

Short communication

Characterization of PEG: LiClO₄ + SrBi₄Ti₄O₁₅ nanocomposite polymer electrolytes for lithium secondary batteries

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Abstract

Nanocomposite polymer electrolytes based on poly (ethylene) glycol (PEG) complexed with lithium perchlorate (LiClO₄) salt and SrBi₄Ti₄O₁₅ (SBT), a ferroelectric ceramic material, as filler are prepared and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential thermal analysis (DTA) and impedance spectroscopic techniques. An enhancement in conductivity is observed with the addition of SBT as filler to the PEG: LiClO₄ salt complex. The PEG: 1.0(LiClO₄) + 12.5 SBT (ball-milled) polymer nanocomposite exhibits maximum room temperature conductivity of $2.4320 \times 10^{-6} \text{ S cm}^{-1}$.

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1. Introduction

In order to develop all-solid-state lithium battery, many research efforts are underway to synthesize true solid polymer lithium electrolytes. In the past few decades, solid polymer electrolytes (SPEs) have gained considerable attention due to their wide range of applications in batteries with high specific energies, sensors and fuel cells [1,2]. Compared with systems based on liquid or gel electrolytes, SPEs are much more stable and have long life characteristics. Poly (ethylene) oxide (PEO) has been a popular choice of polymer matrix for lithium ion conductors [3–8]. Unfortunately, high lithium ionic conductivity has not been attained at ambient temperature with the pristine PEO matrix and, moreover, PEO exhibits very poor mechanical properties. In order to improve the mechanical properties and ionic conductivity of polymer electrolytes, different approaches have been proposed, such as the preparation of polymer blends [9], composite polymer electrolytes by the addition of ceramic inorganic fillers [10–19], organic plasticizers [20], and organically modified ceramics as polymer electrolytes [21]. The

variation of ionic conductivity with salt fraction is an interesting but difficult challenge for both experimental and theoretical research. Most studies have been on high molecular weight [e.g., PEO, with mol wt. $\sim 10^6$] polymers complexed with alkali metal salts. Little attention has been paid to the somewhat low molecular weight polymers. Bearing these facts in mind, we have prepared poly (ethylene) glycol (PEG) of molecular weight 4000, complexed with LiClO₄ salt.

Nanocomposite polymer electrolytes based on polymer containing layered silicates, and polymer containing inorganic ferroelectric nanoparticles, such as BaTiO₃, and Ba_{1-x}Sr_xTiO₃ offer various advantages but the ambient temperature ionic conductivity is not sufficiently high for any practical application [22,23]. The dielectric constant of the dispersoid is also expected to change the ion transport in the polymer electrolyte since its presence modifies the local electric field distribution inside the polymeric composite ionic matrix. In the presence of dispersed ferroelectric particles of dielectric constant higher than that of the basic polymer electrolyte ionic matrix, the electric field lines become modified such that the field is higher near the interface of the polymer due to the high dielectric constant of dispersoid. In the present work, nanocomposite polymer electrolytes based on PEG complexed with LiClO₄ salt and SrBi₄Ti₄O₁₅, a ferro-

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electric ceramic material as filler, have been prepared. These nanocomposite polymer electrolytes have been characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, differential thermal analysis (DTA) and impedance spectroscopic techniques.

2. Experimental

2.1. Ferroelectric fillers and polymer nanocomposite preparation

2.1.1. Preparation of nano sized $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBT) ferroelectric fillers

The ferroelectric ceramic material SBT was prepared by a conventional solid-state reaction [24]. SrCO_3 , Bi_2O_3 and TiO_2 were used as starting raw materials. Stoichiometric quantities of all the raw materials were taken and ground for 4 h. The calcination of all oxides and carbonates was performed at temperatures between 600 and 1050 °C for 6–16 h. The calcination occurs in three steps. The first stage, below 640 °C, is characterized by the reaction of Bi_2O_3 with (i) SrCO_3 to form a solid solution of $\text{SrO-Bi}_2\text{O}_3$ and (ii) part of the TiO_2 to form $\text{Bi}_{12}\text{TiO}_{20}$. During the second stage, above 640 °C and below 800 °C, some of the $\text{SrO-Bi}_2\text{O}_3$ solid solution and $\text{Bi}_{12}\text{TiO}_{20}$ are reduced and SrTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are formed. In the last stage, i.e., above 950 °C, SrTiO_3 and the remaining $\text{SrO-Bi}_2\text{O}_3$ solid solution react with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to give $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$. The as-prepared $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ was ground in a ball mill (Retsch M400) for 15 h using agate balls to reduce the particle size.

