# SYNTHESIS AND CHARACTERIZATION OF SUPERIONIC CONDUCTING GLASSES (AgI)<sub>x</sub>(Ag<sub>2</sub>S)<sub>x</sub>(AgPO<sub>3</sub>)<sub>1-2x</sub>

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## ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SUPERIONIC CONDUCTING GLASSES  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$ . Samples of Superionic Conducting Glasses  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  with x = 0, 0.09,

(Agg)<sub>x</sub>(Ag<sub>2</sub>, S<sub>x</sub>(Agr O<sub>3</sub>)<sub>1,2x</sub>. Samples of superiodic Conducting Glasses (Agf)<sub>x</sub>(Ag<sub>2</sub>, S<sub>x</sub>(Agr O<sub>3</sub>)<sub>1,2x</sub> with x = 0, 0.09, 0.17, 0.23, 0.33, 0.37, 0.41 and 0.44 have been synthesized by rapid quenching method. Some physical properties including crystal structure, thermal behavior, ionic conductivity and transference number have been characterized and measured by using respectively, an X-Ray Diffractometer (XRD), a Differential Scanning Calorimetric (DSC), and an Impedance Spectroscopy (LCR-meter). The diffraction patterns of (AgI)<sub>x</sub>(Ag<sub>2</sub>S)<sub>x</sub>(AgPO<sub>3</sub>)<sub>1-2x</sub> for all compositions of x show only one broad peak indicating that all the samples are good glasses and have an amorphous structure. In general the glass transition temperature T<sub>g</sub> decreases from 398°C to 275°C as x increases. The results of ionic conductivity (s) measured at various frequencies and voltages show a significant increase as x increases. The maximum ionic conductivities are obtained for x=0.44 at different voltages s(0.5 volt)=1.66x10°2 S/cm, s(1 volt)=1.91x10°2 S/cm, s(1 volt)=1.35x10°3 S/cm. The transference number, t<sub>ion</sub> is approximate to 1 indicating that the conduction is essentially ionic in nature.

Key words : Superionic conducting glasses, rapid quenching, ionic conductivity, transport number

#### ABSTRAK

SINTESIS DAN KARAKTERISASI GELAS KONDUKTOR SUPERIONIK (AgI), (Ag,S),  $(AgPO_3)_{1,2*}$ . Cuplikan dari gelas konduktor superionik  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1,2*}$  dimana x = 0; 0,09; 0,17; 0,23; 0,33; 0,37; 0,41; 0,44 telah disintesis dengan metode pendinginan cepat. Beberapa sifat fisis termasuk struktur kristal, sifat termal, konduktivitas ionik dan bilangan transfer telah dikarakterisasi serta dihitung dengan menggunakan peralatan secara berturut-turut dengan X-Ray Diffractometer (XRD), Differential Scanning Calorimetry (DSC) dan Impedance Spectroscopy (LCR-meter). Pola difraksi sinar-x pada suhu ruang dari gelas  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$ untuk semua komposisi x menunjukkan adanya sebuah puncak lebar yang menandakan bahwa cuplikan yang diperoleh memiliki struktur amorf dan merupakan gelas berkualitas baik. Suhu transisi gelas,  $T_{o}$  terlihat menurun untuk semua komposisi x dengan sifat-sifat termal yang berbeda antara gelas dengan dopan maupun dengan gelas tanpa dopan. Secara umum suhu transisi gelas T, menurun dari 398°C ke 275°C dengan bertambahnya x. Hasil pengukuran sifat listrik yang diukur pada tegangan dan frekuensi yang berbeda menunjukkan adanya kenaikan nilai konduktivitas ionik (s) yang berarti dengan pertambahan x. Nilai konduktivitas ionik maksimum dicapai pada x=0,44 yaitu  $s(0,5 \text{ volt})=1,66x10^{-2} \text{ S/cm}, s(1 \text{ volt})=1,91x10^{-2} \text{ S/cm}, s(2 \text{ volt})=2,34x10^{-2} \text{ S/cm}, \text{ sedangkan pada gelas tanpa dopan$ AgPO, yaitu s(0,5 volt)=9,33x10<sup>-8</sup> S/cm, s(1 volt)=1,17x10<sup>-7</sup> S/cm, s(2 volt)=1,55x10<sup>-7</sup> S/cm. Perhitungan bilangan transfer menghasilkan nilai tion mendekati 1 yang menunjukkan bahwa konduksi yang terjadi merupakan konduksi ionik murni.

