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Jurnal Sains Materi Indonesia

Akreditasi LIPI No.: 395/D/2012
Tanggal 24 April 2012
ISSN: 1411-1098

CHARACTERISTIC OF $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ IONIC CONDUCTOR PREPARED BY MELT QUENCHING METHOD

Makhsun[1,2], T. Sakuma[1] and E. Kartini[3]

[1]*Institute of Applied Beam Science, Ibaraki University*
Mito 310-8512, Ibaraki, Japan
[2]*Center for Technology of Radiation Safety and Metrology, Indonesian National Nuclear Energy Agency*
Jakarta Selatan 12070, Indonesia
[3]*Center for Technology of Nuclear Industry Materials, Indonesian National Nuclear Energy Agency*
Kawasan Puspiptek, Serpong 15314, Tangerang Selatan, Indonesia
e-mail: makhsun@batan.go.id

Received: 17 June 2013 *Revised: 26 September 2013* *Accepted: 22 November 2013*

ABSTRACT

CHARACTERISTIC OF $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ IONIC CONDUCTOR PREPARED BY MELT QUENCHING METHOD. Characterization of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ ionic conductor prepared by melt quenching method have been carried out by using X-Ray Diffractometer (XRD), Differential Scanning Calorimeter (DSC) and Inductance (L) Capacitance (C) Resistance (R) meter. X-ray diffraction pattern shows that the compound has a mixture of amorphous and small amount of crystalline form with several Bragg peaks correspond to AgI. The DSC thermograph shows that an endothermic peak at temperature ~420 K matches with the phase transition of AgI which reinforces that a number of AgI are not dissolved in the material of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$. The obtained dc ionic conductivity is around ~10^{-2} S/cm at ambient temperature. The activation energy has two values, 0.20 eV below ~380 K and 0.15 eV above ~380 K.

Keywords: Solid electrolyte, Super-ionic glass, $AgPO_3$, AgI-LiI-$AgPO_3$

ABSTRAK

KARAKTERISTIK KONDUKTOR IONIK $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ DIPREPARASI MENGGUNAKAN METODA *MELT QUENCHING*. Telah dilakukan karakterisasi konduktor ionik $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ yang di preparasi menggunakan metode *melt quencing* dengan menggunakan *X-Ray Diffractometer* (*XRD*), *Differential Scanning Calorimeter* (*DSC*) dan *Inductance (L) Capacitance (C) Resistance* (*R*) *meter*. Data difraksi X-ray menunjukkan bahwa senyawa tersebut mempunyai pola campuran amorf dan kristal dengan beberapa puncak Bragg yang berasal dari AgI. Pola *thermo-graph DSC* juga menunjukkan sebuah puncak endotermik pada suhu ~420 K yang sesuai dengan transisi fasa AgI yang menguatkan dugaan bahwa AgI tidak larut di dalam $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ secara sempurna. Konduktivitas ionik DC pada suhu kamar adalah sekitar ~10^{-2} S/cm. Energy aktivasi mempunyai dua nilai, 0,20 eV di bawah suhu ~380 K dan 0,15 eV di atas suhu ~380 K.

Katakunci: Elektrolit padat, Gelas super-ionik, $AgPO_3$, AgI-LiI-$AgPO_3$

INTRODUCTION

Solid electrolyte with high conductivity is required to develop a solid battery. It is believed that in solid electrolyte the physical processes associated with the ion transport and decoupled of network structures. Solid electrolyte has more advantage than liquid electrolyte namely malleable and not leaking. Glassy solid electrolyte usually consists of a base oxide or chalcogenide-glass that is doped by super ionic conductivity materials. In many compounds the glass and additive components form alloy glass over wide range of compositions [1-4].

Many studies of the super-ionic glass conductivity properties of AgI-$AgPO_3$ system have been reported [5-7]. In order to find better conductivity, we combined AgI and LiI in the mixture of $(AgI)_x(LiI)_y(AgPO_3)_{1-x-y}$. However the study of AgI-LiI-$AgPO_3$ system has not been presented. In the result of our preliminary work, the variation composition of AgI and LiI in that stoichiometry system with x = 0.22, 0.33, 0.44 and y = 0.44, 0.33, 0.22 shows $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ has better conductivity. Therefore we expand the study in the characteristics of this mixture.

Glassy solid electrolytes have several advantages compared with single crystalline/ polycrystalline or ceramic solid electrolyte, such as high ionic conductivity; no grain boundary; wide composition and easy in preparation. A wide composition of glass formers has been used to form different types of local structures. Presence of two glass formers may also enhance the conductivity. Generally, the conductivity increases with the increasing of alkali oxides and halides. Figure 1 shows the Log σ versus $1000/T$ plots of some glassy solid electrolytes comparing to the electrolyte in this work [8-11]. The glassy solid electrolyte of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ in this work was synthesized by melt quenching method and investigated the structure, thermal and conductivity properties as well as estimated the activation energy.

