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Acid catalyst concentration effect on structure and ion relaxation studies of Li_2O–P_2O_5–B_2O_3–SiO_2 glasses synthesized by sol–gel process

P. Muralidharan, M. Venkateswarlu [1], N. Satyanarayana *

Raman School of Physics, Pondicherry University, Pondicherry 605 014, India

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Abstract

Lithium phosphoborosilicate (LPBS) glasses were synthesized through the sol–gel process by varying nitric acid concentrations as a catalyst. The sol–gel process was monitored through XRD and DSC to optimize the LPBS glass forming treatment. Characterization of LPBS glasses was conducted using XRD, FTIR and DSC techniques. Impedance measurements were carried out at different temperatures on LPBS samples synthesized by sol–gel process with various nitric acid concentrations and impedance data were analyzed using Boukamp equivalent circuit software. The conductivity of LPBS samples was calculated from analyzed impedance data and it was found that sample synthesized with 2.5 N nitric acid concentration showed the high conductivity $\sigma = 2.28(\pm 0.02) \times 10^{-7}\ \mathrm{S\,cm^{-1}}$ at 443 K. Activation energy (E_a) is obtained from Arrhenius plots of dc conductivity and it is found to be 0.39 (±0.02) eV for the high conductance sample. Ac conductivity data were analyzed using Jonscher's power law (JPL) and the power law exponent (s) exhibits a low s value for high conducting LPBS sample and a non-linear behavior with temperature. The electric modulus data were fitted with Kohlraush–William–Watts (KWW) stretched exponential function and modulus formalism is used to study the ionic relaxation behavior at different temperatures in LPBS glasses synthesized with varying nitric acid concentrations.

1. Introduction

Solid electrolytes possessing high ionic conductivity are being investigated because of their applicability in the fabrication of various types of solid state ionic devices, like solid state batteries, sensor, electrochromic display etc. [1,2]. Recently, it was found that glassy solid electrolytes show better ionic conductivity than their respective crystalline counter parts and hence amorphous/glassy solid electrolytes are synthesized by varying formers and modifier to former compositions to obtain better ionic conducting materials. Solid electrolytes are synthesized in different single/polycrystalline as well as in amorphous/glassy forms like bulk, powder, sheet, thin films, fibers etc., by various experimental techniques such as melt quench, thermal evaporation, sol–gel process etc. [1–3]. The sol–gel process has many advantages over other methods because using this method tailor made compounds can be synthesized at low temperature with highly homogenous and desired structured [3–8]. Sol–gel process involves importance of many variable parameters such as, precursor chemicals, solvent, water, catalysts, temperature, drying, etc., in the reaction to obtain better solid electrolytes.

* Corresponding author. Tel.: +91 413 26559919x404; fax: +91 413 2655265/655211.
E-mail address: nallanis2000@yahoo.com (N. Satyanarayana).
[1] Present address: Department of Chemical Engineering, NTUST, Taipei, Taiwan.

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Catalysts play an important role in the sol–gel process during hydrolysis and polycondensation reactions and thus, result in determining reaction mechanism and the structure of the polycondensation product. Mineral acids and ammonia are most generally used catalysts in sol–gel processes and other catalysts are acetic acid, KOH, RNH_2 ($R = C_nH_{2n+1}$), KF, HF, titanium alkoxides, vanadium alkoxides, etc. [4]. In sol–gel process, acid catalyst promotes the hydrolysis reaction as an electrophilic by the following reaction [4].

$$(RO)_3SiOR + H_3O^+ \rightarrow (RO)_3SiOH + H^+ + HOR \quad (1)$$

$$H^+ + H_2O \rightarrow H_3O^+$$

$$(RO)_3SiOH + (RO)_3SiOH \rightarrow (RO)_3Si\text{–}O\text{–}Si(RO)_3 + H_2O \quad (2)$$