Kata kunci : Gelas konduktor superionik, pendinginan cepat, konduktivitas ionik, bilangan transfer

# **INTRODUCTION**

The highly ionic conductivity of superionic conducting materials has attracted much interest, because of their use in applications as solid electrolytes in new electrochemical devices such as solid state batteries, fuel cells, memory devices, display panels and sensor [1,2].

Among the superionic conducting materials, AgI crystalline is well known as a typical of superionic conductor

that has a highly ionic conductivity up to  $10^{-2}$  S/cm above its phase transition ( $\alpha$ -AgI)around 147 °C [3]. Since most applications work at ambient temperature, different kind of experiments have been carried out to decrease its transition temperature and to produce the new solid electrolyte materials with high ionic conductivity at room temperature by doped with other ionic salts, such as Ag<sub>2</sub>S, AgBr or AgCl [4-10].

#### Synthesis and Characterization of Superionic Conducting Glasses $(AgI)_{(Ag_{2}S)_{(2})}(AgPO_{3})_{(2)}(D. Sulistyanintyas)$

Superionic conducting glasses (SICG) is one of the solid conductors that has been mostly developed for the last decade since glassy materials have many advantages compared with crystalline counterparts, such as high superionic conductivity at ambient temperature, absence of grain boundaries, ease of thin film formation, strong glass-forming character, low melting point and wide range of composition that gives greater control of properties [3]. Normally, ionic mobilities in the glasses are higher than in the crystalline state because the disorder helps in the creation of conduction pathways, so it is natural to turn attention to ionic glasses [9].

The well known studied of SICG material is based on the silver phosphate (AgPO<sub>3</sub>) group because is not difficult to produce this glass. Pure AgPO<sub>3</sub> consists of tetrahedral anions PO4<sup>-</sup> and shows very low ionic conductivity around 10<sup>-7</sup> S/cm at room temperature. By adding doping salt AgI into glassy AgPO<sub>3</sub>, the ionic conductivity increases until 10<sup>-2</sup> S/cm [6]. Reverse Monte Carlo (RMC) modeling confirms that the increase of the conductivity because of the free volume expansion in the network structure by the presence of a 'salt' component [10].

In this research we have synthesized ternary system of AgI-Ag<sub>2</sub>S-AgPO<sub>3</sub> (ASIX), where the ratio of AgI : Ag<sub>2</sub>S = 1 : 1. These glasses consist of three components: a glass network former (Ag<sub>2</sub>O), metal oxides or metal sulfides acting as a glass network modifier (P<sub>2</sub>O<sub>3</sub>), and a doping salt (AgI and Ag<sub>2</sub>S). In this paper we present an extensive characterization of crystal structure, thermal behavior, ionic conductivity and transference number of the system (AgI)<sub>x</sub>(Ag<sub>2</sub>S)<sub>x</sub>(AgPO<sub>3</sub>)<sub>1-2x</sub> with x = 0, 0.09, 0.17, 0.23, 0.33, 0.37, 0.41 and 0.44 at ambient temperature. It is expected that, the conductivity of these superionic glasses will increase with increasing frequency and composition (x) due to increasing ionic mobility.

