Solid State Ionics 179 (2008) 2137–2141

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Sodium ion motion in NaI–AgPO$_3$ glasses

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ARTICLE INFO

Article history:
Received 2 June 2008
Received in revised form 10 July 2008
Accepted 12 July 2008

Keywords:
Glass
Ionic conduction
Silver phosphate

ABSTRACT

Sodium ion motion in NaI–AgPO$_3$ glasses were investigated by electrical conductivity, NMR chemical shift measurements and X-ray diffraction. The fact that AgI crystal is precipitated at the composition x beyond the glass forming region of the $(\mathrm{NaI})_x(\mathrm{AgPO_3})_{1-x}$ system, and that the crystallization of NaPO$_3$ occurs by keeping the glass at a temperature near the glass transition suggests preferential formation of a chemical bond between silver and iodide ions rather than between sodium and iodide ions. Although the sodium ion conduction is more negligible than that of silver ions in a vitreous state, we show that the ionic conductivity of sodium increases above the glass transition temperature by the line width of the NMR chemical shift.

1. Introduction

It is well known that the ionic conductivity increases with AgI content in an AgI–AgPO$_3$ glass system [1,2]. Addition of NaI, KI [3] and PbI$_2$ [4] instead of AgI in AgPO$_3$ glass also leads to the ionic conduction enhancement. The ionic conductivity enhancement of KI–AgPO$_3$ glass was discussed in terms of the free volume by pressure dependence of ionic conductivity [5]. In a previous paper we reported the effect of iodide addition on the ionic conduction in AgPO$_3$ glass [6]. We verified that the addition of all the iodides examined leads to the enhancement of ionic conduction without exception and that the ionic conductivity increases with increasing valence n of M^{n+} ion from iodide MI$_n$ (M = Li, Na, K, Rb, Cs, Cd and Bi) or, in other words, iodide ion concentration. It is postulated that an ion exchange between Ag^+ and M^{n+} ions occurs, perhaps from MI$_n$ to $(\mathrm{AgI})_n$ in the glass. The conducting species is considered to be an Ag^+ ion. It is conceivable that the contribution of a multivalent ion such as Bi^{3+} from BiI$_3$ to total ionic conductivity is negligible. However, ionic motion of monovalent Na^+ that has a similar ionic radius to Ag^+ cannot be excluded. If so, the transference number of Ag^+ ion might deviate from unity. In fact the isothermal conductivity for the NaI–AgPO$_3$ glass system has a curvature in NaI concentration dependence as shown in Fig. 1. This result agrees well with that obtained by Doreau et al. [3]. It appears like an ionic conduction behavior in the mixed alkali effect. The variation from the linear change of isothermal conductivity is remarkable in the NaI–AgPO$_3$ system among MI–AgPO$_3$ systems examined in our previous study.

The purpose of the present investigation was to elucidate the effect of NaI addition to AgPO$_3$ glass on the sodium ion motion, cation configuration and ion-exchange. We investigated the crystallization process of glasses and Na and Ag NMR chemical shift, and reexamined NaI–AgPO$_3$ glasses by AC impedance spectroscopy.

2. Experimental procedure

A NaI–AgPO$_3$ glass system was prepared with the melt quenching method. The details of the preparation method are described in our previous paper [6]. The glass-forming region was examined by X-ray diffraction. The glass-forming region for the NaI–AgPO$_3$ system is 0 to 22 mol% of NaI contents. Glasses were also prepared using AgPO$_3$ glass and NaI as starting materials. Specimens obtained from both sample preparations were essentially the same, but the glass-forming region from the preparation by AgPO$_3$ glass and NaI was narrower than that from the previous method [6]. The impedance measurements were performed using a Hewlett-Packard Impedance Analyser 4284A between 60 Hz and 1 MHz ranging from room temperature up to the glass transition temperature. ^{23}Na and ^{109}Ag NMR chemical shifts were investigated by using a Bruker MSL-400 NMR spectrometer (9.39 T). NMR spectra of all samples were measured by a single $\pi/2$ pulse technique. ^{23}Na in NaCl and ^{109}Ag in AgNO$_3$ aqueous solution were used as references for the chemical shift.

