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Spectroscopic Analysis and Dosimetric Characterization of Lithium Fluoride (LiF) Crystals

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Abstract

Lithium fluoride (LiF) is an inorganic, non-toxic, and chemically inert compound that has garnered extensive interest across scientific and industrial domains due to its exceptional physical, chemical, and optical properties. Crystallizing in a face-centred cubic (FCC) structure similar to sodium chloride (NaCl), LiF exhibits high thermal stability, with a melting point of 870 °C and a boiling point of 1676 °C. Its low refractive index (~1.4) and good infrared transmission make it ideal for optical applications, particularly in UV and IR spectroscopy. Furthermore, LiF demonstrates low solubility in water and moderate thermal conductivity (~12 W/m·K), reinforcing its stability in diverse environmental conditions.

A key application of LiF lies in radiation dosimetry, where it serves as a highly effective thermoluminescent (TL) material, particularly when doped with elements like magnesium, titanium, or copper (e.g., LiF:Mg,Ti and LiF:Mg,Cu,P). The presence of deep electron traps in its crystal lattice ensures prolonged retention of radiation-induced charge carriers, allowing for accurate and stable dose measurements over time. Importantly, the effective atomic number of LiF (Z_eff ≈ 8.2) closely matches that of human tissue, making it highly suitable for medical and environmental dosimetry.

The sol-gel method of the preparation of the phosphor, particularly the trifluoroacetic acid (TFA)-based route, offers a versatile pathway for preparing phase-pure, nanostructured LiF. This approach allows precise control over particle morphology and size through adjustments in solvent type, salt concentration, and organic surfactants, making it highly suitable for optimizing LiF's dosimetric and optical performance.

Introduction

Lithium fluoride (LiF) is an inorganic, chemically inert, and non-toxic compound that has garnered significant attention in both scientific research and industrial applications due to its stable physical and chemical properties. Structurally, LiF crystallizes in the face-centred cubic (FCC) lattice, adopting a configuration analogous to that of sodium chloride (NaCl), which contributes to its robustness and thermal stability. It exists either as a fine white powder or in the form of transparent, colourless crystals. The compound has a molecular weight of 25.94 g/mol and a density of approximately 2.64 g/cm³**.** Notably, it demonstrates high thermal endurance, with a melting point of 870 °C and a boiling point of 1676 °C, making it suitable for high-temperature applications [1].

Optically, lithium fluoride is distinguished by having the lowest refractive index (~1.4) among common infrared-transparent materials, which makes it highly valuable in optical windows and lenses, particularly in UV and IR spectroscopy. Furthermore, it possesses moderate thermal conductivity (~12 W/m·K) and a thermal expansion coefficient of 32 μm/m·K, factors that influence its behaviour under varying thermal conditions. Its limited solubility in water (0.27 g/100 mL at 293 K) further contributes to its chemical stability in moist environments. Owing to these collective properties, LiF finds application in a diverse range of technologies including optics, nuclear reactors, and more critically, radiation dosimetry**.**

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In the field of radiation measurement, LiF is regarded as one of the most effective thermoluminescent (TL) materials**,** especially in its doped forms such as LiF:Mg,Ti and LiF:Mg,Cu,P. This efficacy stems from the presence of sufficiently deep electron traps within its crystal lattice, which effectively prevent premature loss of trapped charge carriers. These deep traps enable LiF-based TL detectors to retain absorbed radiation energy for extended periods**,** ensuring reliable dose readings even after long post-irradiation intervals [2]. Additionally, one of the most important features of LiF in medical and environmental dosimetry is its tissue equivalence; the effective atomic number ($Z_{eff} \approx 8.2$) of LiF closely approximates that of human soft tissue, thereby ensuring accurate dose estimation with minimal perturbation.

The performance of LiF as a dosimetric material is also closely linked to its structural, optical, and electronic properties**,** which can be effectively studied through spectroscopic techniques**.** Spectroscopic analysis, including photoluminescence (PL), UV-Vis absorption, and infrared (IR) spectroscopy, offers valuable insights into the presence of intrinsic and extrinsic defects, trap levels, and recombination mechanisms responsible for its luminescent behaviour under ionizing radiation. These characteristics significantly influence the sensitivity, linearity, and stability of the dosimetric response.