#### **EXPERIMENTAL METHOD**

#### **Sample Preparation**

Procedures for preparing  $(AgI)_x(Ag_2S)_x$  $(AgPO_3)_{1-2x}$  samples are divided into 2 steps of synthesizing. The first step is to produce glassy AgPO<sub>3</sub> and the second is to produce SICG  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$ . This step is described by the following chemical reaction:

(1) 
$$2NH_4H_2PO_4 \longrightarrow P_2O_5 + 2NH_x + 3H_2O$$
  
 $2AgNO_3 \longrightarrow Ag_2O + NO + NO_2 + O_2$   
 $P_2O_5 + Ag_2O \longrightarrow 2AgPO_3$ 

(2) 
$$_{x}\text{AgI} + _{x}\text{Ag}_{2}\text{S} + _{1-2x}\text{AgPO}_{3} \longrightarrow (\text{AgI})_{x}(\text{Ag}_{2}\text{S})_{x}(\text{AgPO}_{3})_{1-2x}$$

Based on the reference [4],  $(AgI)_x(Ag_2S)_x$ (AgPO<sub>3</sub>)<sub>1-2x</sub> are prepared with molar dopant concentrations of AgI and Ag<sub>2</sub>S 0, 9, 17, 23, 33, 37, 41 and 44% by mixing appropriate amounts of AgI (Alfa Aesar 99.9%), Ag<sub>2</sub>S (Alfa Aesar 99%), AgNO<sub>3</sub> (BDH 169.87), and  $NH_4H_2PO_4$  (Caledon 98%). The mixture was ground together in a mortar, then placed into a porcelain crucible and heated in a furnace.

Two kind of heating treatments have been performed in order to obtain the optimal results. The first group with molar dopant concentration of x = 0, 0.09, 0.17 and 0.23 were heated gradually (150 °C/h) to a temperature of 600 °C for glassy AgPO<sub>2</sub> and up to 850 °C for AgI-Ag<sub>2</sub>S-AgPO<sub>2</sub> mixtures. The melt was kept at this temperature for 2 hours before quenching into a cylindrical hole in a piece of teflon with liquid nitrogen environment. The second group with molar dopant concentration of x = 0.33, 0.37, 0.41 and 0.44 were heated gradually (100 °C/h) to a temperature up to 600 °C. The melt was kept at this temperature for 16 hours and heated again until temperature up to 800°C. The glass specimens were made by casting the melts into a cylindrical rod-brass of 25 mm diameter and 75 cm length and directly quenched into liquid nitrogen.

The colour of the glass varies from a clear, transparent-yellow, orange and dark red transparent glass for x = 0, 0.09, 0.17 and 0.23; while for x = 0.33, 0.37, 0.41 and 0.44 the colour of the samples are dark and opaque. All of the sample preparation and characterization have been performed at the Advanced Materials Laboratory, Technology Center For Nuclear Industrial Materials, BATAN.

# X-Ray Diffraction, Thermal and Electrical Properties Measurements

The structural, thermal and electrical properties of the series of glasses  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$ with x = 0, 0.09, 0.17, 0.23, 0.33, 0.37, 0.41 and 0.44 have been performed by using respectively an X-ray Diffraction, a Differential Scanning Calorimetry (DSC-7, Perkin Elmier) and a Hioki 3522-50 LCR meter at Advanced Materials Laboratory, Technology Center For Nuclear Industrial Materials, BATAN. The x-ray diffraction measurements were performed at room temperature within 2 hours with the wavelength  $\lambda = 1.54$  Å for the CuK $\alpha$ -radiation. For the DSC- measurements, the samples were heated from 50 °C to 500 °C with the heating rate of 10 °C/min and cooled to room at the same rate under helium temperature atmosphere. The glass transition  $T_{g}$ , and the heat flows were determined for all the samples. Powder samples for electrical conductivity measurements were pressed between conductive silver electrodes at 700 Kg/cm<sup>2</sup> into cylindrical pellets 1.5 cm in diameter and approximately 0.2 cm in thickness. Conductance data were recorded at varies frequency from 10<sup>-1</sup> Hz until 105 Hz and varies constant voltage (CV) of 0.1 volt, 0.5 volt, 1 volt and 2 volt.

