

Article



Towards a Correlation between Structural, Magnetic, and Luminescence Properties of CeF3:Tb³⁺ Nanocrystals

Cristina Bartha, Corina Secu, Elena Matei, Catalin Negrila, Aurel Leca and Mihail Secu *

National Institute for Materials Physics, 077125 Magurele, Romania; cristina.bartha@infim.ro (C.B.); cesecu@infim.ro (C.S.); elena.matei@infim.ro (E.M.); cnegrila@infim.ro (C.N.); lec.aurel@gmail.com (A.L.)

* Correspondence:msecu@infim.ro

Received: 1 June 2020; Accepted: 29 June 2020; Published: 3 July 2020

Abstract: In this study, we report on the structural, magnetic, and optical properties of Tb³⁺-doped CeF₃ nanocrystals prepared via a polyol-assisted route, followed by calcination. X-ray diffraction analysis and electron microscopy investigations have shown the formation of a dominant Ce_{0.75}F₃ nanocrystalline phase (of about 99%), with a relatively uniform distribution of nanocrystals about 15 nm in size. Magnetization curves showed typical paramagnetic properties related to the presence of Ce³⁺ and Tb³⁺ ions. The magnetic susceptibility showed a weak inflexion at about 150 K, assigned to the cerium ions' crystal field splitting. Under UV light excitation of the Ce³⁺ ions, we observed Tb³⁺ green luminescence with a quantum yield of about 20%.

Keywords: fluorides; nanocrystals; structure; magnetism; photoluminescence

1. Introduction

Rare-earth-doped nanofluorides are of great interest due to their high potential for application in various fields, e.g., lighting and displays, optical amplifiers, lasers, up-converters, and scintillators ([1–3] and references therein). Nanomaterials showing both luminescence and magnetic characteristics in particular are useful for a wide range of applications, such as multifunctional imaging and simultaneous diagnosis and therapy [4,5].

Among different inorganic fluorides, CeF₃ is one of the most versatile due to its wide range of bulk properties, such as high thermal and chemical stability, high density and resistance to radiation, fast response time, low vibrational energies, etc., and chemical flexibility of the structure allowing high solubility of rare-earth dopant ions. Another major advantage of this compound is related to the large spectrum of possible preparation methods, allowing for its processing in various sizes and morphologies, down to the nanometer scale. The bulk CeF₃ crystal has a hexagonal phase structure: a space group of P3c1 (D_{3d} ⁴) with lattice constants a = 0.713 nm and c = 0.729 nm [5]. It exhibits efficient UV absorption due to the allowed electric dipole 4f→5d transition of Ce³⁺ ions and energy transfer to other rare-earth activators, which is useful for white LED phosphor applications [6–8]. In particular, various synthesis methods have been proposed for Tb3+-doped CeF3 nanocrystals, and the photoluminescence properties and energy transfer mechanism have been extensively investigated [9–12]. A less-studied aspect is related to the magnetic properties, which are strongly correlated with its electronic structure, whereas for the rare-earth dopant ions, these are related to the unpaired electrons in the inner 4f sub-shell. Investigations of the magnetic behavior of CeF₃ crystals are relatively limited and have been described within several models: crystal field theory [13], mixedvalent Ce3+-Ce4+ behavior [14], or super-exchange interaction of cerium ions [15]. Recent investigations of CeF3 nanodisks have revealed an anomalous behavior of the magnetic susceptibility at T \cong 50 K, assigned to the processing-related defects and/or size effects [13–16].

The synthesis route may influence nanocrystals' structure through synthesis-induced defects, but to date, there has been little focus on the structural refinement analysis, and the mixed valency behavior of the cerium ions has been overlooked [17]. These aspects are crucial to understanding the interaction mechanisms relevant for both optical and magnetic properties, and their improvement for possible applications. In addition, the high ratio of ions at the surface (with unsaturated coordination), and the periodicity loss on the surface, result in structural modifications and defects that may affect all the properties, and therefore, knowledge of the nanocrystals' surface properties is highly relevant. The absolute novelty of this study derives from two aspects: (i) the complex structural analysis of terbium-doped cerium fluoride nanocrystals and its correlation with the influence of the material processing method, and (ii) the investigation of the specific magnetic behavior of the nanocrystals.

