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## Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)

## Recent trends in binary and ternary rare-earth fluoride nanophosphors: How structural and physical properties influence optical behavior

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## ARTICLE INFO

## Article history:

Received 19 May 2016

Received in revised form

1 February 2017

Accepted 15 March 2017

Available online 28 March 2017

## Keywords:

Rare-earths

Rare-earth fluoride

Luminescence

Nanomaterials

Photonics

## ABSTRACT

Rare-earth (RE) doped binary and ternary fluoride nanomaterials are currently receiving the highest attention as phosphor materials due to their potential for a wide range of photonic and biophotonic applications. This review article aims providing and introduction to the field and giving a critical overview about the latest developments in this fast evolving field. First, the underlying photoluminescence mechanisms like up- and downconversion (UC and DC), charge transfer (CT) and energy transfer (ET) between optically active trivalent RE ions are explained. Then, the influence of particle size and surface, shape and lattice strain, as well as the crystal phase of the host materials on the optical properties of rare earth based nanomaterials are illustrated. In addition, the effect of surface plasmon resonance (SPR) on the rare earth luminescence is discussed. In the following, different synthesis strategies which have been developed for tuning the crystal phase, shape, size, and morphology of the host nanomaterial are presented. The role of surface modification and functionalization for improving the luminescence intensity, stability, aqueous dispersity/dispersibility and biocompatibility of the materials is discussed. Finally, photonic applications of RE-doped nanofluorides for energy efficient lighting, improved solar cells and biophotonic applications like photodynamic therapy, and biological detection techniques including *in vivo* and *in vitro* bioimaging are presented.

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## Contents

1. Introduction	45
2. Photophysics of trivalent rare earth materials	46
2.1. Direct excitation, energy transfer and charge transfer transition	46
2.2. Quantum-cutting downconversion	48
2.3. Upconversion	48
3. Host materials for luminescent RE <sup>3+</sup>	49
4. Synthesis of binary and ternary RE-fluoride nanoparticles	49
4.1. Thermal decomposition	49
4.2. Hydro/solvothermal method	49
4.3. Co-precipitation method	50
4.4. Microemulsion method	50
4.5. Microwave assisted synthesis	50
4.6. Sonochemical method	50
4.7. Ionic liquid assisted synthesis	51
4.8. Other methods	51
5. Nanoparticle surface modification including functionalization	51

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5.1.	Surface passivation	51
5.2.	Surface functionalization	51
5.2.1.	Amphiphilic polymer based surface derivatization	51
5.2.2.	Silica-coated surface protection	52
5.2.3.	Layer-by-layer assembly	52
5.2.4.	Others	52
6.	Crystal phase, shape and lattice strain	52
6.1.	Tuning of crystal phase and shape	52
6.1.1.	Effect of temperature	52
6.1.2.	Effect of ionic radii	52
6.1.3.	Effect of reactants and synthesis methods	53
6.1.4.	Effect of chelating agent/ligand	53
6.1.5.	Effect of the ionic liquid	54
6.1.6.	Effect of solvent composition	54
6.1.7.	Effect of doping	54
6.2.	Tuning of lattice strain of fluoride host materials	54
7.	Tuning of luminescence properties	54
7.1.	Effect of crystal phase on luminescence	54
7.2.	Effect of core-shell structure on luminescence	55
7.3.	Effect of morphology on luminescence	56
7.4.	Effect of choices of dopant ions on luminescence	56
7.5.	Temperature dependent measurements and other factors	57
7.6.	Tuning of upconversion emission via surface plasmon resonance (SPR)	57
7.7.	How to increase and calculate upconversion quantum yield?	57
8.	Applications	57
8.1.	Photonic applications	57
8.1.1.	Efficient white light emitting materials	57
8.1.2.	Quantum-cutting phosphors for energy efficient lighting and plasma display applications	58
8.1.3.	Upconversion materials and solar cells	59
8.2.	Biophotonic applications	59
8.2.1.	Photodynamic therapy	59
8.2.2.	FRET based and other biological detection	59
8.2.3.	<i>In vivo</i> and <i>in vitro</i> imaging	60
9.	Conclusions and perspectives	61
	Acknowledgements	62
	References	62

## 1. Introduction

Rare-earth (RE) doped nanocrystals have been recognized to hold tremendous promises as luminescent materials for photonic and biophotonic applications [1–8]. The photoluminescent properties of trivalent RE-doped materials are dominated by electronic intraconfigurational  $f-f$  transitions of the RE ion [4]. As the  $4f$ -orbitals of the RE ions are well shielded by the filled  $5s^25p^6$  orbitals, the intraconfigurational transitions are largely independent of the environment. And, unlike in semiconductor nanoparticles, immediate particle size effects affecting the electronic transitions such as quantum confinement cannot be observed for nanocrystals doped with trivalent RE ions. However, for nanomaterials the luminescence dynamics of the trivalent RE ion can be effectively influenced by the particle size, surface, morphology, strain and crystal phase (Fig. 1) [9–14].

For certain applications RE-based phosphors bear some advantages over other classes of the luminescent materials such as organic dyes or semiconductor quantum dots. RE-doped fluorides can be used like organic dyes and semiconductor nanoparticles for biolabelling, drug delivery as well as in (bio-)imaging [15,16]. However, organic dyes generally suffer from photo-instability, chemical degradation, and cannot be attached to the cell for a long period. Another major limitation of organic dyes are their broad absorption and emission bands. These properties limit the application of an organic dye for biological imaging purposes. Semiconductor quantum dots have a higher photostability compared to organic dyes. Furthermore, their emission bands are narrower and the emission colour and quantum yield can be tuned by the

particle size. Yet their bio-application is limited due to the inherent toxicity of most materials [17]. For the excitation of semiconductor materials, normally UV or short wavelength visible light is used; but biological samples often show autofluorescence in this spectral range. In addition, living organisms suffer severe damages upon irradiation with high energy UV light. Many of the outlined drawbacks of organic dyes and semiconductor nanoparticles can be overcome in RE-doped materials. Their advantage lies in the unprecedented photostability, high chemical robustness and low toxicity. RE-doped fluorides also feature narrow excitation and emission bands due to the intraconfigurational  $f-f$  electronic transitions. In addition, the longer lifetime (up to milliseconds) of the excited states makes time-resolved detection possible which is very important for luminescence microscopy and biosensing [18–20]. For all these reasons, RE<sup>3+</sup>-doped binary and ternary fluoride nanoparticles are currently receiving a tremendously growing interest.

In this review article, the developments of trivalent RE<sup>3+</sup>-doped binary and ternary fluoride nanoparticles that took place in the last decade will be discussed. After a short introduction to the photophysics of trivalent RE ions, we will discuss suitable host materials. Then a variety of recently developed synthesis protocols which allow a precise control on shape, size, morphology, lattice strain and crystal phase of the host materials which allow for a decisive tuning of the luminescence of the doped RE<sup>3+</sup> ions will be presented.

Lately, it was realized that surface modification including passivation and functionalization is an effective tool not only to enhance the luminescence efficiency but also to make the

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