



# Study of nanostructure and ionic conductivity of $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$ glass ceramics used as cathode material for solid batteries



M.Y. Hassaan, S.M. Salem, M.G. Moustafa

Department of Physics, Faculty of Science, Al-Azhar University, Nasr City, 11884 Cairo, Egypt

## ARTICLE INFO

### Article history:

Received 8 November 2013

Received in revised form 23 February 2014

Available online 20 March 2014

### Keywords:

NASICON;

$\text{LiVNb}(\text{PO}_4)_3$ ;

Complex impedance;

Double heat treatment;

Ionic conductivity;

Solid batteries

## ABSTRACT

Glass sample with composition  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$  was prepared by quenched melt technique. Double heat treatments performed for different time intervals (12, 18, 24 and 30 h) to obtain glass ceramics with different nanoscale grain sizes. The glassy nature was confirmed from the glass transition temperature using differential thermal analysis (DTA) for the as quenched sample. In addition, the X-ray diffraction (XRD) patterns confirmed the glass nature for the as quenched sample. After heat treatment (HT) the structure of all samples was characterized by XRD. Ionic conductivity and impedance measurements of the derived glass ceramics were systematically investigated. It is observed that the electrical conductivity is enhanced by  $10^3$  times for the heat treated glass sample of 24 h, whereas with further increase of HT time up to 30 h, the conductivity started to decrease. Therefore, the phase observed in the 24 h HT is found more suitable to be used as a cathode material in solid batteries compared to its vitreous counterpart.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently there has been much interest in finding many new glass-based solid electrolytes with high ionic conductivity for applications in solid state batteries, fuel cells, sensor, etc. Several glasses have been shown to have high ionic conductivity and are referred to as superionic conducting glasses [1,2]. Among the glass formers, the phosphates are the best ones and have been widely investigated [3–6].

Moreover, phosphates with the general formula  $\text{A}_m\text{B}_n(\text{PO}_4)_3$  crystallize mainly in the NASICON-type (acronym for “Na Super Ionic Conductor”) structure, where A is an alkali or alkaline earth metal ion and B is one or more metal ions in tri, tetra or pentavalent state [7]. NASICON stands for a well-known family of solid electrolytes of sodium superionic conductor. This family of materials has attracted the attention of researchers looking for ion-selective electrodes or gas sensor devices, fuel cell, batteries, etc. [8,9]. NASICON-type materials have fascinated much awareness in recent past, as they facilitate a large scope for preparing number of materials with variation in their constituent metal ions and composition [10,11].

Several studies have been reported on lithium ion conducting materials with NASICON-type structure because of its high ion conductivity [12–22]. Spectroscopic studies on the structure of NASICON vanadium and niobium phosphate glasses with related structures have been performed by Rao et al. [12]. W. Zhang et al. [13] reported the synthesis and electrochemical properties of Nb containing NASICON-type phases with compositions  $\text{Li}_3\text{V}_2 - x\text{Nb}_x(\text{PO}_4)_3/\text{C}$  ( $x = 0, 0.05, 0.1, 0.15, 0.2, 0.5$ ). To date, there are several articles related to the investigation on substitution effects of divalent (e.g., Co [14] and Mg [15,16]), trivalent

(e.g., Fe [17], Al [18] and Cr [19,20]) and tetravalent (e.g., Ti [21] and Zr [22]) ions in vanadium sites in  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  systems.

In the present work the structure and electrical properties of NASICON-type phase with the composition  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$  is examined to check the enhancement of ionic conductivity of the glass ceramics.

## 2. Experimental

On one hand, glass sample of the composition  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$  was prepared by the quenched melt technique from reagent grade  $\text{Li}_2\text{CO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , respectively. The batch was mixed and milled in an agate mortar and then heated in alumina crucibles at 300 and 600 °C for 2 and 4 h, respectively, in order to decompose the  $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  completely with the emission of ammonia, carbon dioxide gases and water vapor. Then the mixture was cooled, reground and melted at 1200 °C in an alumina crucible for an hour to make sure the complete homogeneity in a preheated furnace. The melt was then poured and rapidly quenched between two copper plates; hammer and anvil. Sheets of opaque black glass samples of 1.5 mm thick were obtained.

