AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **110**, 114119 (2011); doi: 10.1063/1.3669396

View online: http://dx.doi.org/10.1063/1.3669396

View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v110/i11

Published by the American Institute of Physics.

JOURNAL OF APPLIED PHYSICS **110**, 114119 (2011)

Dielectric relaxation and alternating current conductivity of polyvinylidene fluoride doped with lanthanum chloride

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(Received 13 July 2011; accepted 14 November 2011; published online 12 December 2011)

X-ray diffraction (XRD), dielectric constant (ε'), dielectric loss factor (ε''), and ac conductivity (σ_{ac}) of pure and $LaCl_3$-doped polyvinylidene fluoride (PVDF) have been carried out. The dielectric properties have been studied in the temperature and frequency ranges; 140–450 K and $0.1-1000$ kHz, respectively. XRD results reveal that pure and $LaCl_3$-PVDF samples are in the α-phase. The incorporation of La^{3+} ions within the PVDF polymer matrix forms complexes which reduce the order structure of PVDF. Three relaxation processes, namely; ρ, α_a, and α_c were observed for pure PVDF. The first relaxation can be explained based on space charge formation or Maxwell-Wagner polarization. The second one occurs around the glass transition temperature, T_g, and is related to the micro-Brownian motion of the main polymer chain. It becomes broad and shifted to higher temperatures with the doping of $LaCl_3$. The third process appears below the melting temperature of PVDF and can be attributed to molecular motions of the main polymer chain. The behavior of the ac conductivity shows that the conduction mechanism of pure, 5 wt. % and 10 wt. % of $LaCl_3$-doped PVDF samples is follows the correlated barrier hopping (CBH) model, while 3 wt. % of $LaCl_3$-doped PVDF exhibits a small polaron tunneling (SPT) conduction. *© 2011 American Institute of Physics*. [doi:10.1063/1.3669396]

I. INTRODUCTION

Polyvinylidene fluoride, PVDF, has widely been investigated because of its good properties; resistance to chemical, high dielectric permittivity, unique pyroelectric, and piezoelectric properties.[1–3] PVDF was considered as a material with a relatively high permittivity. The polymerization from a melt or a solution leads to the appearance of the so-called non-polar α-phase with a trans-gauche left-trans gauche right ($TGT\overline{G}$). It was reported that the neighboring units of the conformation macromolecules have antiparallel dipole moment.[4] The mechanical stretching of PVDF leads to the transformation of α-phase into β-phase which has a spontaneous polarization due to the parallel alignment of dipoles in neighboring units of the macromolecule acquiring a zigzag trans (TTTT) conformation. So, β-phase of PVDF exhibits ferroelectric properties.[5]

The chemical nature of rare earth (R^{3+}) ions is different compared to the cations of Fe^{3+}, Cr^{3+}, Al^{3+}, etc. This is due to the relatively large size of R^{3+}, low capacity for covalent-bond formation and weak electrostatic interactions between such ions and negative charge ligands. Because of these features of R^{3+} ions, the electronic structure of lanthanides can form complexes with bonds that are mainly ionic (electrostatic) in nature.[6,7] Polymers and polymeric composites have steadily gained growing importance in our daily life. Numerous investigations have been conducted on different polymer-metal composites to understand their physical properties.[8,9] Adding of fillers into a polymer matrix may lead to modify the properties of composites and the polymer structure due to the interphase interaction or formation of interface at the boundary of matrix/filler particles.[10,11] So that stabilization or improvement of mechanical, electrical, and thermal properties of dielectrics can be achieved.[12,13]

Rare earth complexes of europium and samarium are suitable candidates for applications such as light emitting diode, optical fiber, laser materials, and optical signal amplifications. It was found that the rare earth salts have a considerable effect on the structure, optical, and electrical properties of polymers.[14–17] Therefore, the objective of this work is to study the effect of an additive rare earth halides such as $LaCl_3$ on PVDF films to improve the performance of these materials. The x-ray diffraction techniques were used to examine the changes that are produced in the PVDF form. Also, the dielectric properties were investigated for pure and $LaCl_3$-doped PVDF to shed light on their molecular relaxations and conduction mechanism.

