Enhanced dielectric and optical properties of PVDF/$(LaBiFeO_3)_{0.5}$ $(BaTiO_3)_{0.5}$ composite films

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Abstract

The study presents the synthesis and comprehensive characterization of (1-x)PVDF/(x)LaBiFO-BTO composite films, where x varies as 0.05, 0.1, and 0.15, prepared through the solution casting method. X-ray diffraction (XRD) analysis confirmed the presence of various PVDF phases (α, β & γ), while Fourier Transform Infrared (FTIR) spectroscopy validated the existence of distinct vibrational modes associated with these phases. Surface morphology and roughness, evaluated using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), demonstrated an increase in roughness proportional to the LaBiFO-BTO concentration. Optical absorption spectra were used to determine the direct and indirect bandgap energies of the composites by applying Tauc's relation, revealing a decrease in bandgap with the addition of LaBiFO-BTO from 0 to 15 wt%, alongside an increase in Urbach energy. Dielectric measurements indicated a significant enhancement in the dielectric constant at lower frequencies with the 15 wt% LaBiFO-BTO. Dielectric loss was found to decrease with higher filler concentrations in the frequency range of 1 kHz to 1 MHz. Impedance spectroscopy results displayed a distinctive semicircular pattern, indicating specific conduction mechanisms within the composites. AC conductivity analysis, interpreted via Nyquist plots, provided insights into the conduction processes. These findings underscore the potential of LaBiFO-BTO/PVDF composites in applications requiring high dielectric constants and improved electrical properties.

Introduction

Polymer nanocomposites, particularly those involving polyvinylidene fluoride (PVDF), have significantly advanced materials science by enhancing the mechanical, electrical, and optical properties of traditional polymers. PVDF, a semi-crystalline polymer with notable chemical resistance and thermal stability, exists in multiple crystalline forms, with the α β or ν-phase being critical for applications due to its superior properties. Researchers have focused on improving PVDF's performance by incorporating nanomaterials such as BaTiO3, LaFeO3 & BiFeO3 which enhance its crystallinity and introduce multifunctional properties. These PVDF nanocomposites are promising in energy conversion, optoelectronics, sensors, and actuators due to their tailored electrical, optical, and dielectric properties. In this context, the objective is to add LaBiFeO3-BaTiO3 to PVDF to further enhance its dielectric and optical properties.

Preparation of PVDF-LaBiFO-BTO films

Synthesizing (LaBiFeO3)0.5 (BaTiO3)0.5 (LaBiFO-BTO) Polycrystalline Sample

Materials Used:
La2O3, BaCO3, TiO2, Fe2O3, Bi2CO3 (all > 99% purity from Loba Chemicals)

Preparation:
Measure materials in stoichiometric ratios.
Mix using an agate mortar and pestle:
- 2 hours of dry grinding.
- 2 hours of wet grinding in methanol.

Allow methanol to evaporate completely.

Drying:
Dry the precursor in a furnace at 300°C for 12 hours.

Calcination:
Calcine the dried mixture at 1250°C in a high-temperature furnace to form the final polycrystalline sample.

Preparation of PVDF - (LaBiFeO3)0.5 (BaTiO3)0.5 (LaBiFO-BTO) Film

Materials Used:
PVDF (Kynar 720) with molecular weight 5.5 × 10^4 g/mol and density 1.78 g/cm³ (99% purity from HiMedia Laboratories Pvt. Ltd, India).
Dimethyl formamide (DMF) as solvent.