On the other hand, glass–ceramics were prepared by heating the glass plates with a two-step heat treatment on the basis of DTA results. Firstly, the heat treatment was carried out for 2 h at the temperature between the glass transition temperature ( $T_g$ ) and the first crystallization temperature ( $T_{c1}$ ) to form enough crystal nuclei, and then heated up to the temperature above the  $T_{c1}$  to help the crystal growing. The second

step was performed at different periods (12–30 h) to establish the optimum heat treating time.

The regime of glassy specimen's crystallization was selected on the basis of DTA analysis using Shimadzu (DTA) instrument. The bulk densities were measured at room temperature using Archimedes method with carbon tetrachloride as the immersing liquid ( $1.593 \text{ g}\cdot\text{cm}^{-3}$ ). The error in the density measurement is within  $\pm 0.02 \text{ g}/\text{cm}^3$ . XRD measurements of the glass sample and their corresponding glass ceramics were performed using [Rigaku RINT 2100] with  $[\text{CuK}\alpha = 0.1541 \text{ nm}]$  radiation. The maximum current and voltage were 30 mA and 50 kV. FT-IR spectra were measured for all samples in range ( $400\text{--}4000 \text{ cm}^{-1}$ ) using computerized FT-IR spectrophotometer JASCO [FT-IR-300E] and using KBr as a reference material.

In addition, the DC electrical conductivity for glass sample and their corresponding glass ceramics were measured by means of the two-probe technique as well. Silver painted electrodes were pasted on the two faces of polished samples. A Picometer 760 was used to collect the DC data over the temperature range (300–600 K). The sample temperature was measured by a chromal–alumal type K thermocouple which is placed as close as possible to the sample. The error in the DC data is within  $\pm 0.02 \text{ S}/\text{m}$ . The complex impedance measurements were carried out in the frequency range 42 Hz to 5 MHz at 300 K by using HIOKI 1.03 LCR meter.

### 3. Results and discussion

#### 3.1. DTA

In order to identify the characteristic temperatures of the glass sample, thermal analysis was carried out by DTA. Fig. (1) shows the DTA curve of the glass sample of the composition  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$ . The glassy nature was confirmed by the observation of the glass transition temperature in DTA for the as quenched sample. The glass sample exhibit endothermic minimum which represent the glass transition temperature ( $T_g$ ) at around  $480 \text{ }^\circ\text{C}$ , the onset crystallization temperature ( $T_s$ ) at around  $584 \text{ }^\circ\text{C}$  and two successive exothermic peaks corresponding to crystallization temperature ( $T_{c1}, T_{c2}$ ) at around  $664$  and  $784 \text{ }^\circ\text{C}$ , respectively. The significant difference that exists between the glass transition,  $T_g$  and the onset of the crystallization temperature  $T_s$  accounts the thermal stability of the glass sample. The thermal stability ( $\Delta T$ ) parameter is usually employed to estimate the glass stability [23] which is defined by

$$\Delta T = T_s - T_g. \quad (1)$$

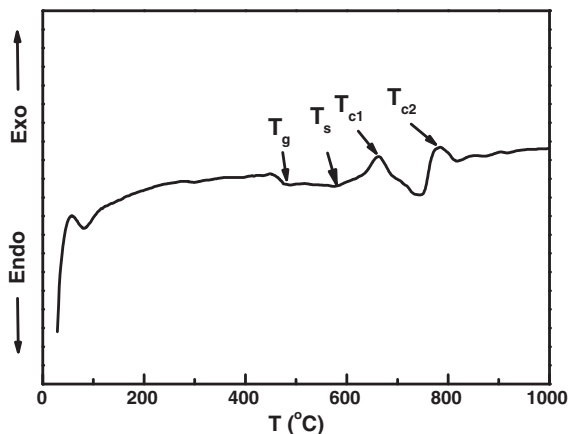


Fig. 1. DTA Curve of  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$  glass.

Table 1

Glass transition temperature ( $T_g$ ), onset crystallization temperature ( $T_s$ ), crystallization peak temperature ( $T_{c1}, T_{c2}$ ), and thermal stability ( $\Delta T, S$ ) for the glass sample.