II. EXPERIMENTAL TECHNIQUES

PVDF of an average molecular weight 534 000 was obtained from Fluka Chemika. Lanthanum chloride, $LaCl_3$ $7H_2O$, was supplied by Sigma-Aldrich, Germany. The PVDF films with different ratios of $LaCl_3$ were prepared by casting as follows: PVDF was dissolved in N-N dimethylformamide (DMF) (reagent grade, Aldrich) at 90 °C for 30 min. $LaCl_3$ was dissolved in absolute ethanol and added to the polymeric solution. The solutions were left to reach a suitable viscosity. When a complete dissolution of the solids was assured, the solutions were allowed to cool at $50-60$ °C for 8 h with

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continuous stirring. The mixture was cast onto glass dishes and kept in the furnace at 50 °C for 24 h to ensure the removal of solvent traces. The thickness of the obtained films was 0.1–0.15 mm. The PVDF films filled with mass fraction, W (wt. %), of 0, 3, 5, 7, and 10 of $LaCl_3$, were obtained. The mass fraction was calculated as

$$W(wt.\%) = \frac{w_f}{(w_p + w_f)} \times 100, \tag{1}$$

where w_f and w_p represent the weight of the filler ($LaCl_3$) and PVDF polymer, respectively.

The x-ray diffraction (XRD) of all samples was performed at room temperature using CuK_α radiation (Rigaku miniflex). The dielectric measurements were carried out using an auto balance bridge type HP 4284A of frequency range from 0.1 to 1000 kHz. All samples were measured by using the four-point method. The samples were heated from 140 to 450 K at a heating rate of 0.5 K/min by using N_2-gas cryostat that can access a temperature range between 100 and 600 K. To make a contact, each sample was coated with silver paste, and short Cu-wires of diameter 0.1 mm were attached to the end of coaxial cables connected to the bridge. The complete range of frequency was scanned during heating using a computer program.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

XRD patterns of pure PVDF and that doped with 3, 5, 7, and 10 wt. % of $LaCl_3$ are shown in Fig. 1. Focusing on pure PVDF, Fig. 1(a), XRD shows a main peak at $2\theta \approx 20°$ which represents a diffraction corresponding to [110]. This is a typical α-phase[18] where the unit cell parameters; *a*, *b*, and *c* are 5, 9.5, and 4.6 Å, respectively. A shoulder peak is observed at $2\theta \approx 18.41°$ in addition to other prominent peaks at $2\theta \approx 26.56°$, 35.75°, and 38.62°. The main peak of PVDF shifts slightly with increasing of $LaCl_3$ content, while all investigated samples are still in the α-form. No peaks were observed at 20.57° or 36.3° which characterize the β-phase of PVDF.[19] It was noticed that the doping of PVDF by $LaCl_3$ decreases the intensity of x-ray diffraction peaks. The change of the intensity of these peaks at different concentrations of $LaCl_3$ can be attributed to the change in the contents of the filler. It means that $LaCl_3$ decreases the ordering character in the crystalline phase of PVDF due to the crosslinking process which can be assigned to the formation of complexes between La^{3+} ions and the fluorine group of the PVDF. It was previously reported that the crosslinking formation within the polymeric materials reduces the degree of crystallinity for some polymers.[20–23] Similar results were observed for PVDF and iodine filled samples due to the interactions between the polymer and the iodine.[24]