2.1.2. Preparation of PEG: $\text{LiClO}_4 + \text{SrBi}_4\text{Ti}_4\text{O}_{15}$ polymer nanocomposites

PEG of molecular weight 4000 (Aldrich) was used without further purification. LiClO_4 (Fluka) was dried under vacuum in an oven overnight at 110–120 °C to remove the moisture prior use. Both ball-milled and as-prepared $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ferroelectric filler were dried at a temperature of 200 °C for 6 h prior to the use. The PEG: x (LiClO_4) samples (where the mole ratio, $x=0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5$ and 2) and PEG: $1.0(\text{LiClO}_4) + y\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ($y=5, 7.5, 10, 12.5$ and 15 wt.% of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$) composites were prepared by a standard solution cast method using methanol (AR grade) as the common solvent [25]. The complex solution was magnetically stirred for 4 h at room temperature, followed by heating to ~50 °C to evaporate the remaining solvent. The viscous solution was then poured into glass dishes and allowed to dry under vacuum overnight at room temperature. The samples were stored in a vacuum desiccator prior to experiment.

2.2. Materials characterization

2.2.1. X-Ray powder diffraction

The XRD pattern for PEG, PEG: $1.0(\text{LiClO}_4)$ and PEG: $1.0(\text{LiClO}_4) + y\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (both as-prepared and ball-

milled with $y=5, 7.5, 10, 12.5$ and 15) samples were recorded using a Philips XPERT diffractometer at a scan rate of 10° per min.

2.2.2. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectra were recorded over the range 500–4000 cm^{-1} by means of a ABB Bomem MB104 spectrometer by pelletizing the samples (diameter = 8 mm, thickness = 2 mm) with KBr (AR grade) using a hydraulic press at 4–5 tons. The FTIR spectra of PEG, PEG: 1.0LiClO_4 and PEG: $1.0(\text{LiClO}_4) + y\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (both as-prepared and ball-milled with $y=5, 7.5, 10, 12.5$ and 15) were recorded.

2.2.3. Differential thermal analysis (DTA)

The DTA thermograms for PEG, PEG: 1.0LiClO_4 and PEG: $1.0(\text{LiClO}_4) + y\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (ball-milled with $y=5, 7.5, 10, 12.5$ and 15) PEG were recorded with a Linseis DTA instrument in the temperature range from 30 to 120 °C at a heating rate of 5 °C per min. The amount of each sample ~10 to 12 mg.

2.2.4. Impedance spectroscopy

Impedance measurements were carried out using a HP 4284A impedance analyzer in the frequency range 20 to 10⁶ Hz with a specially-designed spring press that was fitted with gold plated electrodes and exerted a small pressure on the sample to ensure good contact. The samples were pressed into pellets using Teflon moulds. The experimental spectra were analysed (with an equivalent of) Boukamp's software package [26].

3. Results and discussion

3.1. X-ray diffraction studies

The XRD pattern for PEG shown in Fig. 1(a) displays a prominent peak at a 2θ value of 24°. The pattern for PEG: $1.0(\text{LiClO}_4)$ is shown in Fig. 1(b). The absence of diffraction peaks corresponding to LiClO_4 in Fig. 1(b) reveals that LiClO_4 solvates well in the PEG matrix. The observed decrease in intensity and broadening of the prominent diffraction peak of PEG in Fig. 1(b) suggests decrease in the degree of crystallinity due to intercalated lithium ions. In addition to the decrease in intensity and broadening of the prominent diffraction peaks PEG also exhibits a lower angle shift with the addition of LiClO_4 salt. These observations indicate that the intercalated lithium swells crystalline PEG and hence causes modifications in the long range order.

