CHAPTER 1

INTRODUCTION

1.1 Background

The first observation of conductivity in solid was by Faraday at room and selected temperatures who reported the transport of silver ions through silver sulfide in 1834 (Owen, 2000). The motion of charge carriers in solids gives rise to electricity. The charge carriers can be electrons (or holes) or ions or both. Solids in which the charge carriers are electrons (or holes) are classified as metals, semiconductors and superconductors. If the charge carriers consist of both electrons and ions, they are called mixed conductors. Superionic conductors are a group of materials which exhibit properties characteristics of liquids and solids at the same time (Jurado et. al., 2005). Solid-state ionics has been a very active field of science since the seventies.

Silver iodide (AgI) based fast ion conducting material is one of the best investigated solid ionic conductors (Chandra, 2004). At room temperature, silver iodide exists in the γ-phase with zincblende structure. The *p-d* hybridized Ag-I bonds in the zincblende structure are however weak and are easily broken producing high Ag^+ ion disorder. Above 137°C, γ-AgI undergoes a phase transition to β-AgI. β-AgI has a wurtzite structure where each iodine ion is surrounded by a regular tetrahedron of four silver ions. At 146.5°C, β-AgI is transformed into α-AgI, a body centered cubic structure lattice with two silver ions distributed randomly over many crystallographic sites that enables high Ag^+ ion conductivity (Mohan and Sunandana, 2004). In this work, AgI will be mixed with CuI. Hence, it is necessary to briefly review some CuI properties in order to form hypothesis of the work.

CuI has predominant electron-hole conduction up to 200°C (Kumar, 2002). The *p-d* hybridized bonds are also weak and can be broken easily. Below 369°C, copper iodide exists as γ(zincblende)-CuI, as β(wurtzite)-CuI in the temperature range between 369°C and 407°C. Above 407°C, α-CuI (cubic) exists (Wakamura, 2002). The radius of Ag^+ ion is 1.26 Å and that of Cu^+ is 0.96 Å. This mismatch in cation size leads to the possibility of mixed mobile ion effect controlled ionic conductivity in AgI-CuI system (Kumar et.al, 2003).

1.2 Objectives of the present work

In the present work, pellets of AgI-CuI with different weight percent (wt %) will be prepared and characterized by impedance spectroscopy and X-ray diffraction. The pellets will be prepared by compressing the mixed raw materials at 400 atm pressure. The choice of 400 atm has been determined to be the sufficient pressure to form good pellets.

The mixture will then be sintered at $250\,^0$C for 5 hours. At this temperature γ-AgI will be transformed to α-AgI and Ag^+ ion will be the main conducting species. Hence the AgI-CuI mixture can exist as a mixed conductor. The sintering temperature of $250\,^0$C and sintering time of 5 hours are expected to make the mixture adhere to each other and to "lock" the superionic property of AgI. The conductivity was chosen as the determining parameter since it is the most important parameter which the mixtures must possess particularly for possible application in battery anodes. In summary, the objectives of this work are:

(a) To obtain the composition xCuI-(1-x)AgI, ($0.1 \le x \le 0.4$) that gives the highest room temperature conductivity (σ_{dc}) after the mixtures have been sintered at 250°C for 5 hours.

(b) To understand the conductivity mechanism in the mixed conductor.

(c) To determine the metastability of γ-AgI at room temperature by X-ray diffractogram (XRD).

1.3 Scope of present work

The present dissertation deals with the mixture of AgI-CuI. It is widely known that AgI is the best ion conducting material (Chandra, 2004).

In this work, CuI and AgI were added in different ratios. In the course of obtaining the highest conductivity, it has been found that addition of up to 10 wt % CuI could form a good free standing pellet. Doping with a higher weight percentage of CuI produced a mechanically weak pellet. The room temperature electrical conductivity of a pure AgI pellet heated at 250ºC was $2.00 \times 10^{-6}\,\mathrm{Scm}^{-1}$. Since the crystal lattice of AgI and CuI resemble each other and the atomic radii in the crystal phase are only slightly different, the materials form a complete mixture (Bosko and Rybicki, 2003).

After presenting an overview of AgI-CuI compounds that have been studied, in Chapter two, details of the experiments carried out to prepare the samples and the techniques used to characterize the pellets are presented in Chapter three. Chapter four deals with the electrical properties of the mixtures. Results on conductivity and the temperature relationship are discussed in this chapter. Chapter five reveals the dielectric studies of the mixtures. Chapter six represents the structural characterization of the AgI-CuI mixtures by x-ray diffraction, XRD. Chapter seven is a discussion chapter and chapter eight closes the thesis with relevant conclusions and suggestions for future work.