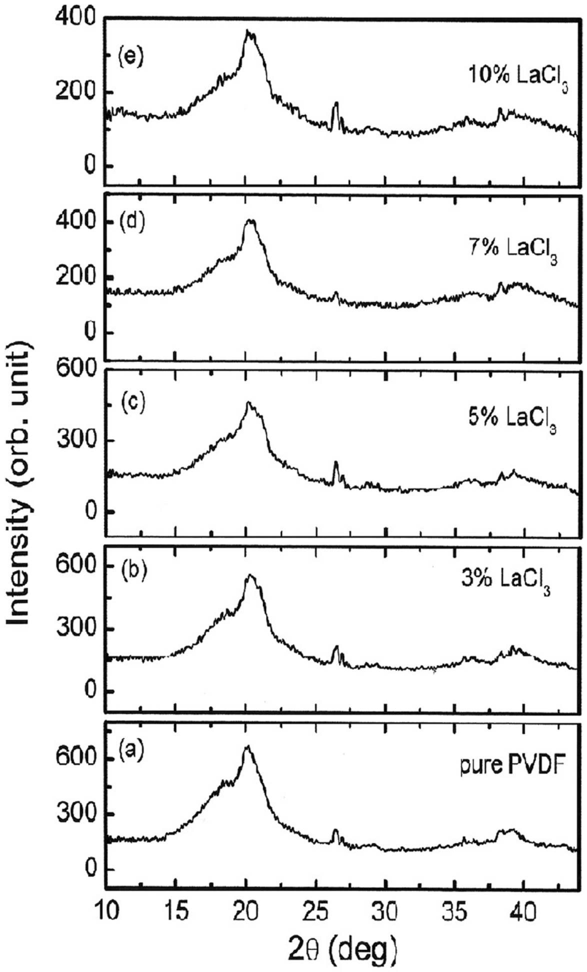

FIG. 1. XRD patterns for pure and $LaCl_3$-doped PVDF: (a) pure PVDF, (b) 3 wt. % $LaCl_3$, (c) 5 wt. % $LaCl_3$, (d) 7 wt. % $LaCl_3$, and (e) 10 wt. % $LaCl_3$.

B. Dielectric relaxation

1. Frequency dependence

Figures 2(a)–2(d) represent the frequency dependence of ε' for pure and $LaCl_3$-doped PVDF at different fixed temperatures. As seen, ε' of all samples decreases with increasing the field frequency due to decreasing number of dipoles which contribute to polarization. The nature of dielectric permittivity related to oscillating free dipoles in an alternating field may be described as follows: at very low frequencies ($\omega \ll 1/\tau$), where τ is the relaxation time, the dipoles follow the field and $\varepsilon' \approx \varepsilon_s$ (value of the dielectric constant at quasistatic fields). As frequency increases ($\omega < 1/\tau$), the dipoles begin to lag the field and ε' slightly decreases. When frequency reaches a characteristic value ($\omega = 1/\tau$), the dielectric constant exhibits relaxation process. At very high frequencies ($\omega \gg 1/\tau$), the dipoles can no longer follow the field and $\varepsilon' \approx \varepsilon_\infty$ (the value of ε' at $\omega = \infty$). The dielectric constant of 3 wt. % of $LaCl_3$-doped PVDF increases slightly compared to that of the pure PVDF. On the other hand, both 5 and 10 wt. % $LaCl_3$-doped PVDF exhibit a pronounced increase of ε' at lower frequencies and higher temperatures. This behavior can be attributed to the existence of multiple configurations of crosslinking formation inside the PVDF matrix with the increase of $LaCl_3$ content.

Figures 3(a)–3(d) illustrate the frequency dependence of ε'' for pure PVDF and that doped with 3, 5, and 10 wt. % of $LaCl_3$ at different temperatures. Pure PVDF undergoes two relaxation processes. The first one is ρ-relaxation, which