The XRD pattern of the as-prepared $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ sample is shown in Fig. 1(c). The position and intensity of the peaks matches well with the reported powder diffraction pattern [27] and this confirms the formation of a single phase of SBT. This compound belongs to the Aurivillius family of oxides and exhibit ferroelectric to paraelectric transition at elevated

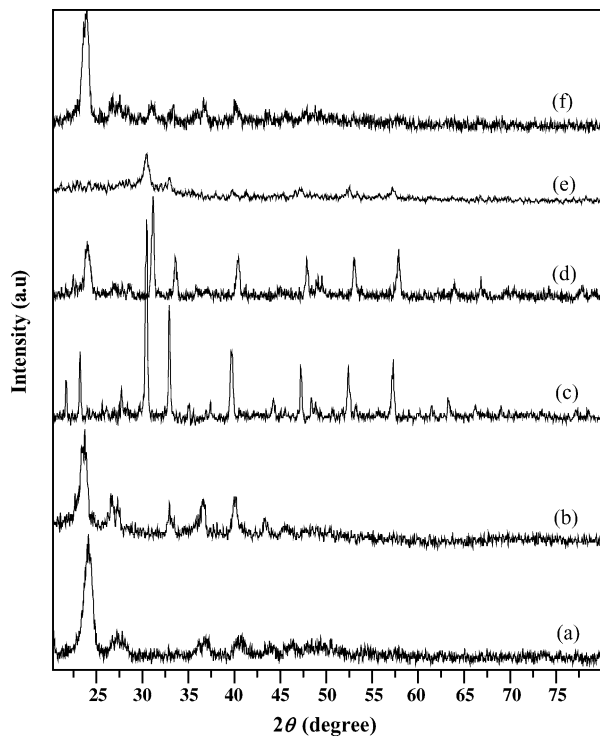


Fig. 1. X-ray diffraction patterns of: (a) PEG; (b) PEG: 1.0(LiClO₄); (c) SBT (as-prepared); (d) PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared); (e) SBT (ball-milled); (f) PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled).

temperature. The crystal structure of SrBi₄Ti₄O₁₅ at room temperature is an orthorhombic system with the space group A2₁am. The refined lattice parameters for the recorded XRD pattern of the as-prepared SrBi₄Ti₄O₁₅ matches well with JCPDS card number 43-0973.

The XRD pattern of PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared) given in Fig. 1(d), shows the reappearance of the dominant diffraction peaks of SrBi₄Ti₄O₁₅ at higher angles with the little reduction in intensity. The XRD pattern of SBT after 15 h of ball milling is presented in Fig. 1(e). The broadening of the dominant diffraction peak of the ball-milled sample of SBT confirms reduction in particle size. The particle size of the as-prepared and ball-milled samples were calculated from the full width half maximum intensity (FWHM) of the characteristic peaks of the SrBi₄Ti₄O₁₅ using the Scherrer formula. The particle size is ~100 and ~20 nm for the as-prepared and ball-milled samples of SBT, respectively.

The XRD pattern of PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled) is shown as Fig. 1(f). As for PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared), the XRD pattern of PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled) also indicates little reduction in the intensity of the characteristic diffraction peaks of SBT. The characteristic diffraction peaks of SBT are not as strong in Fig. 1(e) and revealed the more amorphous nature compared with PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared).