Among the different processes of the synthesis of the crystal, the sol-gel process is a highly efficient and versatile chemical synthesis technique that involves hydrolysis and polycondensation reactions among precursor compounds, typically leading to the formation of a homogeneous polymeric network. Upon subsequent drying and thermal treatment, this network yields various nanostructured materials, including oxide and fluoride powders. Specifically, in the synthesis of metal fluorides, three major sol-gel approaches have been documented: (i) post-fluorination of metal oxides prepared via the sol-gel route, (ii) nonaqueous sol-gel synthesis using pure hydrofluoric acid (HF) as the fluorinating agent, and (iii) formation of metal trifluoroacetate (TFA) followed by their thermal decomposition to yield the corresponding fluorides [3-4].

Among these, the TFA-based route has gained prominence due to its relative safety and ability to control particle morphology. It has been demonstrated that when trifluoroacetic acid (TFA) is employed as the fluorine source, the formation and properties of the gel, as well as the resulting LiF powder**,** are significantly influenced by several key parameters: the type of solvent**,** salt concentration**,** thermal treatment conditions**,** and the presence of organic additives such as oleic acid (OA) surfactants [5-6]. The thermal decomposition of metal trifluoroacetate is a particularly effective pathway, not only for promoting phase-pure LiF formation but also for tailoring the particle size and morphology, which are critical for optimizing luminescent behaviour.

This study focuses on the synthesis and spectroscopic evaluation of LiF crystals, aiming to correlate their physical characteristics with their radiation response. Through detailed spectroscopic investigation, we aim to identify the active luminescent centres and trap states that contribute to the thermoluminescent and photoluminescent behaviour of the material. Additionally, the dosimetric characterization—including parameters such as dose response, fading, and energy dependence—is carried out to assess the practical viability of the synthesized LiF crystals for use in radiation dosimetry.

Experiment:

Lithium fluoride (LiF), a technologically significant material with applications in optics, radiation detection, and energy storage systems, was synthesized using the Sol-Gel method. The Sol-Gel technique is a versatile and low-temperature process widely employed in materials science for the synthesis of homogeneous and fine powders. The fundamental principle of this method lies in the formation of a colloidal suspension (sol) from chemical precursors, which subsequently undergoes hydrolysis and polycondensation to form a gel-like network. The liquid component (solvent) within the gel is then removed, followed by drying and calcination to yield the desired crystalline material. This approach offers precise control over the chemical composition, purity, and microstructure of the final product, making it an effective route for the synthesis of advanced ceramic materials like LiF.

In the present study, Lithium Fluoride was synthesized using lithium acetate dihydrate ($LiCH_3COO \cdot 2H_2O$) as the precursor. Three organic solvents — acetic acid, ethyl alcohol, and ethylene glycol — were employed to

study the influence of solvent nature on the synthesis outcome. Precisely 20 mL of each solvent was used to dissolve 2.28 g of lithium acetate dihydrate (99% purity, obtained from Laba Chemie Pvt. Ltd.) in three separate reaction vessels. To each solution, 1.53 mL of trifluoroacetic acid (TFA, 99.9% purity, supplied by SRI) was added as a complexing agent. The mixtures were magnetically stirred at ambient temperature to ensure complete homogenization, resulting in clear and transparent sols.

These homogeneous solutions were subjected to thermal treatment at 150°C in an oven to promote gelation and solvent evaporation. The resulting dry gels were then calcined at 500°C in a muffle furnace at a controlled heating rate of 10°C per minute. This thermal process facilitated the decomposition of organic components and the crystallization of the LiF phase.

The final lithium fluoride powders obtained from the three different solvent systems were denoted as Sample 1 (1.27 g, acetic acid), Sample 2 (1.25 g, ethyl alcohol), and Sample 3 (1.23 g, ethylene glycol), indicating slight variations in yield possibly due to differences in solvent evaporation rates and sol-gel network formation.

To investigate the structural, morphological, and phase properties of the synthesized LiF samples, detailed characterization was carried out using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)**.** These analyses were conducted at the Department of Physics, Manipur University, Canchipur. XRD was employed to confirm the crystalline phase and purity of the samples, while SEM provided insights into the particle size, shape, and surface morphology of the synthesized LiF powders.

Result and discussions.

The phase purity and crystalline structure of the synthesized lithium fluoride (LiF) powders were investigated using X-ray Diffraction (XRD). The XRD patterns of all three samples—synthesized using different solvents in the Sol-Gel process—exhibit sharp and well-defined diffraction peaks, indicating a high degree of crystallinity.