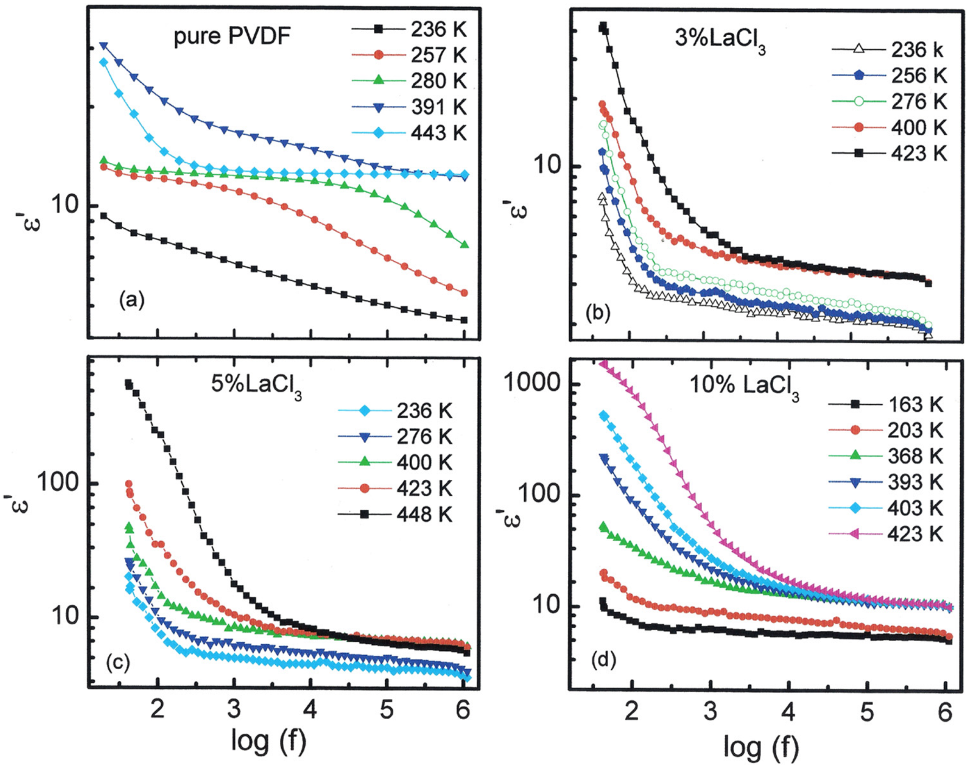

FIG. 2. (Color online) The frequency dependence of ε': (a) pure PVDF, (b) 3 wt. % $LaCl_3$-doped PVDF, (c) 5 wt. % $LaCl_3$-doped PVDF, and (d) 10 wt. % $LaCl_3$-doped PVDF.

occurs at higher frequencies (100 kHz $< f <$ 1000 kHz). It originates from the motion of space charges that are accumulated on the polymer close to the electrodes.[25] The nature of ρ-relaxation process for crystalline regions is due to the chain trapping of interfaces or Maxwell-Wagner polarization.[26] However, in the amorphous parts, ρ-process is related to conductive impurities, injected space charges and electrode polarizations. In semi-crystalline polymers such as PVDF, chain trapping, or Maxwell-Wagner polarization is more likely.[25] For $LaCl_3$-doped PVDF samples, ρ-relaxation can be related to the multiple phases which come from the conformation of the complexes between La^{3+} ions and fluorine group of the main polymer chain. The interactions of different rare-earth metal cations such as La^{3+}, Gd^{3+}, and Nd^{3+} with

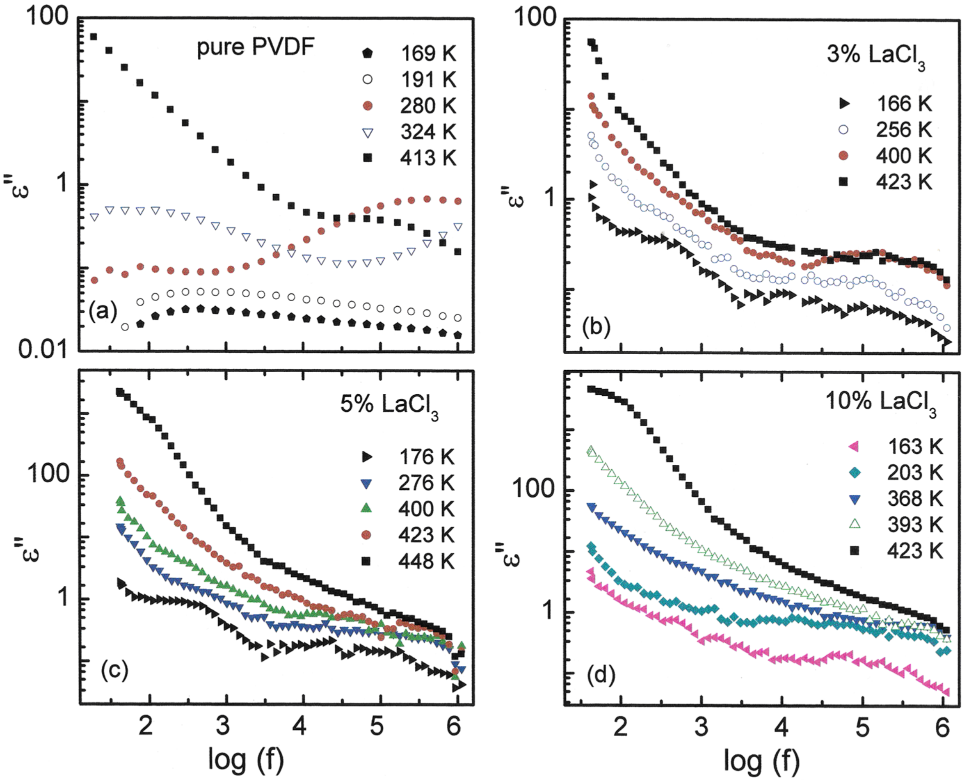

FIG. 3. (Color online) The frequency dependence of ε'': (a) pure PVDF, (b) 3 wt. % $LaCl_3$-doped PVDF, (c) 5 wt. % $LaCl_3$- doped PVDF, and (d) 10 wt. % $LaCl_3$-doped PVDF.

