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Optical and electronic characterization of P(VDF-TrFE)/La₂O₃ nanocomposite films

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Abstract

In this study, the pristine and La₂O₃-embedded poly vinylidene fluoride/trifluoroethylene [P(VDF-TrFE)] thick films were fabricated via solution casting technique and optical and dielectric properties investigated. P(VDF-TrFE)] is a potential candidate for electromechanical and acoustic sensors, actuators, energy harvesting and nonvolatile memory applications. Infrared vibrational spectroscopy (Raman) revealed enhancement of β -phase in the composite films. At room temperature, in the ultraviolet-visible range both the absorption and the optical bandgap (E_g) increased in nanocomposite films. Dielectric properties for nanocomposite films have been measured as a function of frequency in the range of 1 kHz to 1 MHz and temperature in the range from 20 °C to 80 °C. The dielectric results show increase in real and imaginary part of dielectric constant with temperature and volume fraction of La₂O₃ nanoparticles dispersed. The ac and dc activation energies were found to decrease with increase in volume fraction of nanoparticles following Arrhenius relationship. Thus, showing the conduction was thermally activated.

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1. Introduction

Ferroelectric materials are named as ‘smart materials’. Their large piezoelectric compliances, pyroelectric coefficients, dielectric susceptibilities and electro-optic properties make them very attractive for many technological applications such as high energy density capacitors, pyroelectric thermal imaging devices, gate insulators in transistors, electro-optic light valves, thin-film memory elements, multi-ferroic transducers, energy harvesters, etc [1].

Polyvinylidene fluoride (PVDF) is an ideal candidate for important devices such as pyroelectric sensors, electro-optical and electromechanical devices and transducers due to its relatively reasonable high piezo-, pyro- and ferroelectric and optical properties. A fascinating property of this polymer is its polymorphism, where it can exist in several crystalline structures: orthorhombic α -, β -, and δ -phases and monoclinic γ -phase. From technological point-of-view, β -phase is more important and favorable in a scientific community due to its large spontaneous polarization [2]. Upon mechanical drawing, α -phase will transform into β -phase which exhibits a net dipole moment as all C-F dipoles are aligned in the same direction. Thus, are useful in functional devices such as pyro-sensors and imaging devices. In order to enhance the functional properties of PVDF, ferroelectric ceramic powder such as BaTiO₃, PbTiO₃, PbZrTiO₃, and MWCNT are incorporated in the polymer matrix to form 0-3 type composites [3-4]. These ferroelectric composites create a new structure which combines high functional activity of ceramics and high mechanical strength of polymer.

However, these composites are microscopically isotropic and exhibit no directional functionality. Thus requires, a very high poling field to reorient the dipoles towards the direction of applied electric field to make them functional. On the other hand, many efforts have been devoted to enhance the evolution of β -phase by incorporation of clay nanoparticles into PVDF matrix. The increase in β -phase is due to the spatial confinement of the polymer chains imposed by the nanoparticles and amplified by charge-dipole interfacial interactions. Furthermore, experimental results have shown that embedding nano-fillers into polymer leads to significant modifications of the breakdown field, charge transport, and charge distribution of the dielectric materials due to interface effects.

Earlier, it has been reported that the inclusion of non-ferroelectric ceramic TiO₂ in the PVDF matrix contributed to enhancement of pyroelectric activity in the resulting composite [5]. A semiconductor, ZnO, nanoparticles were also imbedded into PVDF matrix. Reports have also shown that addition of nanorods, nano-flowers and walnut shaped ZnO enhanced the optical and structural properties of PVDF and making them attractive for use in pyroelectric detection of electromagnetic radiation including optical parametric devices [6].

Poly vinylidene fluoride/trifluoroethylene [P(VDF-TrFE)] copolymers have also attracted considerable interest as potential polymer candidates for integrated optics applications because of their good electro-optic and nonlinear optical properties. In this paper, preliminary results of investigation of optical and electronic properties of P(VDF-TrFE)/La₂O₃ nanocomposite thick films are presented. The objectives were to see the effects of interfaces of nanocomposites by using UV-Vis and Infrared vibrational and dielectric spectroscopic measurements. The technology and protocol used in the fabrication of La₂O₃ nano-particles are also described.

