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Effect of Synthesis Temperature on Morphological and Luminescent Properties of Lithium Fluoride Crystals

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The precipitation method was used to synthesize pure lithium fluoride crystals using water as solvent at different synthesis temperature, from 10 to 90 °C. The effect of temperature on crystalline structure, sizes of cube like particles, and the luminescent response is reported. The synthesized materials were characterized by scanning electron microscopy and their morphology and size distributions were determined. Particle sizes were found to be dependent on the synthesis temperature, varying from 1.38 to 9.01 μm. A single cubic crystalline phase was determined by X-ray diffraction (XRD) for all synthesized samples. The photoluminescence (PL) spectra as well as UV-Vis absorbance were also analyzed and showed a clear dependence with the particle size. The thermoluminescent (TL) response to X-ray irradiation was studied for an exposition of 43 R. A TL intensity dependence of lithium fluoride crystals with the synthesis temperature is observed. The micro crystalline cube size can be controlled by varying the synthesis temperature.

Keywords: LiF Crystals, Synthesis Temperature, Luminescent Properties.

1. INTRODUCTION

Lithium fluoride (LiF) has become one of the most widely used materials for radiation dosimetry purposes. Many publications have reported the response of LiF in various radiation fields and a wide range of doses, as also the effect of different elements used as dopants.[1–5]

The response of LiF:Mg, Ti (TLD-100) has been extensively studied and compared with many other materials, such as LiF:Mg, Cu, P (TLD-100H).[6,7] Davis et al.[6] irradiated both materials using photon beams from cobalt-60 with energies from 25 to 1100 keV and found the TL responses to be markedly different in energy dependence. In other work Freire et al.[7] found that TLD-100 and TLD-100H present similar reproducibility and well linearity of results, however the TLD-100H shows a higher residual signal and less energy variation. Salah et al.[8] produced nanocrystalline LiF:Mg, Cu, P rods and studied their TL properties for gamma radiation at exposure level up to 10 kGy.

Some authors have paid attention to the dependence of the LiF crystal characteristics as well as the TL response on the preparation method.[9,10] In a recent paper Alharbi et al.[11] synthesized Ag doped LiF using a new chemical co-precipitation method. They used as co-solvent an ethanol:water mixture with different ratios, and found a dependence of the UV-Vis absorbance and photoluminescence response as well as the size of the crystals. The authors report micro and nano crystalline cubes whose size can be controlled between 10 μm–50 nm by varying the solvent:co-solvent ratio. They observed that the larger crystals were grown using water as a solvent, while by using ethanol as co-solvent, increasing ethanol concentration results in a reduced cube particle, down to the nanometric range.

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Also, Vallejo et al.[12] used the co-precipitation method to synthesize pure and Ag-doped LiF crystals and they reported the effect of crystalline cube sizes and Ag concentration on the TL response. They observed two effects, the first concerns with a significant dependence of the TL intensity on the size of the crystals, being larger for the smallest crystals for pure LiF, and second, for Ag-doped samples the TL intensity augmented almost linearly with the Ag concentration. They pointed out that the effect of grain size on the TL response could be explained by the increasing of specific area at the surface of lower grains, giving rise to an enhancement of TL properties as the grain size decreases, due to the fact that during the TL reading a larger area of material is exposed.

In the present work a precipitation method is used to synthesize pure LiF crystals by using different synthesis temperature to control the size of the particle products. The synthesized materials were characterized by XRD and scanning electron microscopy (SEM), and their structure, morphology and size distributions were determined. The effect of temperature on crystalline cube sizes and the luminescent response was investigated.

2. EXPERIMENTAL PROCEDURE

2.1. LiF Crystal Synthesis

Synthesis of LiF crystals was carried out by precipitation, using tri-distilled water as synthesis media. Samples were synthesized at five different temperatures, from 10 to 90 °C.

For the LiF synthesis, lithium chloride (LiCl) and ammonium fluoride (NH_4F) of analytical reagent grade purity were used as precursor materials. All syntheses were carried out using 3.84 N LiCl solution prepared in tri-distilled water. This solution was placed in a glass burette and then dropwise with continuous stirring during 1 hour on a 3.84 N NH_4F solution prepared in a plastic beaker. Each precursor material was dissolved in 50 mL water solvent for a total volume of 100 mL. Then, precipitates were filtered out and washed 25 times in tri-distilled water at room temperature. The final precipitated (about 5 g of LiF) was dried in a convection oven, model ED23 (Binder Inc., NY, USA) at 70 °C for 2 h.

2.2. Sample Characterization

2.2.1. Morphology Analysis

SEM analyses were performed using a scanning electron microscope Zeiss, EVO HD15 LS (Germany) to observe the crystals morphology. Before analysis, LiF crystal samples were metalized by gold sputtering in a Fine Coat Ion Sputter Jeol JFC-1100. The morphology of the samples was observed using secondary electron flux. The accelerating voltage was in the range 5–11 kV and the magnification was 4.00 kX. Particle size distribution was obtained by SEM image analysis using the ImageJ software.