Sample 1: Acetic Acid-based Sol-Gel Route

The XRD spectrum of Sample 1, synthesized using acetic acid as the solvent, reveals four prominent diffraction peaks located at 2θ = 38.767°, 45.068°, 65.637°, and 79.917° (Figure 1). These peaks match precisely with the standard diffraction data for LiF obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) database, confirming the successful synthesis of high-purity LiF. The corresponding Miller indices (hkl) are assigned as (111), (200), (220), and (311) respectively. The sharpness and intensity of the peaks indicate excellent crystallinity and minimal presence of secondary phases or amorphous content.

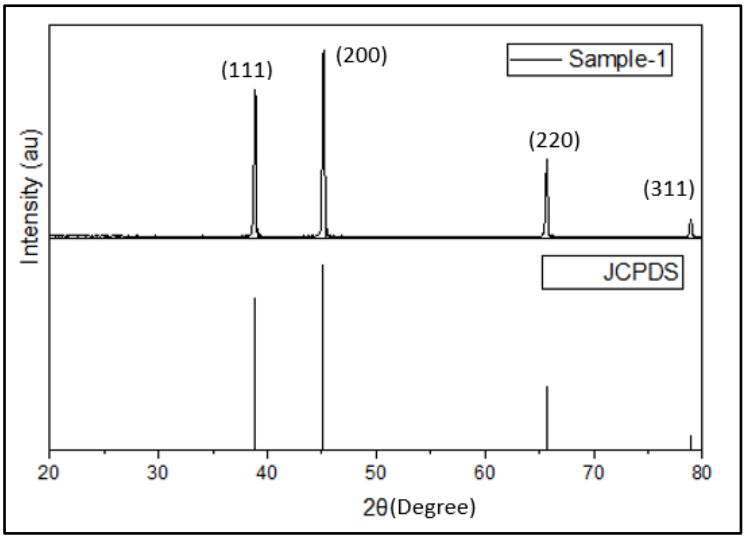


Figure1: The XRD graph of sample-1 with the standard JCPDS graph of LiF.

Sample 2: Ethyl Alcohol-based Sol-Gel Route

The XRD pattern of Sample 2, prepared with ethyl alcohol as the solvent, also confirms the formation of pure crystalline LiF, with peaks observed at 2θ = 38.784°, 45.306°, 65.703°, and 79.079° (Figure 2). These values are

in strong agreement with the standard data reported by Hanawalt et al., 1938, further validating the phase purity also matches precisely with the standard diffraction data of LiF obtained from the JCPDS database. The Miller indices associated with these reflections are likewise (111), (200), (220), and (311). Notably, a slight shift in peak positions compared to Sample 1 suggests minor differences in lattice strain or crystallite size due to the solvent environment during synthesis.

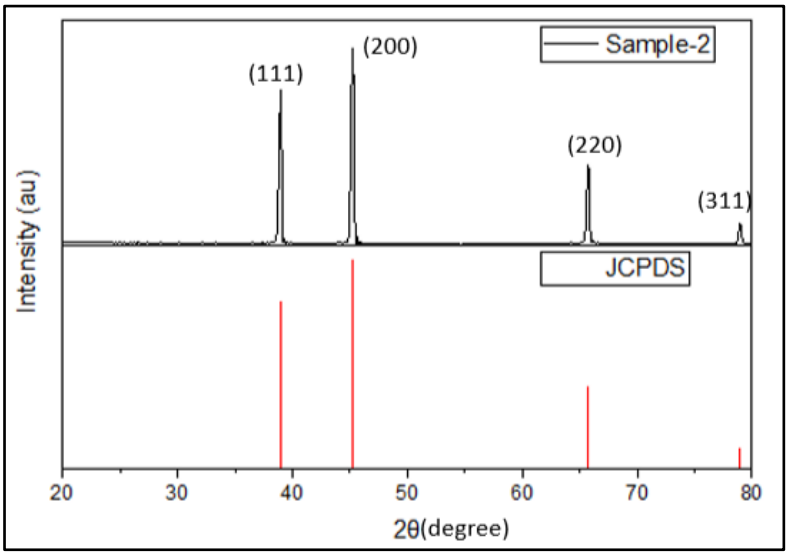


Figure 2: The XRD graph of sample-2 compare with the standard JCPDS Graph of LiF.

