The structural properties and Energy Gap of PVDF/LiAlO$_2$ Nanocomposite Thin Films

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Abstract. Lithium aluminate (LAO), LiAlO$_2$ powders were synthesized by sol-gel method because it was developed for preparing nano-sized at low temperature. The X-ray diffraction (XRD) found out a tetragonal structure for LiAlO$_2$. Various percentages of 1, 2, 3 and 4 wt. were applied to the LAO with polyvinylidene fluoride (PVDF) polymer. The obtained materials were characterized by Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscope (FE-SEM). Structural analysis indicates the presence of polycrystalline phase with nanometre scale. Energy gap were studied and the results shows a decrease in energy gap with the increasing in weight ratio of LAO. This decline in the value of optical energy is due to an increase in the density of the band-gap of localized states.

Keyword: PVDF, LiAlO$_2$, polymer, energy gap

1. Introduction
In high energy density states, the increasing interest in solid batteries is leading many researchers to explore new concepts and related materials. The lithium-ion technology that uses polymer electrolytes as a separator for rechargeable batteries tends to provide the most promising choices [1]. Recently, there has been considerable interest in Al-doping (LiMO$_2$, where M is a transition metal) of lithium intercalation oxides. Theoretically and experimentally, Al transition-metal cation replacement has been shown to increase the cell voltage. Some of Al’s benefits are that it is light, cheap, and non-toxic [2].

Lithium aluminate (LiAlO$_2$) can be used as the best ceramic fillers for polymer electrolytes, and it is primarily used as a possible economical lithium battery cathode in the energy industry in nuclear physics and solid chemistry. LiAlO$_2$ normally crystallizes at ambient conditions, called γ-phase, in a tetragonal structure. Then, in the past few decades, several interesting phases of LiAlO$_2$ have been discovered or synthesized. A low temperature step with orthorhombic symmetry was defined as β-LiAlO$_2$[3]. Lithium aluminate synthesis has essentially been carried out by many methods: sol-gel, solid state, wet chemical, using templates, different precursors and combustion processes [4]. A graphite anode, a lithium-metal oxide cathode, an electrolyte solution containing lithium salts, and a polymeric separator typically consist of a lithium-ion battery [5].

Indeed, for electronic charges, the separator should be electrically insulated and at the same time sufficiently porous to ensure electrolyte uptake to enable ionic conductivity. A necessary requirement for the functioning of the battery is high ionic conductivity. In addition, the high dimensional stability,
as well as good mechanical properties of the polymeric separator at high temperatures is important to avoid a short circuit between the cathode and the anode, which can probably result in a failure of the battery. Several materials such as gel-forming polymers and polymeric separators have been investigated in the literature, such as polyvinylidene fluoride (PVDF), polyethylene oxide (PEO), polypropylene (PP), polyethylene (PE), and copolymers of the latter. PVDF separators obtained by phase inversion methods are used by most batteries on the market today [6].

Metal oxide nanoparticles applied to the polymer material will make a major contribution to the internal components of the battery in terms of electrical conductivity as well as mechanical strength and greater thermal stability thereby contributing to improving the protection of the cell [7,8]. Because of its characteristics, such as the ability to boost lithium ion transfer and electrolyte absorption, nano-silica is one of the most investigated fillers, thus increasing mechanical strength, electrode interface stability, and ion conductivity [9].

A. M. and P. Indolia. S. Gaur (2013) studied the optical characteristics of PVDF-ZnO thin films. This study showed that the optical properties of nanocomposite thin films depends on the ZnO contents and have the best optical properties [10].

The goal of this work is to explore the impact of LAO material on PVDF pristine and PVDF: LAO nanocomposites with different concentrations of LAO optically. The key focus of the present analysis is on the optical band difference of different percentages of PVDF and PVDF:LAO.

2. Experimental part

2.1 Preparation of lithium aluminate LiAlO2:

The LiAlO2 powder synthesis was processed by the chemical method of Sol-gel. First, the mixture was dissolved in (50 ml) using equal quantities of Li and Al nitrates with citric acid (1:1:2) and combined with distilled water, and left to evaporate for 1 day at 70 °C until gelled, then heat-treated for two hours at 650 °C. The powder prepared by sol-gel shows a sponge with a color of white. The stage of heating in the 150 °C, LAO shows a sponge porous structure before the calcination process, these processes may be considered to have a fine and crystalline powder. The calcination temperature (650) °C was proper to get nanosized particles, followed by grinding process to reduce the coarser particles using a large in crucible like container. The resulting prepared powder color was white. Using hot process casting of these composites, this method decreases the prossily-due compacting, which increases composition conductivity in order to decrease volume and improve lithium ion mobility by offering the conductivity direction along with the structure.

2.2 Preparation of PVDF: LAO nanocomposites

The developed nanocomposites were prepared using the method of phase inversion. The casting solution was composed of PVDF powder dissolved in N,N-dimethylformamide (DMF) and various modified LAO concentrations. LAO in the ratio (1, 2, 3, and 4 % wt.) was applied to all the components and combined by stirring to prepare the casting solution for at least 5 hours. By means of a hand-casting knife, the solutions were uniformly cast on a glass substrate and then immersed in a coagulation bath after exposure to the air for a fixed period (one day). To ensure that the excess solvent was extracted, the flat-sheet thin film was kept in the water bath for at least 1 day.