In sol–gel processes, acid catalysts serve to protonate negatively charged alkoxide groups (OR) and enhance the reaction kinetics by rapid completion of hydrolysis (OH). The relative ease of protonation of different alkoxide (OR) ligands (OR = OCH_3, OC_2H_5, OC_3H_7 etc.) can influence the condensation pathway to form linear chain or branched polymer chain. Also, the acid-catalyzed condensation preferentially direct reaction towards terminal ends of the chain rather than middle of the chains that result the formation of less branched polymer chain [4]. The gelation process is greatly influenced by the catalyst and hence, property of the material depends on formation of gel, as in case of ionic conducting materials more open channels structure is required to obtain high conductivity. The above advantages of acid as a catalyst focused our attention in present investigation to prepare lithium phosphoborosilicate glasses through sol–gel process on varying the concentration of nitric acid. Structural characterization through XRD, FTIR and DSC, ionic transport and its relaxation behavior were studied at different temperatures by impedance measurement, ac conductivity power law and modulus formalism on LPBS glasses synthesized with various concentrations of nitric acid as a catalyst.

2. Experiment

2.1. Sol–gel synthesis

Xerogels of LPBS were prepared by the sol–gel process using analar grade tetraethylorthosilicate ($Si(C_2H_5O)_4$), boric acid, orthophosphoric acid and lithium nitrate. The precursors were mixed according to their molecular weight percentage to prepare LPBS samples with various nitric acid concentration, 0.01, 0.1, 1.0, 2.5 and 5.0 N, as a catalyst using the following chemical compositional formula

$$20\%Li_2O - 80\%[10\%P_2O_5 + 90\%(20\%B_2O_3 + 80\%SiO_2)](LPBS) \quad (3)$$

The above composition of LPBS glass was fixed from the earlier studies [9]. Fig. 1 shows synthesis process in the form of a flow chart indicating various stages involved like sol, sol to gel and gel to xerogel formation on maintaining the temperature at 338 K. Xerogels were densified around 678 K at a heating rate of 1 K min^{-1} to form glass. Thus prepared glasses were stored in a vacuum desiccator over anhydrous indicating silica for further investigation.

The X-ray diffraction spectra were recorded for LPBS samples heat treated at different temperatures using a Rigaku miniflex diffractometer with Cu-K_α radiation of wavelength $\lambda = 1.5418$ Å between 70° and 3°, 2θ values, at a scan rate of 2° per minute. FTIR spectra were recorded for LPBS glasses using a Shimadzu FTIR-8300/8700, in range 4000–400 cm^{-1}, 40 scan. The FTIR samples were prepared using KBr pellets at room temperature. DSC curves were recorded using a Mettler Toledo Stare System, Module DSC 821e/500/575/414183/5278, under nitrogen atmosphere at a heating rate of 1 K min^{-1} for the fine powdered LPBS samples placed in an aluminum pan covered with a lid and pressed using the micro pelletizer to form a thin button pellet.

LPBS glassy samples were ground to fine powders with a small amount of isopropanol used as a binding solvent and pelletized under a pressure of 3000 kg cm^{-2} to form pellets of dimension 10 mm dia. and 2–2.5 mm thickness using a Spectra lab pelletizer. The LPBS pellets were coated with graphite paste, graphite suspension in isopropanol, as an electrode on either surface in the form:

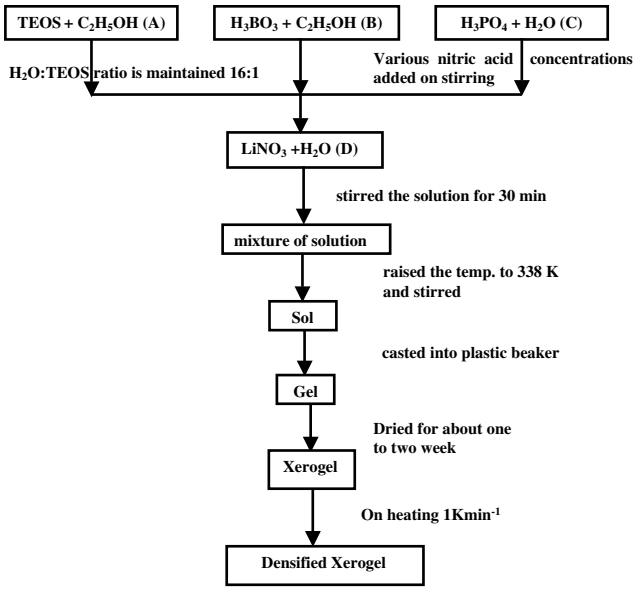

Fig. 1. The flow chart for LPBS sample preparation by sol–gel process.