2.2.2. XRD Analysis

The XRD properties of the samples were obtained using a Bruker D2 Phaser (Coventry, United Kingdom) diffractometer with Cu Kα radiation, which can measure a range of 2θ from 3° to 140°, using a voltage of 30 kV and a current of 10 mA. The samples were prepared by placing the crystals on silicon wafer. The analysis time was 20 min for each of the samples, using the value for 2θ in a range from 30° to 70°, and an increase of 0.020° every 0.5 s. For the analysis of the results, the software Difracc-Commander was used. For parameter interpretation of the spectra, the Difracc-EVA complementary software was used for database comparison.

2.2.3. UV-Vis Absorbance and Photoluminescence Analysis

The UV-Vis absorbance spectra of the samples were obtained using a Cary 5000 UV-Vis-NIR (Agilent Technology, Santa Clara, CA, USA) spectrophotometer, at room temperature. Spectra were recorded between 200 and 1100 nm. The samples were placed in a special container, which compressed the crystals forming a thin film. To avoid losses and to get a better response an integrating sphere was used.

Pellets were made with 4.5 g of LiF powders applying 1.5 tons on a pressing die of 13 mm diameter. Photoluminescence (PL) measurements were carried out by using a 75 W Xe lamp and an Acton Pro 1500i monochromator as excitation source in the 200 to 500 nm range. The fluorescence emission was analyzed with a second Acton Pro 2300i monochromator and a R955 Hamamatsu photomultiplier tube. The system was controlled with a PC where excitation and emission spectra were recorded.

2.2.4. Thermoluminescence Analysis

Thermoluminescent response of samples was measured using a TL Reader Harshaw 3500, Thermo Scientific (UK). First the dosimeters were annealed at 400 °C during 1 h, on a ceramic plate, using a muffle MA12D, Terlab (Mexico). For irradiation an X-ray machine Elity 70E RX-70KUP (C.I. Dental XRay S.A.S., USA) was used to apply 43 R of exposition. After irradiation dosimeters reading was held in an inert atmosphere of nitrogen. A preheat temperature of 50 °C, acquire temperature rate of 10 °C s^{-1} and maximum temperature of 300 °C were used for the glow curve acquisition.

3. RESULTS AND DISCUSSION

3.1. SEM Analysis

Figure 1 shows the synthesis temperature effect on the obtained LiF particle sizes. It is observed that the crystal cube size increases as the synthesis temperature increases. The mean sizes vary from 1.38 to 9.01 μm, as the temperature goes from 10 to 90 °C, respectively (see Table I).