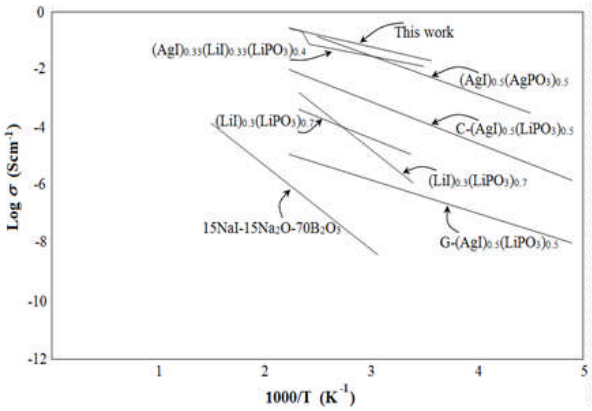

Figure 1. Log σ versus 1000/T plots of some glassy electrolytes

EXPERIMENTAL METHOD

$(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ was synthesized by melt-quenching method in two steps. The first step is synthesizing of $AgPO_3$ with an appropriate amounts of $AgNO_3$ (99.9% KANTO) and $NH_4H_2PO_4$ (99% KANTO) that were mixed and ground together in a porcelain crucible. The mixture was then gradually heated up to 600 ^oC for several hours and quenched into liquid nitrogen. The second step is synthesizing of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ with an appropriate amounts of $AgPO_3$ that was obtained in the first step, AgI (99.999% KOSO) and LiI (99.9% KOJUNDO) in the similar previous preparation, then the obtained sample of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ was milled by high speed milling machine for 20 hours. The activities have been carried out in both of Japan and Indonesia. In Japan the activities were done at the laboratory of applied beam science of Ibaraki University. In Indonesia those were done at Center for Technology of Nuclear Industrial Materials of National Nuclear Energy Agency.

The crystal structure, thermal property and conductivity of the samples were measured by X-ray diffractometer type RINT2000 of RIGAKU Corporation, DSC instrument type DSC-60 of SHIMADZU and LCR meter type HIOKI 3532-80 respectively which were installed at Applied Beam Science Laboratory of Ibaraki University, Japan. The conductivity measurement was done for the powder sample that was pressed between conductive silver electrodes at 70 MPa for about 30 minutes into cylindrical pellets of 1.3 cm in diameter. The electrical conductivity measurements were performed by impedance spectroscopy using two electrodes configuration Ag | sample | Ag. The entire cell was clamped with non-conductive plate and inserted into a special vacuum vessel. The temperature control of the cell was carried out by Ohkura EC5000 thermo-controller using a non-conductive heater wire and a T-type thermocouple attached close to the cell.

RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction patterns of $AgPO_3$, LiI, AgI and $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ at ambient temperature. The XRD patterns of $AgPO_3$ has only a broad peak centered at $2\theta \sim 30^o$ emphasizing its glassy nature. The diffraction patterns of LiI and AgI have crystal structures which are characterized by several Bragg peaks associated with a regular arrangement of their atoms. Whereas the diffraction patterns of the $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ shows the mixture of amorphous and the small of crystalline form with several Bragg peaks correspond to AgI which suggest that a number of AgI are not dissolved in the mixture of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$.

The thermal behavior of $LiPO_3$, LiI, AgI and $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ measured by DSC is shown in Figure 3. The AgI and the $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ thermographs show that they have a similar endothermic peak at temperature ~420 K. The undissolved AgI was also confirmed by DSC, where the thermal behavior spectrum of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ has an endothermic peak at ~420 K which is match with the phase transition of β to α-AgI. The LiI thermograph shows an endothermic peak at temperature ~400 K which is suspected as a phase transition of LiI.

The conductivity properties were investigated from temperatures of 280 to 530 K over frequency range of 20 to 10 kHz. The conductivity data were then collected and plotted in double logarithmic graphs of frequency versus conductivity. The center of the plateau area was used to calculate the dc conductivity. The dc conductivity increases with temperature and obeys the Arrhenius relation,

$$\sigma_{dc}T = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad \text{.....} \quad (1)$$

where:

σ_0 = The pre-exponential-factor of the dc conductivity
E_a = The activation energy for the dc conductivity
k = Boltzmann constant and
T = Absolute temperature

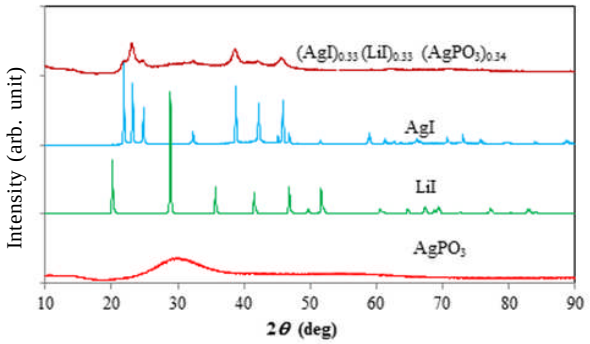

Figure 2. Observed X-ray diffraction patterns of $AgPO_3$, LiI, AgI and $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ at ambient temperature.

