

# Calorimetric Investigations of Lead Free Solder Alloys: Sn-Bi-Sb & Sn-Ga-In



Thesis submitted in partial fulfillment  
for the Award of Degree

**Doctor of Philosophy**

By

*Vikrant Singh*

DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY  
(BANARAS HINDU UNIVERSITY)  
VARANASI – 221005  
INDIA

19141009

2024

### Summary and Major Conclusions

In this study, integral and partial enthalpy of mixing of boundary binaries Ga-Sn, Ga-In and In-Sn system has been measured. It has been done at temperature 673 K-773 K with the variation of dropping elements Sn, In and Sn in Ga-Sn, Ga-In and In-Sn system respectively. 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. 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. SETARAM MHTC 96 LINE EVO drop calorimeter was used for the determination of mixing enthalpy. The NIST standard  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as the calibration material.

The following results were obtained by calorimetric measurement of Ga-Sn, Ga-In and In-Sn system **in Chapter 3**.

- ❖ It has been found that the enthalpies of mixing shows temperature-dependency for two binaries Ga-In & Ga-Sn and is independent of temperature for In-Sn System.
- ❖ Integral and partial mixing enthalpies of Ga-In, Ga-Sn and In-Sn binary systems were investigated using drop calorimeter (MHTC 96 LINE EVO) in the temperature range of 673 K-773 K.
- ❖ Enthalpies of mixing was found to be endothermic for Ga-In and Ga-Sn whereas it was exothermic for In-Sn system.
- ❖ Binary interaction parameters were determined by using R-K Polynomial Fitting, followed by least square optimization. The agreement between the

experimental results and theoretical model was very good. Subsequently, binary interaction parameters were also determined for three of the above systems.

Calorimetric Measurements of enthalpies of mixing of Sn-Ga-In Ternary Alloy System has been done in **Chapter 4** and following conclusions can be drawn:

- ❖ Integral mixing enthalpy and partial mixing enthalpy values were derived from this study on Sn-Ga-In Ternary alloy systems by using drop calorimeter along six of the cross sections at temperatures ranging from 673 K-773 K.
- ❖ It was found that mixing enthalpies were temperature dependent.
- ❖ Iso-enthalpy plots were plotted at constant temperature in the interval of 0.2 kJ. The behavior of both the binaries Ga-Sn and Ga-In affects the majority of the iso-enthalpy curves because In-Sn system is slightly negative or exothermic in nature.
- ❖ It is seen that enthalpy of mixing becomes positive from In-Sn binary towards Gallium corner. As gallium composition increases the enthalpy of mixing increases. All the iso-enthalpy curves are oriented towards In-Sn binary.
- ❖ The enthalpies of mixing of the given ternary system have been calculated using the Kohler, Muggianu, Chou, Toop, and Hillert geometric models and compared with the experimental values.
- ❖ When the values from Redlich-Kister-Muggianu (RKM) model and experiment are compared, it is found that there is a good agreement between them.
- ❖ The data predicted from CALPHAD technique [144] by using THERMOCALC software 2023 (database: SSOL5) is very close to the experimental data for the most of the compositions.

Later in **Chapter 5**, Calorimetric Measurements of enthalpies of mixing of Sn-Bi-Sb Ternary Alloy System has been done and following conclusions can be drawn:

- ❖ Integral and partial mixing enthalpies of Sn-Bi-Sb ternary system were investigated using drop calorimeter (MHTC 96 LINE EVO) in the temperature range of 923 K-1023 K along five of the cross-sections:  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Bi}_x$ ,  $(\text{Bi}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Sb}_x$ .
- ❖ It has been found that the enthalpies of mixing are nearly temperature-independent.
- ❖ The curves representing iso-enthalpy were plotted using the mixing enthalpy values for all the five cross sections.
- ❖ The mixing enthalpy is seen to be more negative when the alloy's composition is nearer to the Sb-Sn binary system and positive when it is nearer to the Bi-Sb binary system. This is so because Sb-Sn binary system has the largest negative mixing enthalpy values among the three binaries, whereas the Bi-Sb alloys have the highest positive enthalpy of mixing values. The binary Sb-Sn affects the majority of the iso-enthalpy curves.
- ❖ This suggests that the Sb and Sn atoms in the given ternary systems sub-lattice may have greater influence on the orientation of the enthalpy of mixing curves.
- ❖ The enthalpies of mixing of the given ternary system have been calculated using the Kohler, Muggianu, Chou, Toop, and Hillert geometric models. When compared with the experimental values, the results are in good agreement.

- ❖ Ternary interaction parameters were determined by using R-K-Muggianu Model, followed by least square optimization. The agreement between the experimental results and theoretical model was very good.
- ❖ The data predicted from CALPHAD technique [144] by using THERMOCALC software 2023 (database: SSOL5) is very close to the experimental data for the most of the compositions.