## **RESULTS AND DISCUSSION**

#### **X-Ray Diffraction**

Figure 1 and Figure 2 show the diffraction patterns of  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  for x = 0, 0.09, 0.17, 0.23 and x = 0.33, 0.37, 0.41, 0.44, respectively. The patterns show only a broad peak indicating typical amorphous material or characteristic of glassy state. This result confirms the successful preparation of glass samples containing no crystallinity. The diffraction patterns for all compositions of x show a broad peak centered around  $2\theta \sim 30^\circ$ . This peak is related to the Bragg peak in the crystalline AgPO<sub>3</sub>, the parent material.



**Gambar 1.** X-Ray duffraction Patterns of  $(Agl)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  with x = 0, 0.09, 0.17 and 0.23 at room temperature.

The lower angle in Figure 2 is slightly higher than is shown in Figure 1 because of difference setting in instrument and small angle scattering. With increasing the doping salts concentration (x), the intensity of the broad peak becomes weaker because of less glass component in higher x composition.



**Figure 2.** X-ray diffraction patterns of  $(AgI)_x$  $(Ag_2S)_x(AgPO_3)_{1-2x}$  with x = 0.33, 0.37, 0.41 and 0.44 at room temperature.

## **Glass Transition**

The heat flow measurements measured by DSC give glass transition temperature,  $T_{g}$  for all compositions of x. This is appropriate with glassy state patterns as shown by X-ray diffraction. Figure 3 shows the composition dependence of the glass transition temperature  $T_{g}$  upon heating.



*Figure 3.* . The glass transition temperature of  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  as a function of mol %  $(AgI+Ag_2S)$  upon heating (closed circle). The closed square is the Tg obtained by E. Kartini et al. [5] and the closed triangle is the Tg obtained by Reau et al. [8].

As shown in Figure 3, the glass transition temperature,  $T_g$  decreases rapidly as the amount of dopant salt increases from x = 0.09 to 0.33, and it changes slowly until x = 0.44. A similar trend was also observed in ternary system of AgI-Ag<sub>2</sub>S-AgPO<sub>3</sub> glasses [5,8], but the glass transition  $T_g$  was much lower because of different quenching techniques and different sample geometries (hence different cooling rates). The decrease of  $T_g$  when (AgI+Ag<sub>2</sub>S) is increased is attributed to the expansion of phosphate chains that increase the free volume expansion, and reduce the ability to maintain phosphate links as temperature increases.

## **Ionic Conductivity**

Figure 4 shows conductivity value of  $AgPO_3$  glass at varies frequency from 0.1 Hz to 100 kHz, and varies constant voltage from 0.1 volt to 2 volt. Logarithm of conductivity in  $AgPO_3$  glass increases with increasing constant voltage value. A similar trend of conductivity pattern is also observed for other constant voltage values. At constant voltage CV = 0.1 volt, the conductivity increases in the range of log frequency from -1 to 0, followed by flat (plateau) between log frequency = 0 and 2, and then sharply increases at higher frequencies. The plateau area shows



Figure 4. AC-Conductivity of AgPO<sub>3</sub> glass at room temperature.

#### Synthesis and Characterization of Superionic Conducting Glasses $(AgI)_x(Ag_2S)_x(AgPO_3)_{1,2x}(D. Sulistyanintyas)$

that the conductivity does not depend on the frequency. This was known as frequency independent area or DC-conductivity. However, at higher frequency, for different voltages the conductivity sharply increases and overlaps when frequency was increased further indicating that the AC conductivity really depends on frequency.