2. Experimental Procedures

2.1. La₂O₃ nanoparticles fabrication

Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and is very easy to control the particle

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size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and is less hazardous. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors [7]. In this study, the hydrothermal synthesis of La_2O_3 nanoparticles was utilized. Lanthanum Oxide nano particles were prepared using transparent aqueous solutions of 0.1 M Lanthanum chloride ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$) and 0.1 M potassium hydroxide (KOH) as precursors (no surfactants were used). Potassium hydroxide solution was added dropwise to 20 ml of the transparent 0.1 M lanthanum chloride solution with stirring until the solution was turned translucent colloidal form keeping the pH at 10.00. After vigorous stirring for 1 h, the colloidal solution was transferred into a Teflon lined stainless steel autoclave of 100 cc capacity, then sealed and maintained at 200 °C for 8 hrs. A schematic of the Teflon lined stainless steel autoclave utilized for the fabrication of nanoparticles is illustrated in Fig. 1. Subsequently, the resultant pale white solid product (La_2O_3 nanoparticles) was centrifuged, washed with distilled water and ethanol to remove the ions possibly remaining in and finally dried at 300 °C in air. The chemical reaction takes place as follows:

Fig. 1. Stainless steel autoclave.

2.2. Materials, preparation and devices

The 0-3 connectivity nano-composite films were fabricated using the solution cast technique. The first step is the preparation of P(VDF-TrFE) [70/30 mol%] solution (Pmix) by dissolving it in a suitable amount in methyl-ethyl-ketone (MEK) at around 60 °C. A requisite amount of La_2O_3 nanoparticles were then added to Pmix to form a mixture (nPMix), and this mixture is ultrasonically agitated for several hours to break-up the agglomerates and disperse La_2O_3 uniformly in the Pmix. The obtained nPMix composite solution is kept in a suitable container (flat petri dish) for the solvent to evaporate. The films so obtained were annealed for 2-3 hours in the air, at 110 °C for the present case. A full-face silver electrode was deposited on the film to form M-I-M device then the film was cut into 10 mm x 10 mm sized element for testing. The electroded samples were poled at 100 °C with about 50 kV/cm voltages for 2 hours.

Fig. 2. A summary of composite film fabrication process.

After the poling process, the samples were short circuited and annealed at 50 °C for 2 hours. The flowchart of the fabrications processes is depicted in Fig. 2. The thickness of the obtained films was approximately 0.32 mm. Composite films filled with volume fractions (Φ) of 0%, 2%, 5%, and 8% of La_2O_3 nanoparticles were fabricated. The volume fraction was calculated as follows:

$$\Phi(\text{vol.}\%) = \frac{m^p \rho^r}{m^p \rho^r + m^r \rho^p} \times 100 \quad (1)$$

where m^p and m^r are the mass of P(VDF-TrFE) and La_2O_3 , respectively. ρ^p and ρ^r are the density of P(VDF-TrFE) and La_2O_3 , respectively.

2.3. Dielectric study

The samples were poled under an applied electric field of 5 kV/cm. Both the real and imaginary parts of the dielectric constant (ϵ' , ϵ'') for a poled samples at a frequency values of 100 Hz, 1 kHz, 10 kHz, and 100 kHz were measured as a function of temperature, range from 20 °C to 80°C using QuadTech 1620 LCR meter. The samples were heated to approximately 80°C and the temperature dependence of the dielectric data (capacitance and $\tan\delta$) was measured at a rate of 3°C/min. Values of dielectric constant (ϵ') and dielectric loss (ϵ'') were then calculated for each value of the capacitance. The dielectric constant, dielectric loss ϵ'' , and ac conductivity (σ_{ac}) are determined by the following relation:

$$\epsilon' = \frac{Ct}{\epsilon_0 A} \quad (2)$$

$$\epsilon'' = \epsilon' \cdot \tan \delta \quad (3)$$

$$\sigma_{ac} = \epsilon_0 \omega \epsilon'' \quad (4)$$

where C is the parallel capacitance of samples at signal frequency of 1 kHz. $\tan\delta$ is the electric loss tangent, A is the electrode area, t is the thickness of sample, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum, ω is the angular frequency of the applied signal [8]. According to the Arrhenius law the ac conductivity is strongly dependent on temperature and the ac activation energy (E_{ac}) can be obtained from:

$$\sigma_{ac} = \sigma_0 \exp(-E_{ac} / kT) \quad (5)$$

where σ_0 is a pre-exponential term and represents the high temperature limit of conductivity, while k and T are the Boltzmann constant and the absolute temperature, respectively