Sample 3: Ethylene Glycol-based Sol-Gel Route

For Sample 3, which employed ethylene glycol as the solvent, the XRD peaks appear at 2θ = 38.767°, 45.068°, 65.637°, and 79.917° (Figure 3), which are identical to those of Sample 1 and are in agreement with the JCPDS standard data. This consistency reaffirms the reproducibility of the Sol-Gel method and its effectiveness in synthesizing phase-pure lithium fluoride, regardless of the choice of polar organic solvent.

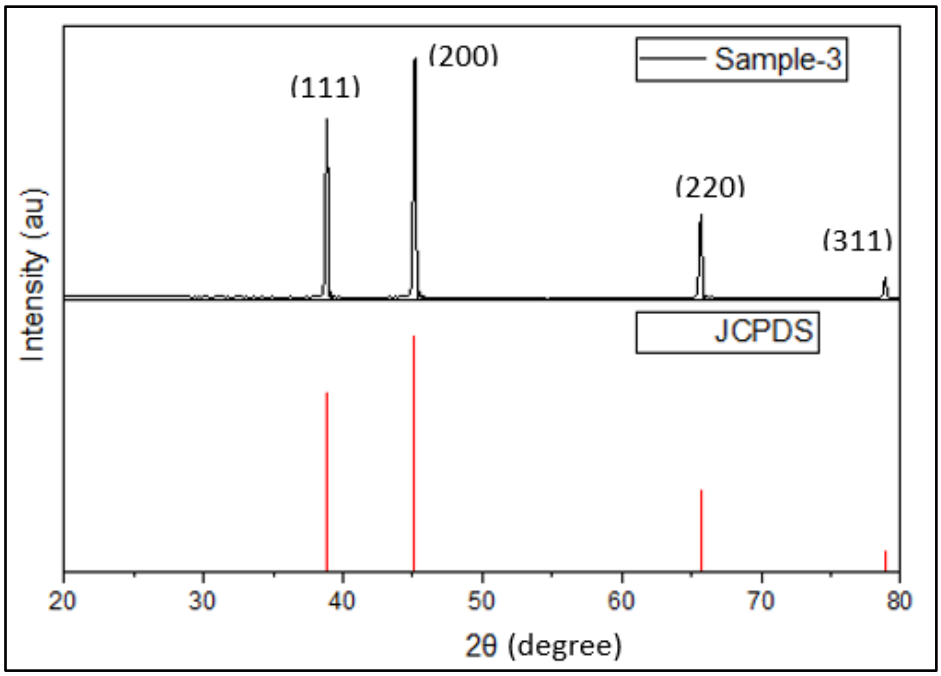


Figure 3: The XRD graph of sample-3 with standard JCPDS graph of LiF.

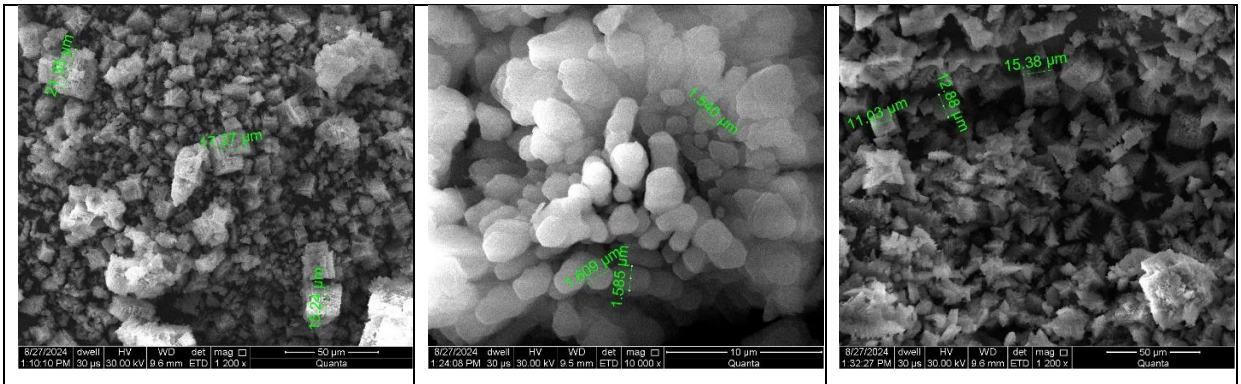
All three samples exhibit diffraction peaks corresponding to the face-centred cubic (FCC) structure of LiF, with the same Miller indices (111), (200), (220), and (311). The near-identical peak positions and sharpness across

the three samples imply that the crystalline phase remains stable across different solvent conditions. Minor variations in peak intensities and positions are likely due to differences in precursor-solvent interactions, evaporation kinetics, and gel formation behaviour, which can subtly influence the microstructural evolution during thermal processing.