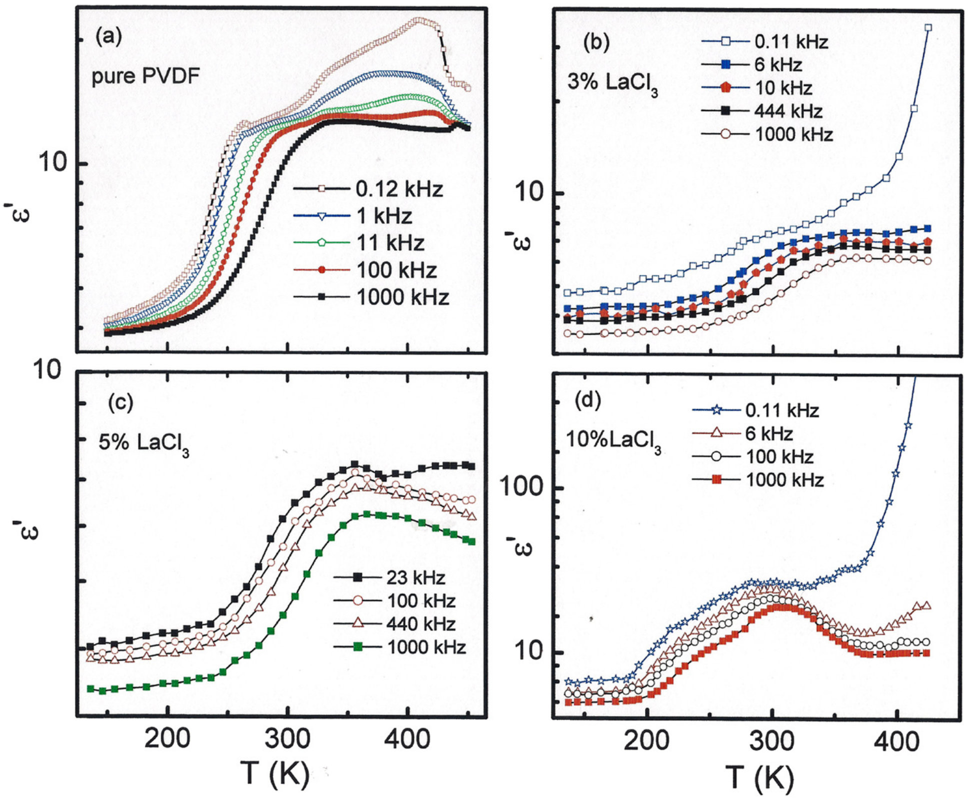

FIG. 4. (Color online) The temperature dependence of ε': (a) pure PVDF, (b) 3 wt. % $LaCl_3$-doped PVDF, (c) 5 wt. % $LaCl_3$- doped PVDF, and (d) 10 wt. % $LaCl_3$-doped PVDF.

different polymeric materials were previously studied, and the formation of complexes between these cations and ligand polar groups was suggested.[25,27,28] The second process is α_c-relaxation that occurs below the melting temperature of PVDF (Ref. 29) and may be related to the molecular motions of the main polymer chain.[30] Such peak does not appear for $LaCl_3$-doped PVDF within the studied range of temperatures.

2. *Temperature dependence*

Figures 4(a)–4(d) show the temperature dependence of ε' for pure PVDF and that loaded by 3, 5, and 10 wt. % of $LaCl_3$ at some selected frequencies. The dielectric constant of pure and $LaCl_3$-doped PVDF increases with temperature and exhibits a shoulder within the temperature range of