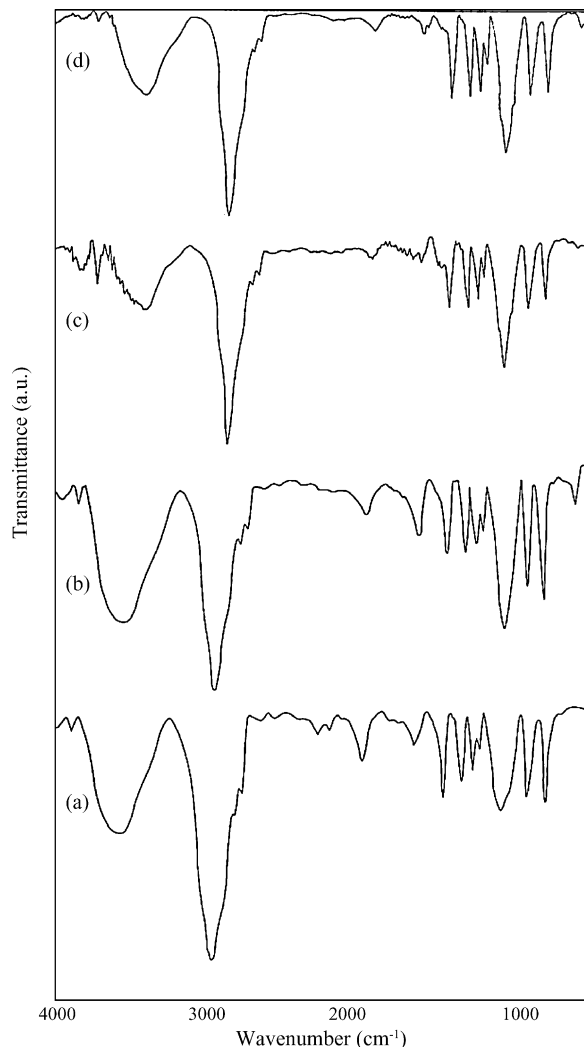


Fig. 2. FTIR spectra for: (a) PEG; (b) PEG: 1.0(LiClO₄); (c) PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared); (d) PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled).

3.2. FTIR spectroscopic studies

The FTIR spectra of PEG, PEG: 1.0(LiClO₄), PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (as-prepared), and PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled) are shown in Fig. 2(a)–(d), respectively. Changes such as reduction in the band width and increase in the intensity of the C–O–C stretching band of PEG at 1111 cm⁻¹ and reduction in the intensity of the bands observed at 1969, 2166 and 2238 cm⁻¹ of PEG in Fig. 2(a) with the addition of LiClO₄ Fig. 2(b) clearly confirms the formation of polymer salt complex. The C–O–C stretching (~1110 cm⁻¹), CH₂ rocking (~950 cm⁻¹) and CH₂ wagging (1150–1350 cm⁻¹) modes of PEG are usually employed as an indicator of the Li⁺-PEG polymer interaction. Addition of both as-prepared and ball-milled ferroelectric SBT fillers in the PEG: 1.0(LiClO₄) polymer salt complex produce a reduction in the band width and an increase in intensity of the C–O–C stretching mode of PEG, as shown

in Fig. 2(c) and (d), respectively. This indicates some minor structural changes in the PEG: 1.0(LiClO₄) polymer salt complex on the addition of SBT ceramic fillers.

3.3. Differential thermal analysis (DTA)

The DTA was performed to observe the changes in the melting temperature (T_m) of the prepared samples. Generally, a low glass transition temperature (T_g) indicates the existence of a greater amount of amorphous phase. The melting temperature of the polymer is also related to T_g , as the T_g decreases, there is a slight decrease in the T_m . The DTA thermograms in Fig. 3(a) and (b) clearly indicate a slight shift in the melting endothermic peak T_m , towards a lower value with the LiClO₄ salt content in PEG. In addition to the reduction in T_m , the melting endotherms also exhibit broadening. The DTA thermograms of PEG: 1.0(LiClO₄) + y SrBi₄Ti₄O₁₅ (ball-milled samples with $y=5, 7.5, 10, 12.5$ and 15) given in Fig. 3(c)–(g) indicated no appreciable change in T_m . With increase in the concentration of the filler however, there is an increase in the width of the endotherms. Decrease in the crystallinity is clearly noted from the broad endotherm obtained for the samples containing high filler content. Hence, it is found that the addition of filler inhibits crystallization of the polymer from amorphous to crystalline phase. As the wt.% of filler, increases there is an increase in the intramolecular attraction, and transient cross-links are formed in the polymer matrix. Accordingly, there is a decrease in the flexibility