The frequency dependences of the AC conductivity known as *Universal Frequency Response (UDR)* has been developed by Jonscher [11]. One of several models to analyze the AC-conductivity is described by the following equation:

$$\sigma \approx f^s \tag{1}$$

where  $\boldsymbol{\sigma}$  is conductivity value, s is an exponent power and f is frequency.

Based on the earlier results for either ionic crystalline or silica glass, there is one equation for superionic conducting glass [12]:

$$\sigma = \sigma_{\rm o} f^{\rm s} \tag{2}$$

By making them into Logarithm terms, the equation (2) becomes a linear equation:

 $Log \sigma = S Log f + Log \sigma_0$  (3)

where  $\text{Log } \sigma_0$  indicates the conductivity at frequency 1 Hz.

The equation (3) is used to fit the conductivity data by dividing into 3 frequency ranges, respectively at low frequency  $(S_1)$ , middle frequency  $(S_2)$  and high frequency  $(S_3)$ , in which each range has a specific pattern and a differential physical meaning. The ionic jump occurs at the low frequency range, DC-conductivity usually occurs at the middle frequency range and ionic vibration occurs at higher frequency range. The result of fitting parameters for low, middle and high frequency ranges notated by  $s_{01}$ ,  $s_{02}$  and  $s_{03}$ , respectively are shown in Table 1.

Table 1. Exponent Power and Conductivity of AgPO3 Glass.

CV	Sı	$S_2$	S3	Log	Log	Log	
[volt]	Logf [-1-1]Hz	Logf [1-2]Hz	Logf [2-5]Hz	σ <sub>01</sub> [S/cm]	σ <sub>02</sub> [S/cm]	σ <sub>0</sub> β [S/cm]	
0.1	0.05	0.02	022	-6.62	-6.62	-7.07	
05	0.03	0.02	022	-657	-659	-7.03	
1	0.03	0.03	02	-653	-653	-693	
2	0.03	0.02	0.18	-6.45	-6.46	-6.81	

The value of  $S_1$  and  $S_2$  at CV = 0.5 volt, 1 volt and 2 volt as shown in Table 1 are lower than  $S_3$ . It means that frequency dependent of the conductivity at low and middle frequency ranges are lower than for higher frequency. At higher frequency range, all values of  $S_3$  are almost same for all CV, indicating that conductivities become highly. Conductivities obtained at frequency 1 Hz varies from  $s(0.1 \text{ volt})=8.51 \times 10^{-8} \text{ S/cm}$ ,  $s(0.5 \text{ volt})=9.33 \times 10^{-8} \text{ S/cm}$ ,  $s(1 \text{ volt})=1.17 \times 10^{-7} \text{ S/cm}$  and  $s(2 \text{ volt})=1.55 \times 10^{-7} \text{ S/cm}$ . DC-conductivity value that observed by taking the plateau regime with the lowest value of S that close to 0 is

 $3.47 \times 10^{-7}$  S/cm. In this case the AgPO<sub>3</sub> glass does not show a superionic character.

Figure 5 shows the AC-conductivity of  $(AgI)_{0.23}(Ag_2S)_{0.23}(AgPO_3)_{0.54}$  at room temperature. Almost similar trend of conductivity results as for AgPO<sub>3</sub> glass in figure 4 was also observed for x=0.23, where the logarithm conductivity increases with increasing frequencies and the constant voltage value. At constant voltage, the DC-conductivity was observed in the range of log frequency from -1 to 1, and it increases slowly between log



frequency = 1 and 3, and then sharply increases at higher frequencies. The conductivity overlaps for different voltages at above log frequency = 4 and it is indicating that universality respond was achieved in this frequency.