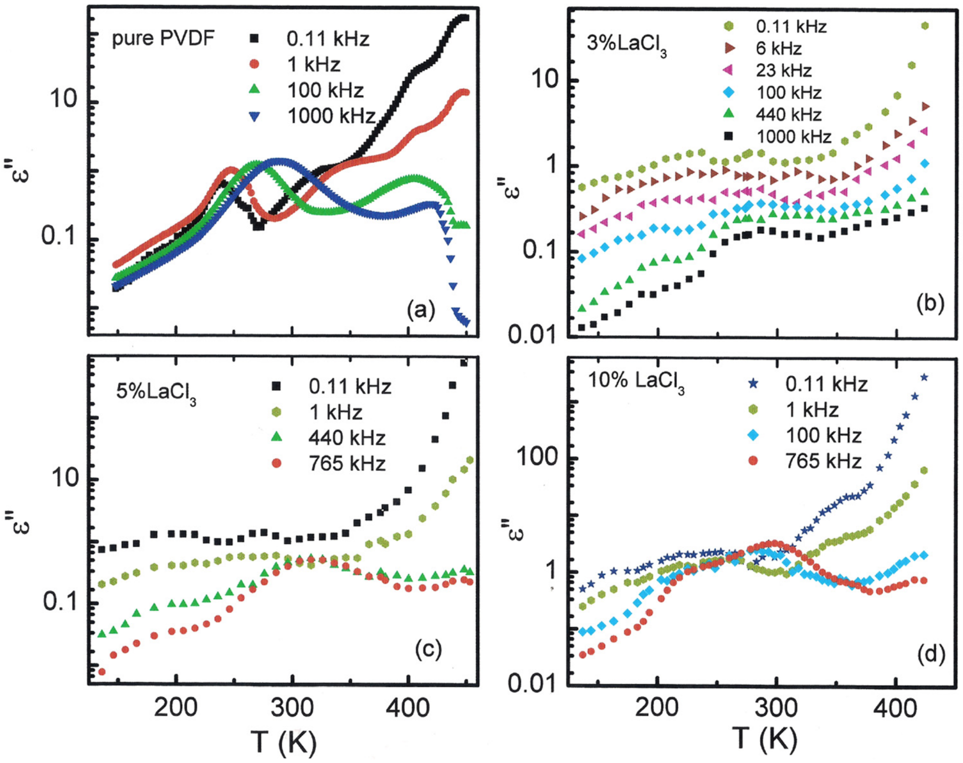

FIG. 5. (Color online) The temperature dependence of ε'': (a) pure PVDF, (b) 3 wt. % $LaCl_3$-doped PVDF, (c) 5 wt. % $LaCl_3$-doped PVDF, and (d) 10 wt. % $LaCl_3$-doped PVDF.

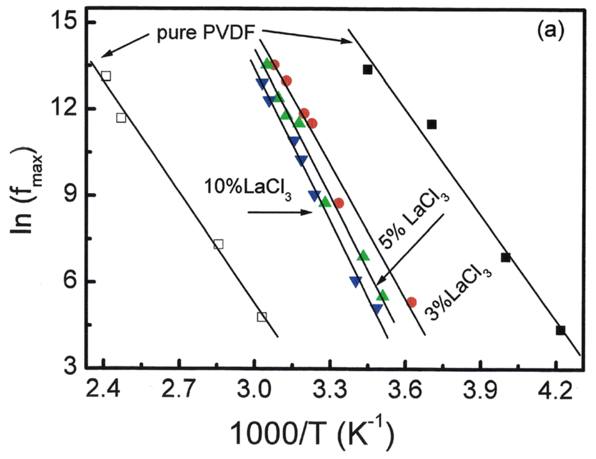

FIG. 6. (Color online). The variation of $ln(f_{max})$ versus $1000/T$ for pure and LaCl$_3$-doped PVDF samples.

240–300 K. This shoulder is associated with the glass transition temperature, T_g, of PVDF (Ref. 31) and can be interpreted according to the micro-Brownian motion of the main polymer chain.[30,32] It becomes broader and shifts to higher temperatures with increasing of LaCl$_3$ content. The increment of T_g due to the increase of LaCl$_3$ content inside the polymer matrix is probably a results of the interaction between La^{3+} ions and fluorine group which restricts the PVDF chain mobility. The formation of these immobilized polymer shells around La^{3+} ions increases the crosslinking density. Consequently, the degree of crystallinity of LaCl$_3$-doped PVDF samples decreases. Moreover, ε' of pure PVDF shows another peak around 420 K as seen in Fig. 4(a) and can be interpreted according to α_c-process. The disappearing of α_c-relaxation for LaCl$_3$-doped PVDF within the studied range of temperatures is in consistent with the shift of T_g towards higher temperatures.

TABLE I. The activation energies (in eV) of α_a-relaxation process for pure and LaCl$_3$-doped PVDF samples.