3. Results and discussions

Fig. 2 shows the X-ray diffraction profiles for the quenched NaI–AgPO$_3$ system. As shown in the figure, no Bragg peaks were observed

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doi:10.1016/j.ssi.2008.07.013

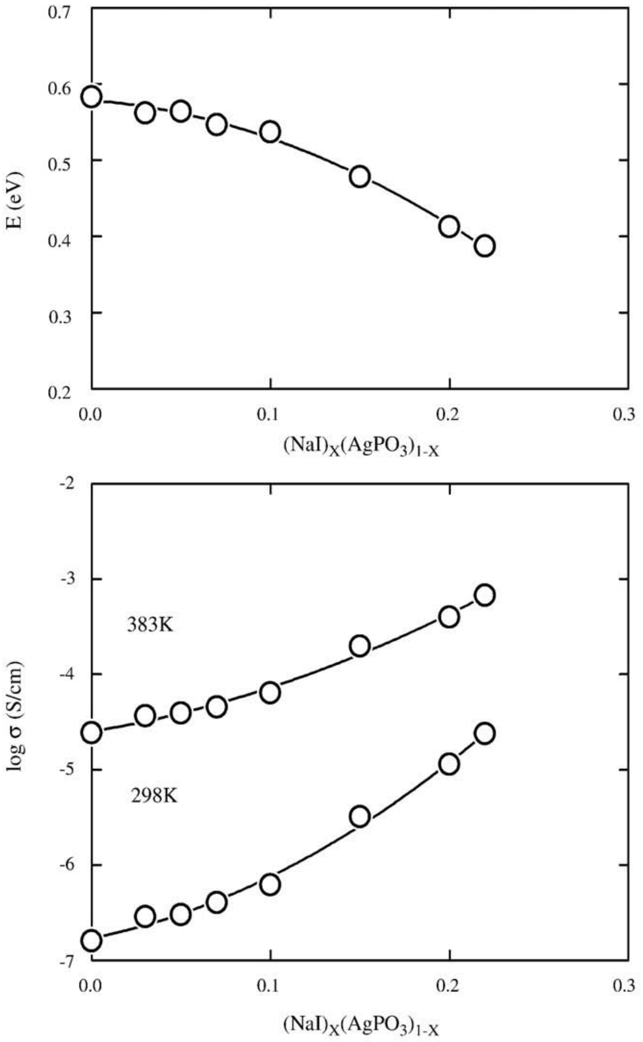

Fig. 1. Isothermal ionic conductivity and its activation energy for NaI–$AgPO_3$ glasses.

by X-ray diffraction profiles below 30 mol% of NaI, although the quenched samples became opaque when 25 mol% or more of NaI was added. The Bragg peaks identified as β-AgI were found in the sample containing 35 mol% of NaI. The melt separated into two parts, a less viscous and clear upper part and a viscous fluid in the bottom when the NaI concentration was more than 40 mol%. As shown in the figure, the quenched sample from the upper part of the melt mainly included β-AgI while the crystalline phase from the bottom was identified as a mixture of β-AgI and $NaPO_3$ by X-ray diffraction. These results suggest that the melt from the starting materials NaI, Ag_2O and P_2O_5 induced an exchange reaction between silver and sodium ions.