Table 2 shows the result of fitting parameters for low, middle and high frequency ranges with x = 0.23 and notated by  $s_{01}$ ,  $s_{02}$  and  $s_{03}$ , respectively. As shown in Table 2 frequency dependent of the conductivity at low and middle frequency range are lower than for higher frequency. At higher frequency range, all values of  $S_3$  are almost same for all CV, indicating that conductivities become higher. Conductivities obtained at frequency 1 Hz varies from  $s(0.1volt) = 3.98x10^{-7}$  S/cm,  $s(0.5 volt) = 5.01x10^{-7}$  S/cm,  $s(1volt) = 7.94x10^{-6}$  S/cm and  $s(2volt)=1.02x10^{-6}$  S/c. DC-conductivity indicated by the plateau regime with the lowest value of S that close to 0 obtained at CV = 0.1 volt is  $2.51x10^{-7}$  S/cm. Although the ionic conductivity at x = 0.23 increased one order higher than AgPO<sub>3</sub> glass, in this case it does not show a superionic character.

Table 2. Exponent Power and Conductivity of  ${(AgI)}_{_{0.23}}$   ${(Ag_2S)}_{_{0.23}}{(AgPO_3)}_{_{0.54.}}$ 

CV	S1	$S_2$	S <sub>3</sub>	$Log \sigma_0$	$Log \sigma_{\mathbb{R}}$	$Log\sigma_{0}$	
[volt]	Logf	Logf	Logf	[S/cm]	[S/cm]	[Sam]	
	[-1-1]Hz	[14]Hz	z [4-5]Hz				
0.1	-0.05	0.02	04	-65	-66	-64	
05	-004	0.07	034	-64	-6.6	-63	
1	0.04	0.08	028	-63	-65	-5.1	
2	-0.05	0.08	03	-627	-64	-5.99	



*Figure 6.* AC-Conductivity of  $(AgI)_x(Ag_2S)_x (AgPO_3)_{1-2x}$  with x = 0, 0.09, 0.17 and 0.23.



with x = 0.33, 0.37, 0.41 and 0.44.

The ionic conductivity for other higher doped glasses system (x>0) compared with undoped glass (x=0) is shown in Figure 6 for the first group of samples (x=0,0.09,0.17 and 0.23) and Figure 7 for the second group of samples (x = 0.33, 0.37, 0.41 and 0.44). Both figures show that the logarithm conductivity as a function of logarithm frequency increases with increasing mol% dopant salts (AgI + Ag<sub>2</sub>S). The conductivity significantly increases at x <sup>3</sup> 0.33 and it reaches maximum at x = 0.44 where the solubility limit of this system is obtained [8,9]. As shown in Figure 7 and listed in Table 3, the ionic conductivities for x  $\geq 0.23$  are higher than  $10^{-3}$  S/cm indicating a superionic behavior. The highest conductivity of  $2.34 \times 10^{-2}$  S/cm was



**Figure 8.** The logarithm of the conductivity of  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1.2x}$ ] as a function of mol%  $(AgI+Ag_2S)$ .

obtained for  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  with x=0.44 at frequency 1 Hz and constant voltage 2 volt. This value is 5 order magnitudes higher than the ionic conductivity of the undoped glass AgPO<sub>3</sub>.

Figure 8 shows the logarithm of conductivity as function of mol% of dopant salt (x) and frequencies. For x < 0.44 the conductivity increases with increasing frequency, but it overlaps at higher concentration. It shows that the conductivity is frequency independent for x > 0.44. In general the conductivity increases significantly We can see here that heating treatment for 24 hours to the samples (second group of samples) give a better quality results than for heating treatment for 6 hours (first group of samples).

### The Ionic Transference Number

As one of the application of the superionic glass is to be used for a solid electrolyte in a rechargeable battery. [13]. One of the criteria of the solid electrolyte, that the conductivity must be from the ionic contribution and not the electronic contribution. When the solid electrolyte has more electronic conductivity, when it is combined with electrodes will be short circuited. Therefore, one of the requirement of the solid electrolyte is the transference number is close to unity. Transference number is calculated by definition that the transference number of a particle is the ratio of the conductivity due to it and the total conductivity [1]. Assume the total conductivity,  $\sigma_{r}$ , of a sample is due to ionic,  $\sigma_{ion}$ , and electronic,  $\sigma_{e}$ , so that conductivity contributions,

Table 3. AC-Conductivity of  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  at frequency 1 Hz.