Sample	$E(\alpha_a)$
Pure PVDF	1.05 ± 0.09
3 wt. % LaCl$_3$	1.34 ± 0.09
5 wt. % LaCl$_3$	1.47 ± 0.07
10 wt. % LaCl$_3$	1.52 ± 0.05

Figures 5(a)–5(d) depict the temperature dependence of ε'' for pure PVDF and that contains 3, 5, and 10 wt. % of LaCl$_3$ at different fixed frequencies. It is noticed that ε'' of pure PVDF increases gradually with temperature and reaches a maximum peak within the temperature range of 240–300 K. This peak is due to α_a-relaxation which ensures that the dipoles relaxation is associated with T_g. The height of this peak changes and shifts to higher temperatures with increasing of frequency and LaCl$_3$ content. Furthermore, ε'' of pure PVDF shows a second peak around 420 K due to α_c-relaxation which ascribed to the changes in confirmation below the melting temperature. This result is in consistent with the behavior of $\varepsilon'(T)$ [see Fig. 4(a)].

The temperature dependence of the maximum loss peak frequency, f_{max}, is displayed in Fig. 6. The behavior of f_{max} can be described by Arrhenius equation:[33]

$$f_{max} = f_0 \exp\left(-\frac{E}{kT}\right), \tag{2}$$

where f_0 is a characteristic constant parameter for a particular relaxation process, k is the Boltzmann's constant, and E is the activation energy. The calculated values of E are listed in Table I. It was found that the value of the activation energy of α_c-relaxation for pure PVDF is 1.2 eV which is higher a little bit than that of α_a-relaxation ($\approx$1.05 eV). These values are in disagreement with those reported

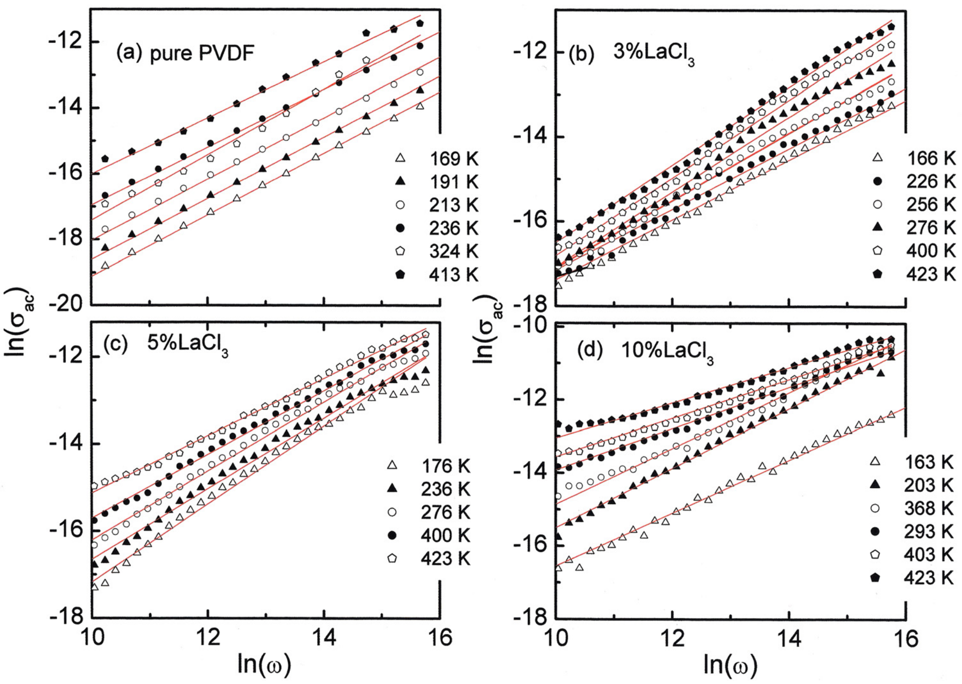

FIG. 7. (Color online) The frequency dependence of σ_{ac}: (a) pure PVDF, (b) 3 wt. % LaCl$_3$-doped PVDF, (c) 5 wt. % LaCl$_3$-doped PVDF, and (d) 10 wt. % LaCl$_3$-doped PVDF. The solid red lines are the fitting according to Eq. (4).

earlier[30,34,35] may be due to the existence of the micro-inhomogeneities inside the sample. The values of the activation energy of α_a-relaxation for $LaCl_3$-doped PVDF increase with $LaCl_3$ content. This is another evidence for the enhancement of T_g with doping.