Finally, according to Drude model, the dc conductivity can be obtained using Ohm's law as:

$$\sigma_{dc} = It / VA \quad (6)$$

where I is the current in Ampere and V is the applied voltage over the sample in volt. Two terminal measurements were performed for dc current measurement utilizing Kethley model 6517 electrometer.

2.4. Optical Characterizations

FTIR spectral analysis in the range from 500-4000 cm^{-1} was carried out by Thermo Nicolet FTIR spectrometer with a resolution of 8 cm^{-1} using Globar (ETC Everglo) as source of IR Radiation. FT-Raman spectra were recorded with a portable Horiba scientific Raman micro spectrometer in the range from 250-2500 cm^{-1} using 785nm laser source.

The UV spectra were taken by Hitachi model U-2900 double beam spectrophotometer. According to Tauc's power law, the optical energy band gap (E_g) in UV region can be obtained from:

$$\alpha = \frac{\beta}{h\nu} (h\nu - E_g)^n \quad (7)$$

where n is an empirical index equal to $1/2$ for a quantum mechanically allowed direct transition and 2 for indirect transition during optical absorption and β is a constant with α as absorption coefficient.

3.1. Infrared spectroscopic characterizations

Infrared vibrational studies were carried out to investigate the formation of β -phase before and after the incorporation of La_2O_3 nanoparticles in P(VDF-TrFE) matrix. The characteristic vibration bands were analyzed with in the wavelength range of $500\text{--}4000\text{ cm}^{-1}$. Figure 3 shows the FTIR spectra of pure P(VDF-TrFE) and 2%, 5%, and 8% vol. of La_2O_3 nano particles dispersed composite films.

Fig. 3. FTIR spectra of pure P(VDF-TrFE) and 2%, 5%, and 8% vol. of La_2O_3 nanocomposite films.

Fig. 4. Raman spectra of pure P(VDF-TrFE) and 2%, 5%, and 8% vol. of La_2O_3 nanocomposite films.

It is evident from Fig. 3 that peaks intensity of various peaks could not be differentiated with increasing nano-powder content. However, It can be elucidated from Fig. 4 that there is gradual changes in intensity of Raman spectra at 831 nm when the La_2O_3 content in the films increases. It is worth mentioning and note-worthy result that Raman bands at 831 cm^{-1} shows the presence of β -phase in P(VDF-TrFE) film [10]. The intensity of this band increases with increase of La_2O_3 nano-particle content in the films. This variation in Raman intensities observed in the spectra at different compositions can be attributed to the formation of more β -phase in the nanocomposites. It proves that the incorporation of La_2O_3 can enhance the β -phase

without the need of high poling voltage which is a promising indicator of the increased ferroelectric property of the material. Thus, it is attractive nanocomposites for optical, ferroelectric and pyroelectric applications.

3. Results and Discussion

3.2. UV-Vis spectroscopic measurements

The UV spectra of nanocomposite films with wavelength of incident light are shown in Fig. 5. The absorbance of nanocomposite films increases with increase of concentration of dispersed nanoparticles in P(VDF-TrFE) film. The increase of absorbance is attributed to the presence of nanoparticles which absorb the incident light [9].

The optical band gap of nanocomposite films was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 6 and extrapolating the linear portion near the onset of absorption edge to energy axis. The optical energy gap increases with increase in concentration of nanoparticles dispersed in P(VDF-TrFE) films as is evident from Fig. 6. From the Fig. 6, the values obtained of optical band gap are tabulated in table 1.

Fig. 5. UV-Vis optical absorption spectra of P(VDF-TrFE) and La_2O_3 -P(VDF-TrFE) nanocomposite films.

