

Role of Secondary Nucleation on Structural and Optical Properties of Rare-Earth Doped Nanoparticles Morphed via Ionic Liquids

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Abstract

Herein, phase pure, template free rare-earth ($\text{RE}^{3+} = \text{Eu}^{3+}, \text{Ce}^{3+}$) doped BaF_2 nanoparticle are synthesized using ionic (IL) liquid assisted solvothermal method. Here IL is used not only as capping/templating agent but also sometime as a reaction partner. As-prepared cubic shaped $\text{BaF}_2:\text{Eu}^{3+}$ nanoparticles are calcined at different temperatures such as 200°, 400° and 800°C. Interestingly, lattice strain, morphology and optical property are drastically changed at 800°C. Lattice strain is changed from tensile to compressive strain beyond 400°C calcinations temperature. At high temperature, cubic-shaped morphology is changed to step like structure due to secondary nucleation. Thereafter, photoluminescence excitation and emission intensities are completely vanished at 800°C. Thermally stimulated luminescence (TSL) and thermally stimulated exo-electron emission (TSEE) measurements are performed to understand the role of defects in luminescence quenching.

Rare-earth doped nanomaterials have been getting tremendous attention for last decades for several applications including the optoelectronic, magnetic and in vivo/in vitro bio-imaging applications. Unlike semiconducting and organic based nanomaterials, rare-earth doped nanomaterials show size independent optical properties. However, photophysical processes of RE^{3+} doped nanomaterials are considerably dependent on the host matrix, crystal phase, morphology and core-shell structure. Amongst various host materials, fluoride based host materials are considered as better candidate for the doping of RE^{3+} ions due to high thermal and chemical stability, high refractive index and large band gap.

For obtaining the fluorides based nanomaterials various synthesis strategies have been developed like solvothermal, hydrothermal, micro-emulsion, thermal decomposition method, IL assisted and so on. ILs are preferably considered over the conventional molecular solvents due to negligible vapor pressure, high thermal stability, large liquidus range and large electrochemical window. Their physical and chemical properties can credibly be tuned by changing the alkyl chain length, cation-anion combinations and viscosity. In this way, ILs are also accepted as “green and designer” solvent. In case of nanomaterials designing, ILs are not only employed as reaction medium and capping/templating agent, however can also be utilized as reaction partner. For instances, BF_4^- and PF_6^- possessed ILs are used as fluorinating agent in synthesis of RE^{3+} doped binary/ternary fluorides nanoparticles. These anions (BF_4^- and PF_6^-) containing ILs on hydrolysis at high temperature, release the F^- ions in solution due to weakly coordinating cationic counter ion.

Herein, 1% Eu^{3+} doped BaF_2 nanoparticles are prepared using task specific $[\text{C}_2\text{mim}]^+\text{Br}^-$ IL at 150°C for 3 hours reaction time. In addition, 0.1% Ce^{3+} doped BaF_2 nanoparticles are also prepared by using $[\text{C}_4\text{mim}]^+\text{BF}_4^-$ IL, where ILs are not only used as a reaction partner but also as a fluorinating agent. Thereafter, as-prepared nanoparticles were calcined at different temperatures such as 200°, 400° and 800°C and then studied the structural and optical properties of as-prepared and calcined materials using PXRD, SEM, TEM and spectrofluorometer. There are

significant changes in lattice strain, morphology and optical properties of the calcined nanoparticles are noticed. PXRD results indicate that as-prepared bare and $\text{BaF}_2:\text{Eu}^{3+}$ nanoparticles with or without IL synthesized are pure cubic phase. PXRD patterns are evidently matching with JCPDS card no-C4-452 (Figure 1).

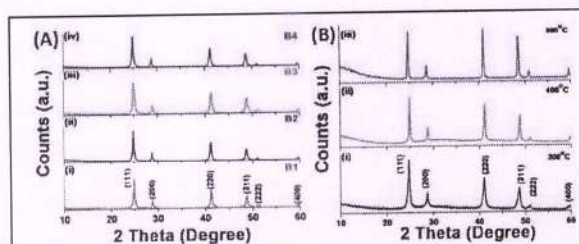


Figure 1. (A) PXRD patterns of as-prepared nanoparticles: i) BaF_2 without IL, ii) BaF_2 with IL, iii) $\text{BaF}_2:\text{Eu}^{3+}$ with IL and iv) $\text{BaF}_2:\text{Eu}^{3+}$ without IL; (B) PXRD patterns of calcined $\text{BaF}_2:\text{Eu}^{3+}$ nanoparticles prepared using $[\text{C}_2\text{mim}]^+\text{Br}^-$ IL: i) 200°C, ii) 400°C and iii) 800°C.

In addition, there is no change in crystal phase of calcined nanoparticles which is appearing with increasing the calcination temperature (Figure 1B). It means BaF_2 host matrix is thermally stable even at 800°C (Figure 1B). It is found that crystallite size of bare BaF_2 nanoparticles with no IL are bigger compared to the BaF_2 nanoparticles prepared using IL (Table 1). From this it is clearly evident that IL is acting as a capping/templating agent.

Lattice strain results depict that tensile strain of bare BaF_2 (B2) and $\text{BaF}_2:\text{Eu}^{3+}$ (B4) nanoparticles synthesized using IL have more tensile strain than that of BaF_2 (B1) and $\text{BaF}_2:\text{Eu}^{3+}$ (B3) nanoparticles which are synthesized without IL. Moreover, lattice strain of $\text{BaF}_2:\text{Eu}^{3+}$ nanoparticles with IL which are calcined at different temperatures are also determined. Results reveal that tensile strain is obtained till 400°C and then compressive strain is found for nanoparticles which are calcined at 800°C (Figure 2B and Table 1).

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