The sharpness of the diffraction peaks across all samples indicates a high crystalline nature of the synthesized powders. No additional peaks were observed, implying the absence of impurity phases or unreacted precursors.

Furthermore, the calculated density values of the synthesized powders—2.65 g/cm³ for Sample 1 and Sample 3, and 2.64 g/cm³ for Sample 2—are consistent with the reported theoretical density of bulk LiF (~2.64 g/cm³), further supporting the formation of stoichiometric and pure LiF.

The surface morphology and microstructural features of the synthesized lithium fluoride (LiF) powders were investigated using Scanning Electron Microscopy (SEM). The SEM micrographs for all three samples—Sample 1, Sample 2, and Sample 3—are depicted in Figure 4. These images provide valuable insight into the particle size distribution, shape uniformity, and degree of agglomeration of the final products synthesized via the Sol-Gel route and subsequently calcined at 500°C



Sample: 1	Sample:2	Sample :3

Figure 4: The SEM images of samples 1,2 and 3.

The SEM image of Sample 1 reveals a heterogeneous microstructure with irregular particle shapes and sizes. The particle size distribution is relatively broad, ranging from 15.24 µm to 21.35 µm. The particles appear to be agglomerated, which is commonly observed in materials processed via the Sol-Gel method, especially when the drying and calcination processes induce particle clustering due to capillary forces and sintering. The relatively larger particle size in this sample suggests incomplete grain growth control or inefficient dispersion during gel formation.

In contrast, Sample 2 exhibits a homogeneous particle morphology, with uniformly sized and well-dispersed grains. The particle sizes are significantly smaller, ranging narrowly from 1.540 µm to 1.6409 µm, which is nearly an order of magnitude smaller than those of Samples 1 and 3. This fine and uniform morphology indicates a more efficient gel formation and particle nucleation process, likely due to the lower viscosity and higher volatility of ethyl alcohol as a solvent, which enhances molecular mobility and promotes uniform drying and decomposition. The absence of significant agglomeration in this sample also suggests a more favourable thermal decomposition profile of the gel, yielding finer LiF grains.

The SEM image of Sample 3 reveals a heterogeneous morphology, similar to Sample 1, with particle sizes ranging between 11.03 µm and 15.38 µm. The particles are irregular in shape and exhibit a moderate degree of agglomeration. Ethylene glycol, being a high boiling point and viscous solvent, tends to slow down gelation and solvent evaporation, which can lead to larger and less uniform particle sizes. This explains the intermediate particle size range of Sample 3 when compared to the other two samples. The morphology observed is indicative of less efficient control over nucleation and growth processes during synthesis.

Conclusion

The synthesis and characterization of lithium fluoride (LiF) powders using the Sol-Gel method with different polar organic solvents—acetic acid, ethyl alcohol, and ethylene glycol—have revealed critical insights into the influence of solvent choice on the phase purity, crystallinity, and microstructural features of the final product. X-ray Diffraction (XRD) analysis confirmed that all three samples exhibit sharp and well-defined diffraction peaks that align with the standard JCPDS data for LiF, indicating the successful formation of phase-pure, highly crystalline materials with a face-centred cubic (FCC) structure. The identical Miller indices (111), (200), (220), and (311) observed in all samples affirm the reproducibility and robustness of the Sol-Gel method for synthesizing LiF, irrespective of the solvent used. Minor shifts in peak positions and intensities reflect subtle variations in crystallite size and lattice strain arising from the differing solvent chemistries.

Complementary Scanning Electron Microscopy (SEM) analysis further demonstrated that the choice of solvent significantly affects the morphology and particle size distribution of the synthesized powders. While Samples 1 (acetic acid) and 3 (ethylene glycol) displayed heterogeneous structures with larger, irregular, and moderately agglomerated particles, Sample 2 (ethyl alcohol) exhibited a highly homogeneous morphology with the smallest and most uniform particle size distribution. The superior dispersion and fine particle formation in Sample 2 can be attributed to the lower viscosity and higher volatility of ethanol, which promote rapid gelation, uniform drying, and efficient thermal decomposition.

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