The crystallization process by thermal treatment for NaI 20 mol% glass is shown in Fig. 3. Crystallization occurs above 523 K for 9 h annealing. Annealing for only 2 h led to crystallization at 523 K whereas, the crystalline phase appeared following 27 h annealing at 493 K. It is clear that the Bragg peaks we obtained from various annealing conditions were the same and came from the $NaPO_3$ crystal. The quench of the supersaturated melt and the annealing process at an appropriate temperature within the glass-forming region accompanied the phase separation and resulted in crystallization of AgI and $NaPO_3$. Therefore the chemical formula of these glasses is formally presumed to be $(AgI)_x(NaPO_3)_x(AgPO_3)_{1-2x}$ rather than $(NaI)_x(AgPO_3)_{1-x}$ so that AgI and $NaPO_3$ crystals precipitate from the melt, because of the increase of AgI and $NaPO_3$ components. In fact, the AgI–$NaPO_3$ system could not form homogeneous glass but rather

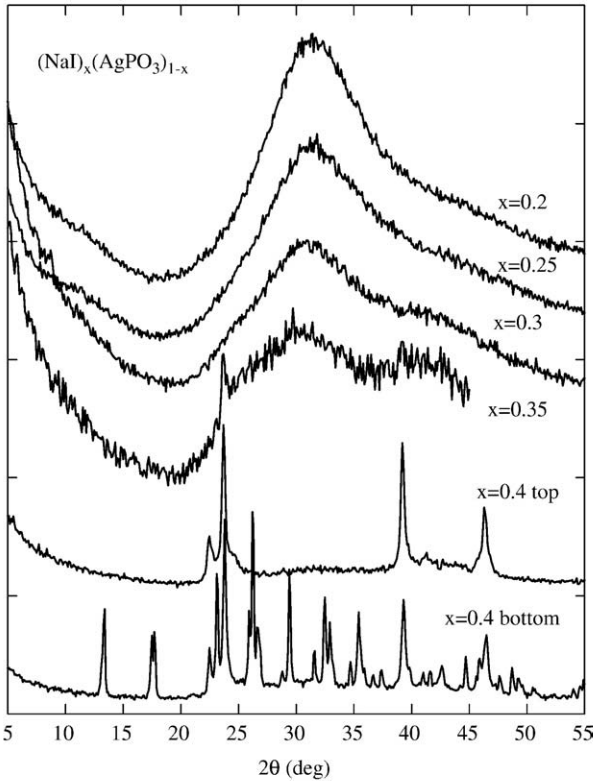

Fig. 2. X-ray diffraction profiles from $(NaI)_x(AgPO_3)_{1-x}$ system. “top” and “bottom” of $x=0.4$ means quenched samples obtained from the upper and lower parts of the melt, respectively.

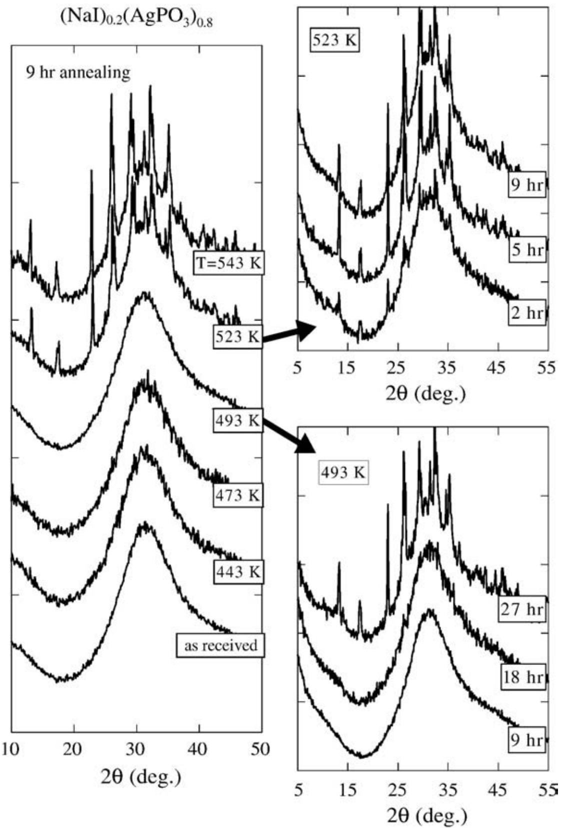

Fig. 3. X-ray diffraction profiles of $(NaI)_x(AgPO_3)_{1-x}$ system after annealing at several temperatures.