Sample	$T_g$ ( $^\circ\text{C}$ ) $\pm 2$	$T_s$ ( $^\circ\text{C}$ ) $\pm 2$	$T_{c1}$ ( $^\circ\text{C}$ ) $\pm 2$	$T_{c2}$ ( $^\circ\text{C}$ ) $\pm 2$	$\Delta T$ $\pm 2$	S $\pm 2$
Glass	480	584	664	784	104	30.67

According to Saad and Poulain [24] the thermal stability parameter (S) which reflects the resistance for devitrification of glass and it is defined by

$$S = (T_c - T_s) (T_c - T_g) / T_g. \quad (2)$$

In the above equation ( $T_c - T_s$ ) is the rate of devitrification transformation of glassy phase. The value of  $\Delta T$  and S, calculated from Eqs. (1) and (2) respectively, are presented in Table (1). This reveals that the glass sample has high thermal stability and good glass forming ability.

#### 3.2. Density and molar volume

The density is a powerful tool to explore the changes in the structure of the materials. The density ( $\rho$ ) of the glass and glass ceramic samples is listed in Table (2). The molar volume  $V_m$  ( $\text{cm}^3/\text{mol}$ ) for all samples is calculated by using the formula;

$$V_m = M / \rho \quad (3)$$

where M and  $\rho$  are the molecular weight in ( $\text{g}/\text{mol}$ ) and the measured density ( $\text{g}/\text{cm}^3$ ), respectively. The molar volume for all samples are listed in Table (2). From Table (2), it is clear that the molar volume decreased gradually with increasing HT time.

It is observed that the density of the glass sample exhibit small value than that of the HT samples, where their density increased gradually with increasing HT time. The increase in density of glass ceramics may be due to the rearrangement of molecules causing structural changes in glass ceramics. That is to say, the structure is more closely packed in glass ceramic than that in glass [25]. This result is in good agreement with a reported work elsewhere [26].

#### 3.3. X-ray diffraction (XRD)

XRD analysis was employed to characterize their amorphous and/or crystalline nature of the glass and glass ceramic samples. Fig. (2) shows XRD patterns of  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{1.7}(\text{PO}_4)_3$  glass and glass ceramics. In the case of as quenched sample Fig. (2) shows broad humps around  $2\theta = 25$  with no indication of diffraction peaks. This confirms the amorphous nature of the glass sample. After HT number of peaks are observed and they are identified to be  $\text{LiVNb}(\text{PO}_4)_3$  (JCPDS card 51–1660) with a structure close to monoclinic and  $\text{LiV}(\text{P}_2\text{O}_7)$  crystals (JCPDS card 85–2381) with a structure close to monoclinic also. It is clear that the major phase is  $\text{LiVNb}(\text{PO}_4)_3$ , which indicates the formation of NASICON compound after HT process. In order to distinguish between

Table 2

Density ( $\rho$ ), molar volume ( $V_m$ ), normal site concentration (N), distance between two stable sites ( $\lambda$ ), and pre-exponential factor ( $\sigma_0$ ) for glass and its glass ceramic samples.

Sample	$\rho$ ( $\text{g}/\text{cm}^3$ ) $\pm 0.02$	$V_m$ ( $\text{cm}^3/\text{mol}$ )	N ( $\times 10^{21} \text{ cm}^{-3}$ ) $\pm 0.01$	$\lambda$ (nm) $\pm 0.01$	$\sigma_0$ ( $\times 10^3 \text{ s m}^{-1}$ )
Glass	2.62	72.18	8.34	0.493	0.252
HT 12 h	2.69	70.30	8.57	0.489	0.139
HT 18 h	2.78	68.02	8.85	0.483	0.428
HT 24 h	2.82	67.06	8.98	0.481	0.992
HT 30 h	2.89	65.43	9.20	0.477	0.156

Download English Version:

<https://daneshyari.com/en/article/1481038>

Download Persian Version:

<https://daneshyari.com/article/1481038>

[Daneshyari.com](https://daneshyari.com)