3. Results and discussions

3.1 X-ray diffraction analysis

The X-ray diffraction spectra for lithium aluminate LiAlO2 (LAO) synthesis by sol-gel method are reported in Figure 1. The X-ray spectra indicates the formation of tetragonal structure LiAlO2 with card No.(JCPDSNO.) 96-100-8167, and the secondary phase Al2O3 has orthogonal structure with card No. (JCPDS 96-100-0443).

The main peaks at 22.25°, 24.3°, 28.19°, 33.35°, 34.63°, 50.12°, 56.25°, 61.34°, 72.44°, and 78.41° corresponding to (101), (110), (111), (012), (200), (220) (130), (302) (332), and (330) indicates the
formation of pure LiAlO$_2$. Some extra secondary peaks (secondary phases of Al$_2$O$_3$) are seen adjacent to the peak features and may be due to the presence of the impurity process. In Table 1, the structural properties are explained as full width at half maximum (FWHM), index plane, and grain size that agree with [11,12].

![X-ray diffraction spectra of LiAlO$_2$](image)

**Figure 1.** X-ray diffraction spectra of LiAlO$_2$.

**Table 1.** The structural properties of LiAlO$_2$ and Al$_2$O$_3$ powder.

| 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | G.S (nm) | $d_{hkl}$ Std.(Å) | Phase              | hkl   | card No. |
|-----------|--------------|-------------------|----------|-------------------|---------------------|-------|----------|
| 21.2941   | 0.3083       | 4.1692            | 26.2     | 4.1650            | Orthor.Al$_2$O$_3$  | (020) | 96-100-0443 |
| 22.2577   | 0.3084       | 3.9909            | 26.3     | 3.9953            | Tetra.LiAlO$_2$     | (101) | 96-100-8167 |
| 23.4526   | 0.2312       | 3.7902            | 35.1     | 3.7931            | Orthor.Al$_2$O$_3$  | (111) | 96-100-0443 |
| 24.3007   | 0.2698       | 3.6598            | 30.1     | 3.6557            | Tetra.LiAlO$_2$     | (110) | 96-100-8167 |
| 28.1938   | 0.3084       | 3.1626            | 26.6     | 3.1613            | Tetra.LiAlO$_2$     | (111) | 96-100-8167 |
| 29.4273   | 0.3084       | 3.0328            | 26.6     | 3.0495            | Orthor.Al$_2$O$_3$  | (022) | 96-100-0443 |
| 30.5837   | 0.2698       | 2.9207            | 30.5     | 2.9782            | Orthor.Al$_2$O$_3$  | (121) | 96-100-0443 |
| 31.7401   | 0.1927       | 2.8169            | 42.9     | 2.8099            | Orthor.Al$_2$O$_3$  | (013) | 96-100-0443 |
| 33.3590   | 0.3084       | 2.6838            | 26.9     | 2.6885            | Tetra.LiAlO$_2$     | (012) | 96-100-8167 |
| 34.0529   | 0.2313       | 2.6307            | 35.9     | 2.6521            | Orthor.Al$_2$O$_3$  | (031) | 96-100-0443 |
| 34.6311   | 0.3469       | 2.5881            | 24.0     | 2.5850            | Tetra.LiAlO$_2$     | (200) | 96-100-8167 |
| 36.9053   | 0.2699       | 2.4336            | 31.0     | 2.4306            | Orthor.Al$_2$O$_3$  | (113) | 96-100-0443 |
| 39.6035   | 0.5011       | 2.2738            | 16.9     | 2.2387            | Orthor.Al$_2$O$_3$  | (004) | 96-100-0443 |
| 41.6079   | 0.3854       | 2.1688            | 22.1     | 2.1693            | Orthor.Al$_2$O$_3$  | (123) | 96-100-0443 |
| 43.4196   | 0.2312       | 2.0824            | 37.0     | 2.0825            | Orthor.Al$_2$O$_3$  | (040) | 96-100-0443 |
| 48.7775   | 0.3469       | 1.8655            | 25.1     | 1.8746            | Orthor.Al$_2$O$_3$  | (133) | 96-100-0443 |
| 50.1267   | 0.4626       | 1.8184            | 19.0     | 1.8279            | Tetra.LiAlO$_2$     | (220) | 96-100-8167 |
| 56.2555   | 0.5782       | 1.6339            | 15.6     | 1.6349            | Tetra.LiAlO$_2$     | (130) | 96-100-8167 |
| 59.6861   | 0.3470       | 1.5480            | 26.4     | 1.5516            | Orthor.Al$_2$O$_3$  | (151) | 96-100-0443 |
| 61.3436   | 0.3084       | 1.5100            | 29.9     | 1.5116            | Tetra.LiAlO$_2$     | (302) | 96-100-8167 |
| 70.1707   | 0.3469       | 1.3401            | 28.0     | 1.3441            | Orthor.Al$_2$O$_3$  | (323) | 96-100-0443 |
| 72.4449   | 0.3855       | 1.3036            | 25.5     | 1.3049            | Tetra.LiAlO$_2$     | (322) | 96-100-8167 |
3.2 Atomic force microscopy for LiAlO₂ powder