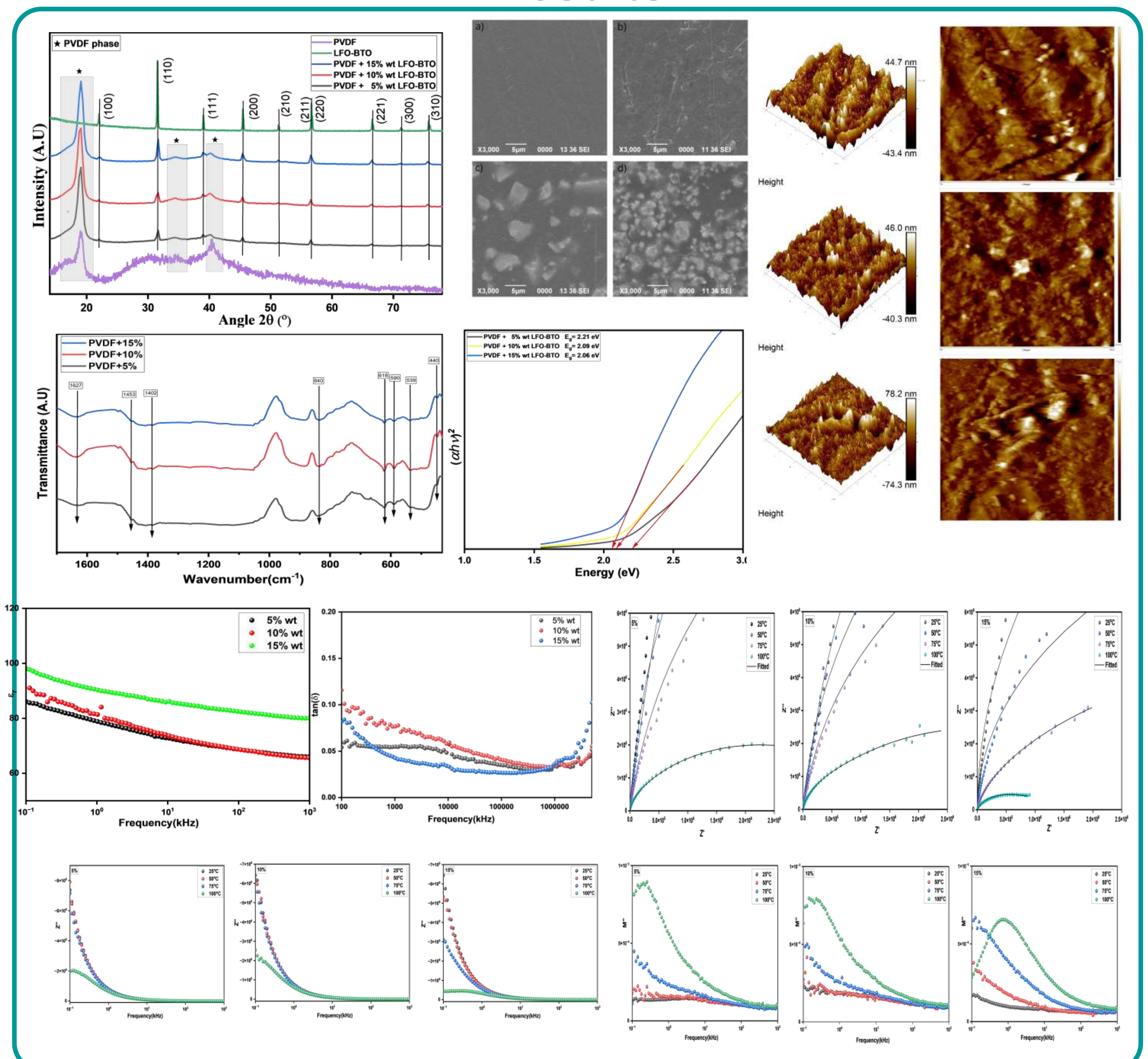
Composite Preparation:
Add LaBiFO-BTO to the PVDF solution to create composite films with concentrations of 5, 10, and 15 wt%.
Pour the resulting mixture into a petri dish.

Drying Process:
Dry the mixture in an oven with controlled heating to ensure complete solvent removal.
Peel the dried polymer film from the petri dish.

Characterizations

- **X-ray Diffraction (XRD) Analysis:** The instrument used for the XRD study is Bruker D8 Advance (Powder) with an operating range of 2θ = 12°-80°
- **Scanning Electron Microscopy (SEM):** The instrument used for the SEM study is JEOL JSM 6390LV with an operating voltage of 20 kV and magnification scale of 5μm
- **Atomic Force Microscopy (AFM):** The instrument used for the AFM study is Bruker Multimode Scanning Probe Microscope, capable of imaging in 2-D and 3-D surface topography and the scale bar of 5 μm
- **Fourier Transform Infrared (FTIR) Spectroscopy:** The instrument used for the FTIR study is Perkin Elmer SPECTRUM 100 and FORNTIER IR with a spectral range of 420 - 1700 cm⁻¹ (ATR mode).
- **UV-Visible-Near Infrared (UV-VIS-NIR) Spectroscopy:** The instrument used for UV-Visible study is Perkin Elmer LAMBDA 750 UV-Vis NIR Spectrophotometer with spectral range of 200 - 800 nm
- **Dielectric & Impedance Spectroscopy:** The instrument used for this study is LCR N4L, Model: PSM-1735 (UK) and the frequency range of 100 Hz - 1 MHz

Results



Conclusions

Synthesis and Structural Analysis:
PVDF/(LaBiFeO3)0.5-(BaTiO3)0.5 composites were synthesized using the solution casting method.
LaBiFO-BTO crystallized in the cubic phase with space group P m -3 m, and maintained its cubic perovskite structure when incorporated into the PVDF matrix.
The presence of PVDF (α, β, and γ) phases was confirmed by XRD and FTIR analysis.

Morphological Analysis:
SEM analysis indicated a homogeneous distribution of LaBiFO-BTO particles within the PVDF matrix.
AFM studies showed significant surface topographic changes with varying LaBiFO-BTO concentrations, where higher filler content increased the Ra and Rq values.

Optical Properties:
Increasing LaBiFO-BTO concentration from 5% to 15% resulted in a decrease in the direct band gap from 2.21 eV to 2.06 eV.

Dielectric Properties:
Dielectric study revealed that composites with 15 vol% LaBiFO-BTO exhibited the highest dielectric constant (εr ~ 98), which is approximately six times greater than pure PVDF (εr ~ 13.81) with minimal loss <0.05 in the frequency range 1kHz to 1MHz.
Nyquist plot analysis showed that the diameter of semi-circular arcs decreased with higher LaBiFO-BTO content, indicating improved semiconducting behavior and interconnectivity.

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