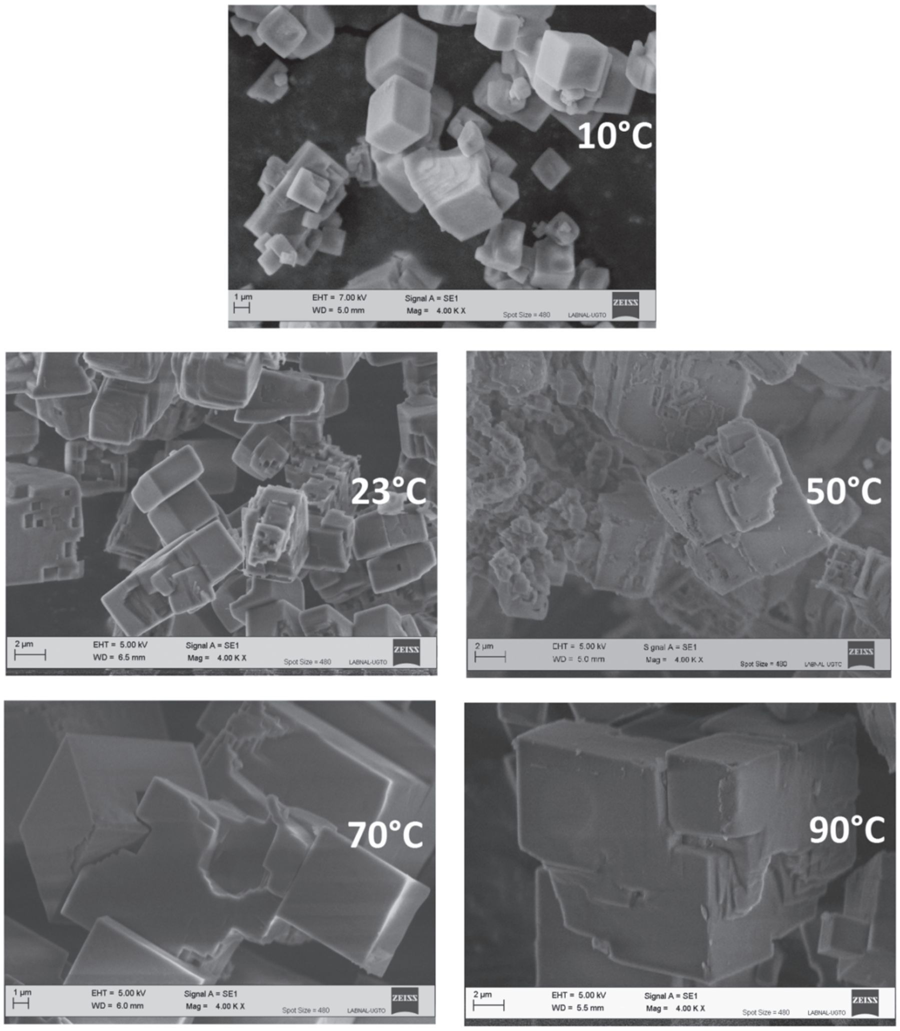

Figure 1. SEM images of pure LiF crystals synthesized at different temperatures.

These results can be compared to that reported using a precipitation method with a co-solvent ethanol:water as synthesis media.[11,12] The authors report that cube size can be controlled by varying the solvent:co-solvent ratio. In this work we have demonstrated that the cube size can be controlled varying the synthesis temperature and using just water as synthesis media. In both cases, the observed effect can be attributed to changes in solubility (due to temperature or solvent polarity modifications), which determines the crystal growth dynamics.

Table I. Mean size of LiF crystals as a function of synthesis temperature.

Sample	Temperature (°C)	Mean size (μm)	Standard deviation (μm)
T1	10	1.38	0.90
T2	23	4.10	1.40
T3	50	4.60	2.43
T4	70	8.90	3.73
T5	90	9.01	2.56

3.2. XRD Analysis

Figure 2 shows the XRD pattern for pure LiF samples synthesized at different temperatures. All curves show well defined peaks at $2\theta = 38°$, 45° and 66°. All samples show a complete cubic phase, however the peaks show slight changes according to the temperature of synthesis. In the curve T1 obtained at 10 °C, peaks are significantly wider than the others, which means either a small sizes of crystal or lower crystallinity grade (see Table II). The assumption of a small crystal size at lower temperatures is confirmed by the SEM analysis, where a mean size of 1.38 μm was obtained for the sample at 10 °C.

3.3. UV-Vis Absorbance and Photoluminiscence Analysis

Figure 3 shows the UV-Vis absorption spectra for LiF crystals synthesized using five different temperatures. A broad band centered in 436 nm is observed showing some dependence on the temperature. The results show a clear monotonic dependence of the intensity of the absorbance as a

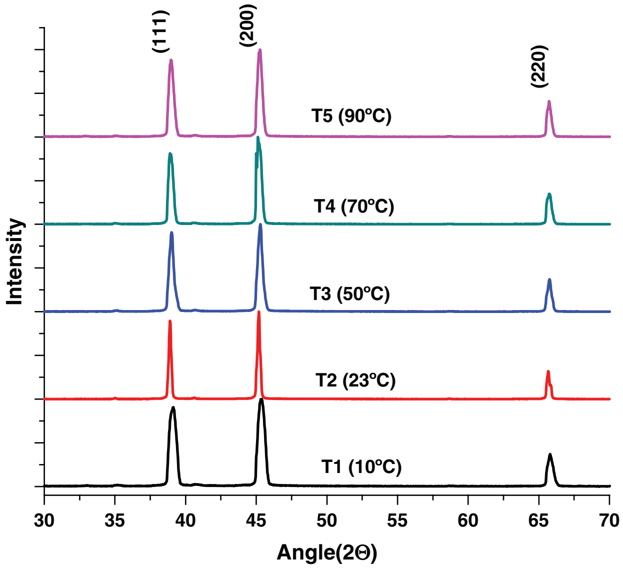

Figure 2. XRD pattern of pure LiF crystals synthesized at different temperatures.

Table II. Half widths of the peaks obtained by XRD and shown in Figure 2.

Sample	Half widths (angle 2θ)
T1 (10 °C)	0.606
T2 (23 °C)	0.237
T3 (50 °C)	0.422
T4 (70 °C)	0.422
T5 (90 °C)	0.448

function of the temperature of synthesis, which could be associated to the size of the crystals. The band observed in 436 nm is well known[13] to be characteristic of LiF, corresponding to F_2 color centers.