C. Ac conductivity

It was found that the ac conductivity at low temperatures can be described as:[36,37]

$$\sigma_t = \sigma_{dc} + \sigma_{ac}(\omega), \tag{3}$$

$$\sigma_{ac}(\omega) = \sigma_t - \sigma_{dc} = A\omega^s, \tag{4}$$

where σ_{dc} is the dc (or low frequency) conductivity, σ_t is the total conductivity, s is the universal exponent, and A is a pre-exponential factor. The dc conductivity is subtracted by extrapolating $\sigma(\omega)$ to the $f \rightarrow 0$. The study of the temperature dependence of the exponent s is expected to be helpful in elucidating the microscopic dielectric relaxation mechanism. There are two distinct mechanisms that have been proposed for relaxation phenomena. One is the quantum mechanical tunneling (QMT) of electrons or polarons through the barriers separating localized states. The second is the classical hopping over the same barriers. The correlated barrier hopping (CBH) model was suggested by Pike[38] to explain the ac conduction mechanism. Small polaron tunneling (SPT) model may be proposed for a covalent solid like PVDF if the addition of a charge carrier to a site causes a large degree of local lattice distribution.

To determine the dominant ac conduction mechanism, the frequency dependence of σ_{ac} at low temperature side of α_a-relaxation process has been considered in Figs. 7(a)–7(d). Based on Eq. (4), the plots of $\ln(\sigma_{ac})$ versus $\ln(\omega)$ yield straight lines of different slopes, i.e., of s. The values of s were listed in Table II to show the temperature dependence of the exponent, s, of α_a-relaxation process for both pure and $LaCl_3$-doped PVDF. The values of s for pure PVDF at low temperature are in consistent with those reported earlier.[30] It is to be noted that the values of s decreased with increasing temperatures for 5 and 10 wt. % of $LaCl_3$-doped PVDF samples. A similar trend of s is observed for pure PVDF except at T = 413 K. This trend of s emphasizes that the CBH is the most suitable mechanism to explain the behavior of the ac conduction in these samples. On contrast, the s values for 3 wt. % of $LaCl_3$-doped PVDF increase with increasing temperatures. This indicates that the conduction mechanism of this sample could be SPT.

TABLE II. The values of the exponent, s, for pure and $LaCl_3$-doped PVDF samples at different temperatures according to the fitting of Eq. (4).

Pure PVDF		3 wt. % $LaCl_3$		5 wt. % $LaCl_3$		10 wt. % $LaCl_3$	
T (K)	S	T (K)	s	T (K)	s	T (K)	S
169	0.939	166	0.760	166	0.910	163	0.816
191	0.933	226	0.728	176	0.898	203	0.727
213	0.925	256	0.807	236	0.809	368	0.765
236	0.883	276	0.899	276	0.793	393	0.567
324	0.773	400	0.933	400	0.732	403	0.529
413	0.853	423	0.929	423	0.659	423	0.483

IV. CONCLUSIONS

XRD patterns show that all investigated samples are in the α-phase. The addition of $LaCl_3$ to PVDF causes a reduction of the crystallinity due to increasing the crosslinking density. The outcome results of the temperature and frequency dependence of ε' and ε'' of pure PVDF revealed three relaxation processes. The first one is ρ-relaxation, which can be explained according to the Maxwell-Wagner polarization. The second is α_a that occurs around T_g due to the micro-Brownian motion of the main polymer chain. The third process is α_c which locates around 420 K and associates with the molecular motions of the main polymer main. The disappearing of the α_c-relaxation for $LaCl_3$-doped PVDF samples is in consistent with the increase of T_g due to the complexes formation between La^{3+} ions and fluorine group of PVDF matrix. Finally, ac conductivity (σ_{ac}) of the investigated samples reveals that the CBH is the most probable conduction mechanism at α_a-relaxation process for both pure PVDF and that doped with 5 and 10 wt. % of $LaCl_3$. While the conduction mechanism of 3 wt. % of $LaCl_3$-doped PVDF is SPT type.

ACKNOWLEDGMENTS

The authors would like to thank Professor Dr. A. Loidl and Professor Dr. P. Lunkenheimer for using their lab facilities, Experimental Physik V, University of Augsburg, Germany.

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