	CV	x=0	x=0.09	x=0.17	x=023	x=033	x=037	x=041	x=0.44
	[volt]	[S/cm]							
	0.1	851x10 <sup>8</sup>	4.47x10 <sup>7</sup>	1.41x10 <sup>7</sup>	398x10 <sup>7</sup>	243x10 <sup>3</sup>	6.03x10 <sup>3</sup>	1.14x10 <sup>2</sup>	1.66x10 <sup>2</sup>
ľ	05	933x10 <sup>8</sup>	5.01x10 <sup>7</sup>	1.58x10 <sup>7</sup>	5.01x10 <sup>7</sup>	-	-	-	-
	1	1.17x10 <sup>7</sup>	1.02x10 <sup>7</sup>	5.01x10 <sup>7</sup>	794x10 <sup>6</sup>	2.82x10 <sup>3</sup>	8.13x10 <sup>3</sup>	1.45x10 <sup>2</sup>	1.91x10 <sup>2</sup>
	2	155x10 <sup>7</sup>	9.12x10 <sup>7</sup>	3.16x10 <sup>7</sup>	1.02x10 <sup>6</sup>	3.09x10 <sup>3</sup>	1.02x10 <sup>2</sup>	1.62x10 <sup>2</sup>	234x10 <sup>2</sup>

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$$\sigma s_{\rm T} = \sigma_{\rm ion} + \sigma_{\rm e} \qquad (4)$$

The fraction of the conductivity due to ions or electrons is given by,

$$t_{\rm ion} = \sigma_{\rm ion} / \sigma_{\rm T} \tag{5}$$

$$t_{\rm a} = \sigma_{\rm a} / \sigma_{\rm T} \tag{6}$$

where  $t_{ion}$  and  $t_{e}$  are referred to the ionic and electronic transference numbers.

In order to understand the ionic conductivities of this glassy system, it is important to measure the ionic transference number of these series of glasses  $(AgI)_{x}(Ag_{2}S)_{x}(AgPO_{3})_{1-2x}$  with x = 0.33, 0.37, 0.41 and 0.44. For this measurement we prepared in two kinds of pellets for each glass. At both sides of the first pellet were coated by silver powder. This arrangement allows both ionic and electronic conductivities are to be flown and the total conductivity  $\sigma_{_{\rm T}}$  is measured. On each side of the second pellet was coated by silver powder and carbon powder, respectively. The combination of carbon powder and silver powder respectively is used for blocking the ionic flow and sustain only electronic conduction. In this arrangement, the electronic contribution  $\sigma_{a}$  was measured. From both data, we can determine the ionic transference number of the superionic glass. Table 4 shows the measured data of ionic conductivity  $\sigma_{ion}$ , electronic conductivity  $\sigma_{e}$  and the ionic transference number  $t_{ion}$ . The results show that the conductivity of superionic glasses  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  are bout 87% to 97% (close to unity) indicating that the conductivity is essentially ionic due to the contribution of the silver ions [1, 8].

#### CONCLUSION

Superionic conducting glasses  $(AgI)_x(Ag_2S)_x(AgPO_3)_{1-2x}$  with x = 0; 0.09; 0.17; 0.23; 0.33; 0.41 and 0.44 have been successfully synthesized by rapid quenching method. The diffraction patterns for all compositions show amorphous structure. The addition of the doping salt  $(AgI + Ag_2S)$  into the  $AgPO_3$  glass induces effects, such as decreasing the glass transition and increasing the electrical conductivity. The transference number,  $t_{ion}$  approximate to 1 proves that the conduction is essentially ionic. It can be concluded here that this glass shows a superionic behavior and can be used as a solid electrolyte in a rechargeable battery.

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