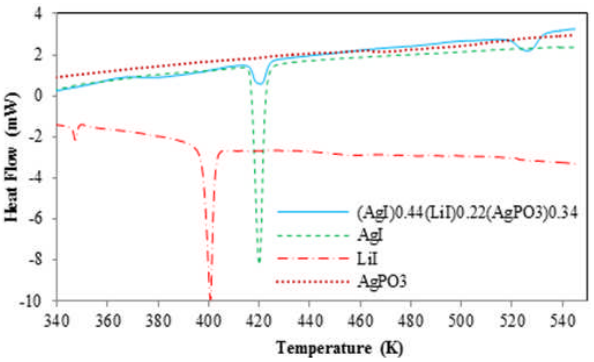

Figure 3. Differential scanning calorimetry pattern of $AgPO_3$, LiI, AgI and $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$

Temperature-dependent conductivity curves of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$, AgI and LiI were shown in Figure 4. The conductivity of AgI increases sharply at temperature above 420 K. There were significant differences of conductivity at temperature below 420 K and above 420 K. The lower conductivity is around 10^{-5} S/cm and increase sharply to around 10^{-1} S/cm at above 420 K. It occurs due to the structural property of AgI, where the β-AgI has transformed into the α-AgI phase.

The temperature-dependence conductivity curve of LiI shows that the conductivities of LiI slightly increase from room temperature until temperature of ~400 K and increase sharply at temperatures higher than 400 K. It is match with the endothermic peak of DSC data of

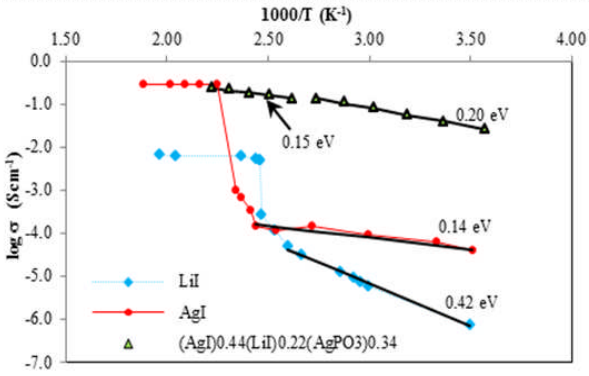

Figure 4. Reciprocal temperature dependence of the dc conductivity and calculation of the activation energy of $(AgI)_{0.44}(LiI)_{0.22}$ $(AgPO_3)_{0.34}$, AgI and LiI.

LiI as shown in Figure 3, where the temperature of 400 K was suspected as a phase transition of LiI. The conductivity of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ is around 10^{-2} S/cm at room temperature and increases slightly with increasing temperatures. The phase transition of AgI and LiI did not appear in the temperature-dependent conductivity curves of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ due to the highly conductivity of the $(AgI)_{0.44}(LiI)_{0.22}$ $(AgPO_3)_{0.34}$ at room temperature.

Super-ionic conductor $(AgI)_{044}(LiI)_{0.22}$ $(AgPO_3)_{0.34}$ prepared by melt quenching method has an irregular arrangement and disorder of atoms in the molecular structures. The high conductivity of $(AgI)_{0.44}(LiI)_{0.22}(AgPO_3)_{0.34}$ can be understood as implication of disordered arrangement of Ag and Li ions in the molecule structures where Ag or Li ions can easily jump to the vacant site [12-13]. As the temperature increases, the number of vacant sites becomes larger. At high temperature, the frequency of electric field applied across to the sample could make some distortion of local disorder [14].

By the Eq. (1), the activation energy, E_a for dc conductivity can be extracted, as shown by the solid line in Figure 4. The activation energy of $(AgI)_{0.44}(LiI)_{0.22}$ $(AgPO_3)_{0.34}$ has two values, 0.20 eV below ~380 K and 0.15 eV above ~380 K. The lower value is similar to the activation energy of AgI (0.14 eV), indicates that the conduction mechanisms is mainly due to silver ions, whereas the higher value is above the activation energy of AgI but below to that of LiI (0.42 eV), indicates that several lithium ion contribute in the conduction mechanisms. The low and high activation energy is determined by the different conduction mechanisms between lithium and silver ions. Earlier reports by P. Maas and P. Devendra *et al*. mentioned that when more than one type of mobile ions is present, the properties of glasses change to follow the dominant ion transport. This diffusivities change is shown in the changes of its activation energy [15-16].

CONCLUSIONS

Adding the AgI and LiI to the $AgPO_3$ by melt quenching method increased several magnitudes of the conductivity (~10^{-2} S/cm). The difference in the activation energy for temperature below and above of 380 K indicates that the different conduction mechanisms are operative between LiI and AgI. The changing occurs arround the temperature that was suspected as phase transition of LiI (400 K).

ACKNOWLEDGEMENTS

One of the authors (M.) wishes to express his thanks for financial support to the JSPS RONPAKU (Dissertation PhD) program. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Japan, Grant-in-Aid for Scientific Research (C), 24510117.

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