2O_3 at the drop temperatures. The measured enthalpies of mixing are plotted against dropping element and found endothermic in nature for all the compositions in the case of Ga-Sn and Ga-In while exothermic nature have been observed In-Sn system. The binary interaction parameters are

determined for all the three boundary binary system using RK-Polynomials. These interaction parameters are used for the calculation of the ternary interaction parameters in **chapter-4**.

In **Chapter-4**, the integral and partial enthalpy of mixing for Sn-Ga-In ternary alloy systems were measured by the help of drop calorimeter along six of the cross sections at different temperatures of 673 K, 723 K and 773 K. Pieces of pure tin were dropped into molten $Ga_{0.25}In_{0.75}$, $Ga_{0.50}In_{0.50}$, $Ga_{0.75}In_{0.25}$ alloys and pieces of pure Indium into $Ga_{0.25}Sn_{0.75}$, $Ga_{0.50}Sn_{0.50}$, $Ga_{0.75}Sn_{0.25}$. In order to calculate the interaction parameter, Redlich-Kister-Muggianu (RKM) model was used which considers the substitutional solution mechanism. Geometric models i.e. Kohler, Muggianu, Chou, Toop, and Hillert have been used to calculate the integral mixing enthalpies and compared with experimental data. It is also observed that the data predicted from CALPHAD technique is very close to the experimental data for most of the composition range. It has been seen to be a good agreement between the theoretical models and results of this study.

In **Chapter-5**. The integral and partial mixing enthalpies of Sn-Bi-Sb system were determined using the drop-solution calorimeter (MHTC 96 LINE EVO, SETARAM Instruments, France). At 923 K,973 K, and 1023 K, calorimetric measurements of the Sn-Bi-Sb system were made along five of the cross sections. Pieces of pure tin were dropped into molten $Sb_{0.25}Bi_{0.75}$, $Sb_{0.50}Bi_{0.50}$, $Sb_{0.75}Bi_{0.25}$ alloys; Bismuth into $Sb_{0.50}Sn_{0.50}$ and Antimony into $Bi_{0.50}Sn_{0.50}$. Using the calorimetric data, partial and integral thermodynamic properties were determined. It was found that mixing enthalpies were temperature independent. The substitutional solution Redlich-Kister-Muggianu(RKM) model was used to derive the interaction parameter based on ternary enthalpy values. It is also observed that the data predicted from CALPHAD technique is very close to the experimental data for most of the composition range. When the estimated and measured values are compared, it is found that there is a good agreement between them.

The overall conclusions of this work have been presented in **Chapter-6** followed by scope for the future work.