Atomic force microscopy (AFM) was performed to measure the average diameter and the grain size for the samples in the shape of a pellet by using AA3000 scanning probe Microscopy by Angstrom Advanced Inc (USA). The AFM pictures morphology for the surface of the LiAlO₂ NPs in the two and three dimensions are shown in Figure 2a and b. The pictures are shown a uniform surface; indicate that the particle has uniform dimensions.

The average diameter on the surface is found by granularity cumulating distribution chart to be 82.65 nm for LiAlO₂ as shown in Figure 2c.

![AFM micrograph for LiAlO₂ powder](image)

**Figure 2.** AFM micrograph for LiAlO₂ were (a) 2D, (b) 3D and (c) Granularity cumulation distribution chart.

3.3 Field Emission Scanning Electron Microscope (FE-SEM)

Typical sample findings from the field emission scanning electron microscope (FE-SEM) are shown in Figure 3. PVDF pure and PVDF: LiAlO₂ 1% thin film FE-SEM picture demonstrates that the sample consists of large agglomerated clusters. It can be seen under high magnification that each cluster consists
of multiple spherical nanoparticles, each of which has a smooth surface. The addition of LAO to the PVDF has a significant impact on the morphology of the film. As the content of LAO increased, the size and density of the pores increased.

In Figure 3a, the film is relatively smooth and flat with small and few pores. More bigger pores were formed when 1% LAO was added into the PVDF solution, as shown in Figure 3b.

(A) Pure PVDF thin film

(B) PVDF:LAO 1% thin film

Figure 3. SEM images of (a) pure PVDF and (b) PVDF : LiAlO₂ 1% thin film.

3.4 Optical band gap

For pristine PVDF and PVDF: LAO composite films, the optical band gap can be obtained by taking into account the linear portion of the UV-Visible spectrum at the absorption edge. It is obvious from Figures 4 and 5 that all samples display absorption edges that are red-shifted with LAO nanoparticles. Figure 4, 5 and Table 2 are shown the energy gap variation with Various LAO proportions (1, 2, 3, and 4 % wt.) nano-powder. The results show a decrease in the energy gap(direct band gap) due to an increased in inter atomic spacing which decrease the potential, this inturn reduce the energy band gap. Tauc plots identified direct PVDF:LAO band gaps in nanocomposite films:

\[ f(\hbar \nu) = (\alpha \hbar \nu)^2 \]

Where \( \alpha \) is the absorption coefficient which was determined by the following expression:

\[ \alpha(v) = 2.303 \left( \frac{A}{l} \right) \]
When $A$ is the optical absorbance, and $t$ is the thickness of the polymer nanocomposite thin film and it is approximately equal to 3.5mm.

Doping may affect the optical band gap; the low energy gap was due to high density of localized state. Impurities are the increase in doping due to dopants, as the chemical composition changes during doping. A shift in the energy distribution of the permissible states cannot have a general rule such as after impurities are added, the band gap will decrease [10].

![Figure 4. Energy gap of pure PVDF thin film.](image)

**Table 2.** The Energy gap of PVDF:LAO thin film.

| Sample      | Energy gap (eV) |
|-------------|-----------------|
| PVDF        | 5.73            |
| 1 %         | 5.54            |
| 2 %         | 5.50            |
| 3 %         | 5.45            |
| 4 %         | 5.33            |

PVDF:LAO

The band-gap is a non-approved energy zone. The density of states versus energy depends on the substance's chemical composition; if the chemical composition is changed, at least, in principle, the state density distribution should change. Dopants are impurities, because, by doping, the chemical composition changes. A change in the energy distribution of the permissible states cannot have a general rule such as: after the introduction of impurities, the band-gap would decrease. Generally, these
impurities are called dopants, which in the band-gap produce permissible shallow states. Shallow states have small energies of ionization; and when the doping density is high, a band is formed by dopant states. If the valence or conduction band edge is very close to this band, the band gap will decrease [10].

4. Conclusion
Lithium Aluminate (LiAlO$_2$) has been successfully prepared using sol-gel. The dependency of the optical properties of nanocomposites on LiAlO$_2$ material has been investigated. As the content of LiAlO$_2$ increases, the optical band gap for this process for direct transitions decreases. The structural changes

**Figure 5.** Energy gap of PVDF:LiAlO$_2$ thin film.
that occur after adding LiAlO$_2$ nanoparticles may be correlated with this activity. Due to the inclusion of LiAlO$_2$ nanoparticles, there is a drop in the optical energy gap of nanocomposites. The decrease in the optical distance indicated by the energy of optical activation can be associated with a decrease in network disorder.

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