Fig. 6. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for P(VDF-TrFE) and La_2O_3 -P(VDF-TrFE) nanocomposite films.

Table 1

Optical energy band gap (E_g) of P(VDF-TrFE) and La_2O_3 - P(VDF-TrFE) nanocomposite films.

Sample	E_g (eV)
P(VDF-TrFE)	2.65
+2 vol.% La_2O_3	2.80
+5 vol.% La_2O_3	3.08
+8 vol.% La_2O_3	3.15

3.3. Dielectric Measurements

Fig. 7 (a-b) shows the dielectric constants ϵ' and the dielectric loss constant ϵ'' versus the frequencies (log f) at different temperatures of P(VDF-TrFE) samples, respectively. The behavior of ϵ' at lower frequencies shows high values at lower frequencies then decrease sharply over the entire frequency. The decrease of ϵ' in higher frequencies region may be due to the fact that the dipoles cannot follow the fast variation of the applied field. Fig. 8 shows the dielectric constants ϵ' and the dielectric loss constant ϵ'' versus the temperature at specific frequencies. As expected in ferroelectrics, these parameters (ϵ' , ϵ'') increase with increase in temperature and increasing concentration of nanoparticles in the films.

Fig. 7. (a, b): Real part of dielectric constant (ϵ') (b) Imaginary part of dielectric constant (ϵ'') vs. frequency of pure P(VDF-TrFE) at different temperature.

Figure 9 and 10 show the AC conductivity (log scale) and DC conductivity (log scale), respectively, plots as a function of $1000/T$ ($^{\circ}\text{K}^{-1}$) for all samples at a frequency value of 10 kHz. As can be seen from Fig. 9 and 10, the value of AC conductivity (σ_{ac}) and DC conductivity (σ_{dc}) increase with the increase in temperature. The ac and dc activation energies were measured by taking the slope of fitting curves in Fig. 9 and 10, respectively. It was

Fig. 8. Real part of dielectric constant (ϵ') and imaginary part of dielectric constant (ϵ'') vs. temperature of all nanocomposite films at 10 kHz.

Fig. 9. $\text{Ln}(\sigma_{ac})$ versus $1000/T$ for pure P(VDF-TrFE) and La_2O_3 -doped P(VDF-TrFE).

found that the ac and dc activation energies decrease with increase in volume fraction of nanoparticles following Arrhenius relationship. The ac and dc activation energies plotted versus volume fraction as shown in Fig. 11, the results indicate the conduction was thermally activated. The results of ac and dc activation energy of all samples are summarized in Table 2.

Table 2

The results of ac activation energy (E_{ac}) and dc activation energy (E_{dc}) of P(VDF-TrFE) and La_2O_3 - P(VDF-TrFE) nanocomposite films.

Sample	E_{ac} (eV)	E_{dc} (eV)
P(VDF-TrFE)	0.29	0.92
+2 vol.% La_2O_3	0.20	0.84
+5 vol.% La_2O_3	0.19	0.65
+8 vol.% La_2O_3	0.15	0.41

Fig. 10. $\ln(\sigma_{dc})$ versus $1000/T$ for pure P(VDF-TrFE) and La_2O_3 -doped P(VDF-TrFE).

Fig. 11. ac and dc activation energy versus volume fraction of P(VDF-TrFE) and La_2O_3 -P(VDF-TrFE) nano-composite films.

5. CONCLUSIONS

La_2O_3 nanoparticles were synthesized and fabricated via hydrothermal method without any surfactants. Their nanocomposite films with co-polymer P(VDF-TrFE) were fabricated via solution casting method. A noteworthy finding was the enhancement of β -phase by incorporation of nanoparticles into P(VDF-TrFE) matrix. From technological point-of-view, β -phase is more important and favorable for a scientific community due to its large spontaneous polarization. The optical band gap increased with increase in La_2O_3 nanoparticles.

The dielectric constant (ϵ') and dielectric loss (ϵ'') decreased with the frequency of applied signal and increased with temperature and volume fraction of La_2O_3 nanoparticles dispersed. The ac and dc activation energies were found to decrease with increase in volume fraction of nanoparticles following Arrhenius relationship.

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