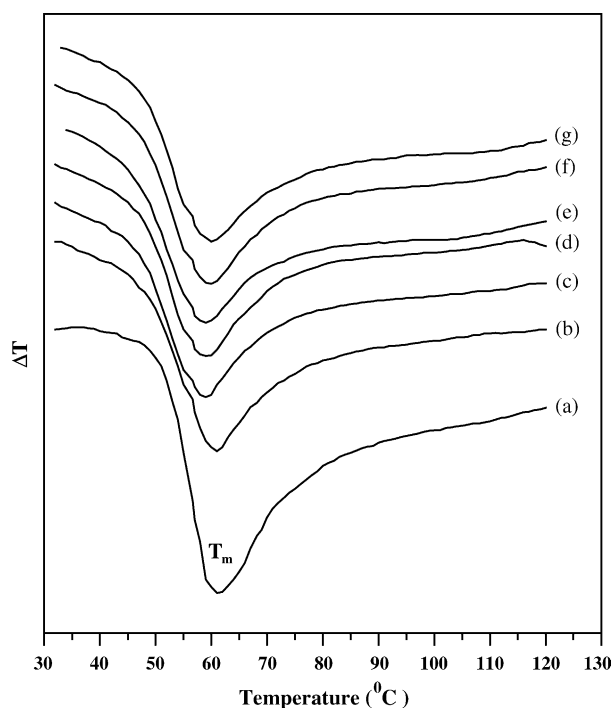


Fig. 3. DTA thermograms of: (a) PEG; (b) PEG: 1.0(LiClO₄) and PEG: 1.0(LiClO₄) + y SrBi₄Ti₄O₁₅ (ball-milled) with (c) $y=5$, (d) $y=7.5$, (e) $y=10$, (f) $y=12.5$ and (g) $y=15$ wt.%.

of the polymer matrix and hence the mechanical stability of the polymer matrix increases.

3.4. Conductivity measurements

The ionic conductivity of the prepared electrolyte samples was derived from the complex impedance plot. The bulk resistance of the electrolyte is the intercept of the arc on the real axis and was determined using the frequency response analyser software. A typical impedance spectroscopy plot (Cole–Cole; Z'' versus Z' plotted in linear scale) for the PEG: 1.0(LiClO₄) sample measured at room temperature is given in the inset of Fig. 4. The conductivity isotherms for the PEG: x LiClO₄ samples ($x=0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5$ and 2) measured at room temperature are shown in Fig. 4. PEG 4000 has a low ionic conductivity ($\sim 2.2797 \times 10^{-8}$ S cm⁻¹) at room temperature. The ionic conductivity for the polymer–salt complexes increases with the salt concentration and reaches a peak value of 3.2933×10^{-7} S cm⁻¹ for a mole ratio of $x=1$, where x is the ratio of ether oxygens to Li, and then decreases with further increase in salt concentration. The initial increase in conductivity in the low concentration system is due to the increase in charge carriers as the number of free cations increases, and also to a decrease in the degree of crystallinity (X_c) with increase in salt concentration. The further decrease in conductivity at higher salt concentration could be due to an increase in the ion–ion interaction that hinders the motion of Li⁺ ions and stiffening of polymer chains as a result of cross links formed by cations and salt precipitation [2].

The SBT ceramic fillers were added to the PEG: 1.0(LiClO₄) polymer salt complex as it exhibits the

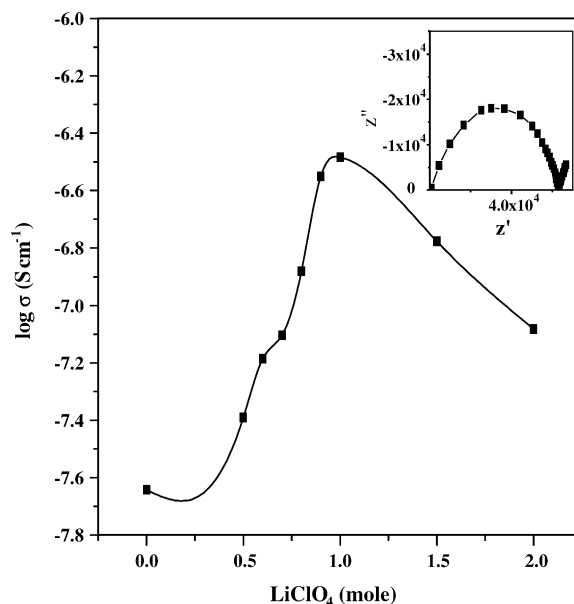


Fig. 4. Ionic conductivity vs. LiClO₄ mole ratio of PEG: x (LiClO₄) samples (where, $x=0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5$ and 2); the Cole–Cole plot for PEG: 1.0(LiClO₄) is shown in the inset.

