Ionic Liquid Based Synthesis of Quantum Cutting $NaGdF_4$ Nanocrystals and their Spontaneous Phase Transition

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Abstract

Herein imidazolium based ionic liquids with tunable alkyl chain length are employed to prepare Eu^{3+} doped $NaGdF_4$ nanocrystals with tunable shape, morphology and most importantly crystal phase. Hexagonal $NaGdF_4$ nanoparticles are obtained when 1-ethyl-3-methylimidazolium bromide ILs[C_2mim]Br is used. However, in case of ionic liquids with longer alkyl chains such as butyl, octyl or decyl extremely small nanoparticles of the cubic polymorph form, which then convert even at room temperature to the thermodynamically stable hexagonal modification. The hexagonal nanomaterial shows a substantial quantum cutting efficiency (154%) whilst in the cubic material, the effect is negligible.

Energy efficient and environmentally benign lighting devoid of mercury is the need of the hour. Though compact fluorescent lamps (CFLs), which consume less energy and have a longer rated life replaces classic incandescent lamps successfully but it also uses Hg as discharge medium. Environmentally benign noble gases, such as Xe can be an alternative to Hg, butgreater energy loss during conversion of the shorter wavelengths to visible light, and the lower discharge efficiency of Xe compared to Hg, limits its application. But phosphors exhibiting quantum yields greater than 100% may be useful to make Xe-based CFLs competitive. This can be achieved by a two-photon down-conversion process based on a combination of two different rare-earth ions, *i.e.* Gd^{3+} and Eu^{3+} in $NaGdF_4$:Eu^{3+}, where the excitation energy is transferred via a two-step process from the quantum cutter (Gd^{3+}) to the emitting ion (Eu^{3+}), resulting in the emission of two visible photons.[1,2]

On the other hand, ionic liquids (ILs)which are normally described as "green" and "designer solvents" draw a tremendous attention in academia and industries.[1-2]Normally ILs are composed of distinct cations and anions and they are a widely tunable class of compounds with interesting properties like negligible vapor pressure, wide liquidus range, good thermal stabilities, considerable electrical conductivities and wide electrochemical window. Though they are extensively used in organic catalysis, electrochemistry, f-element separation and many other applications, their use in inorganic materials synthesis has just begun but holds great promises.[1-2]

Here, an easy, yet highly phase selective synthesis of oxygen free Eu^{3+} doped $NaGdF_4$ nanocrystals with high quantum cutting efficiency is presented. Synthesis only needs stirring an aqueous solution of the starting materials and a task-specific IL such as [C_2mim]Br (1-ethyl-3-methyl imidazolium bromide) for one hour at room temperature. This synthesis protocol not only meets with the requirements of "Green Chemistry" but also offers the possibility of easy scale-up for industrial manufacturing. Tuning of the crystal phase of $NaGdF_4$ can be achieved even at room temperature by judiciously choosing the IL. The extremely small, less thermodynamically stable nanoparticles of $NaGdF_4$spontaneously convert at room temperature without applying external stimuli like heating to the thermodynamically more stable hexagonal phase which also has the higher quantum efficiency.

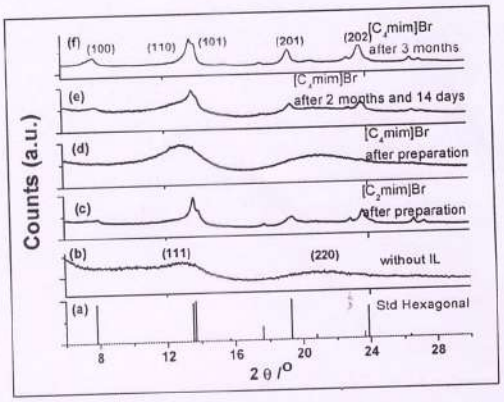

Figure 1: (a) Hexagonal database pattern (JCPDS card no-27-699), b) doped $NaGdF_4$: Eu^{3+} prepared without IL, c) in presence of 1.0 mol% [C_2mim]Br at RT, d)) in presence of 1.0 mol% [C_4mim]Br at RT, e and f) $NaGdF_4$:Eu^{3+} doped sample in presence of [C_4mim]Br but measured after 2 months 14 days and 3 months respectively.

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