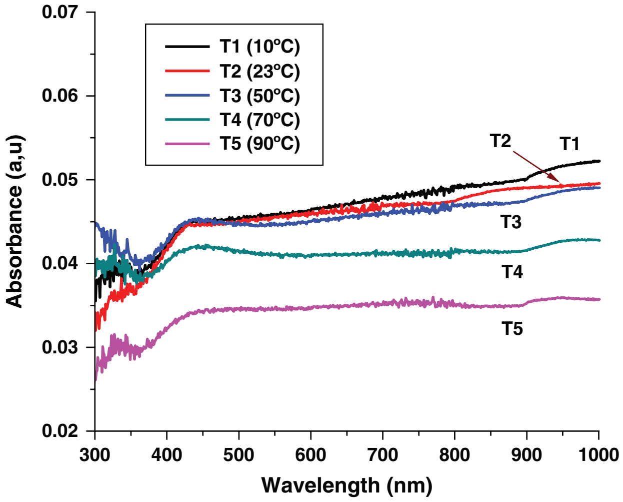

Figure 3. UV-Vis absorption spectra of pure LiF samples at different temperatures.

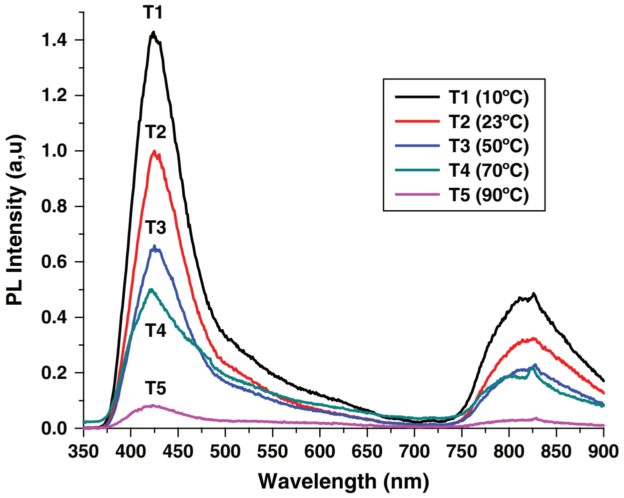

Figure 4. PL emission spectra of pure LiF samples at different temperatures.

PL emission spectra, under 325 nm excitation, of synthesized LiF samples using different temperatures are presented in Figure 4. The PL emission spectra shows two peaks corresponding to two emissions bands centered in 423 nm and 825 nm, respectively. Both peaks correspond to emissions due to intrinsic defects and aggregates, generated by F_2 color centers.

3.4. Thermoluminiscence Analysis

The TL response intensity of the synthesized crystals was measured for an exposition of 43 R using an X-ray source during a total time of 52 s. Figure 5 shows the glow curves for pure LiF crystals synthesized at different temperatures. A TL peak at 230 °C is observed in all cases, except for the sample at 90 °C, which is shifted to 212 °C. No significant differences were observed in the glow curve structure, neither in the characteristic energy, since all glow curves exhibit a single peak around the same temperature, about 200 °C. However, the smallest crystals, (1.38 μm), corresponding to samples synthesized at 10 °C show the highest

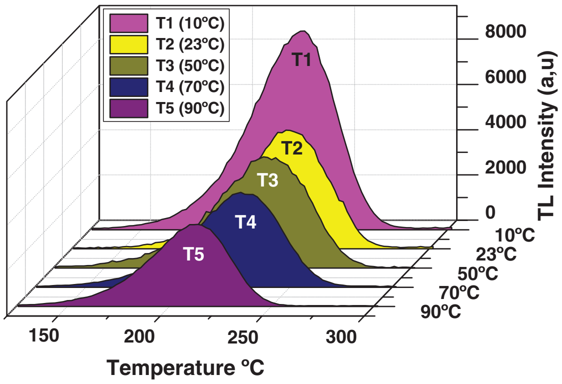

Figure 5. TL intensity curves of pure LiF synthesized at different temperatures.

intensity, which could be explained by the increasing of specific area at the surface of lower grains, giving rise to an enhancement of TL properties as the grain size decreases, due to the fact that during the TL reading a larger area of TL material is exposed.[12]

4. CONCLUSIONS

Undoped LiF crystals were synthesized and the effect of temperature on crystalline cube sizes was studied. We found a clear dependence of the crystal size on the synthesis temperature. We found that the mean crystal size increases as the synthetization temperature increases. This dependence can be attributed to changes in solubility due to the temperature, which favors different dynamics of crystal growth. No changes were observed in the morphology beyond the difference in crystal size.

The PL emission and the UV-Vis absorbance spectra show a clear dependence on crystal size. Both the UV-Vis absorbance and the emission increases as the crystal size decreases. The TL response to X-ray irradiation was also studied for an exposition of 43 R.

A thermoluminescent intensity dependence of lithium fluoride crystals with the synthesis temperature was observed. Also, it is important to stress the relevance of having a synthesis method that is simpler than when using co-solvents as synthesis media.

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