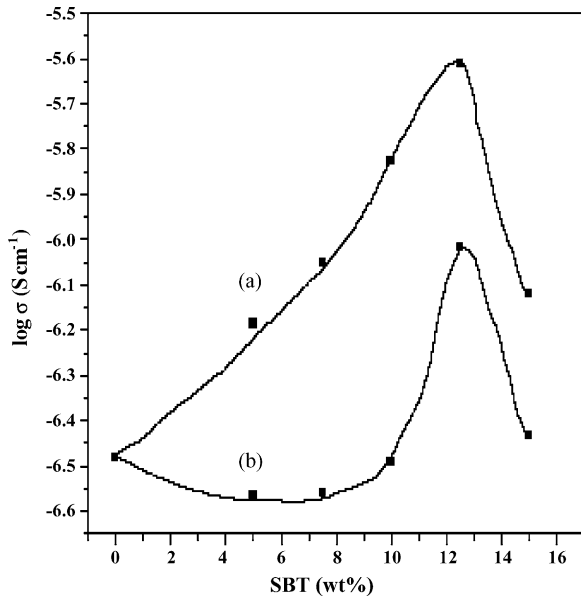


Fig. 5. Ionic conductivity vs. SBT wt.% of: (a) PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (ball-milled), y = 5, 7.5, 10, 12.5, 15; (b) PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (as-prepared), y = 5, 7.5, 10, 12.5, 15.

highest conductivity. Conductivity data for PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (ball-milled with y = 5, 7.5, 10, 12.5 and 15) are displayed in Fig. 5(a). The conductivity increases with increase in wt.% SBT and exhibits a maximum room temperature conductivity of $2.4320 \times 10^{-6} \text{ S cm}^{-1}$ for PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled). Further addition of SBT results in a decrease in conductivity. The variation of conductivity of PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (as-prepared with y = 5, 7.5, 10, 12.5 and 15) is displayed in Fig. 5(b). The conductivity decreases initially with addition of SBT and then increases with the increase in wt.% SBT and displays a maximum room temperature conductivity of $9.5764 \times 10^{-7} \text{ S cm}^{-1}$, and then decreases (Table 1). In general, the PEG: 1.0(LiClO₄) + y(SBT) (as-prepared with y = 5, 7.5, 10, 12.5 and 15) polymer composite had a lesser conductivity than the PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (ball-milled with y = 5, 7.5, 10, 12.5 and 15) nanocomposites. The increase in a order of maximum conductivity value for the ball-milled samples when compared to the as-prepared

Table 1

Ionic conductivity of PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅

Filler concentration, y (wt.%)	Conductivity σ_{RT} (S cm ⁻¹)	
	As-prepared	Ball-milled
5	2.72151×10^{-7}	6.5099×10^{-7}
7.5	2.74391×10^{-7}	8.83046×10^{-7}
10	3.21665×10^{-7}	1.49263×10^{-6}
12.5	9.5764×10^{-7}	2.4320×10^{-6}
15	3.6876×10^{-7}	7.5499×10^{-7}

Both as-prepared and ball-milled with y = 5, 7.5, 10, 12.5 and 15.

sample is due to the effect of ball-milling on the fillers, which decreases the crystallinity of the fillers thus increasing the conductivity of the polymer samples.

4. Conclusions

The PEG: (LiClO₄) + SrBi₄Ti₄O₁₅ polymer nanocomposite electrolytes have been prepared with various mole ratios of LiClO₄ and different wt.% of SrBi₄Ti₄O₁₅ ferroelectric ceramic filler (both ball-milled and as-prepared) by a standard solvent-casting technique. This process results in homogenous samples. Conductivity measurements reveal that for PEG: x(LiClO₄) samples (where, x = 0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5 and 2 mole ratio of LiClO₄ to PEG) PEG: 1.0(LiClO₄) exhibits a maximum room temperature conductivity of $\sim 10^{-7} \text{ S cm}^{-1}$. The addition of ferroelectric fillers in PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (y = 5, 7.5, 10, 12.5 and 15) gives an enhancement of conductivity. The conductivity of PEG: 1.0(LiClO₄) + y SrBi₄Ti₄O₁₅ (ball-milled) samples show an increase in conductivity with addition of SBT (ball-milled) ceramic fillers and reaches a maximum conductivity value but the conductivity decreases with the higher filler content. A maximum room temperature conductivity of $2.4320 \times 10^{-6} \text{ S cm}^{-1}$ is observed for PEG: 1.0(LiClO₄) + 12.5 SrBi₄Ti₄O₁₅ (ball-milled) polymer nanocomposite. The conductivities for PEG: 1.0(LiClO₄) + ySrBi₄Ti₄O₁₅ (as-prepared) polymer nanocomposites are always lower than those of PEG: 1.0(LiClO₄) + y(SBT) (ball-milled) polymer nanocomposites.

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