Herein, we report on the structural, magnetic, and optical properties of Tb³⁺-doped CeF₃ nanocrystals prepared via a polyol assisted route. X-ray diffraction and electron microscopy techniques have been used for the structural and morphological characterization of the nanocrystals, whereas photoelectron spectroscopy was employed for the nanocrystals' surface analysis. Magnetic and optical properties (e.g., photoluminescence, quantum yield) have been presented and discussed.

2. Materials and Methods

2.1. Samples Preparation

For the preparation of Tb (8 mol%)-doped CeF₃ nanocrystalline powders, we used the chemical precipitation technique at room temperature mediated by the ethylene glycol solvent, similar to [18]. The raw materials Ce(NO₃)₃ · 6H₂O (99.5%), Tb(NO₃)₃ · xH₂O (99.9%), NH₄F (99.99%), and anhydrous ethylene glycol (99.8%) were used for the synthesis. Initially, a first solution was prepared by dissolving 0.102 g of NH₄F into 10 mL of ethylene glycol. Then, 0.3261 g Ce(NO₃)₃ · 6H₂O (99.5%) and 0.0358 g Tb(NO₃)₃ · xH₂O (99.9%) were dissolved into 5 mL of ethylene glycol. This second solution was slowly dropped into the first one, and the mixture was stirred for 1 min at room temperature until a transparent colloidal solution had formed. At the end, the nanoparticles were isolated by centrifugation of the colloidal solution, washed to remove the remaining reagent, and dried at 80 °C in air. Further annealing of the CeF₃:Tb powder was performed in open atmosphere for 1 h at 400 °C.

2.2. Samples Characterization

For the X-ray diffraction (XRD) measurements, we used a BRUKER D8 ADVANCE (Billerica, Massachusetts, USA), type X-ray diffractometer. The XRD pattern was recorded in the 20 to 60° range with 0.05° step and 3 s integration time. For the phase composition analysis and crystal structure refinement, we used the Rietveld method and a dedicated software (MAUD) [19,20], and starting parameters from PDF 04-005-7362 (Ce0.75F3) and PDF 00-008-6551 (CeO1.66) files from the ICDD Powder Diffraction Files database [21]. The morphology of the samples was studied using a Zeiss MERLIN (Jena, Germany) Compact scanning electron microscope (SEM) with a GEMINI column, whereas for the chemical composition analysis, we used an EVO 50 XVP microscope from Zeiss equipped with an energy dispersive X-ray system (EDX) Quanta Bruker 200. For the magnetic properties' characterization, we used a superconducting quantum interference device (SQUID), and we measured the sample magnetization dependence on both magnetic fields up to 3 T, and on temperatures ranging from 5 to 300 K. A powder sample (17 mg) of CeF₃:Tb³⁺ was measured using a standard capsule, and its magnetic contribution (about 4%) was subtracted from the total magnetic signal. The temperature dependence of the magnetic susceptibility was measured under magnetic fields of 0.1 and 5 T applied perpendicularly to the sample. For the XPS measurements, we used a multianalysis SPECS system dedicated to surface analysis, equipped with a non-monochromatic source that provides a uniform X-Ray flux on the sample surface. The electron analyzer was a PHOIBOS150, with a 150 mm radius and a multichanneltron detector operating in large area mode and very low angular acceptance of 5° around the normal. The spectra of C1s, O1s, Ce3d, F1s, Tb3d, and Tb4d lines were recorded using a Pass Energy of 10 eV, while the extended spectrum was

recorded using a Pass Energy of 50 eV. For the spectra fitting and analysis, we used the Spectral Data Processor v.2.3 software (XPS International, Marlborough, Massachusetts, USA) and Voigt functions. In order to minimize the contamination, the XPS spectra were recorded on freshly calcinated samples after having been stored for 24 h in the high vacuum chamber. For the photoluminescence (PL) spectra, we used a FluoroMax 4P spectrophotometer (HORIBA Jobin Yvon, Kyoto, Japan); the spectra were corrected for the spectral sensitivity of the experimental set-up. The chromaticity analysis and quantum yield characterization were performed using the Quanta-Phy accessory of the spectrophotometer".

3. Results and Discussion

3.1. Structural and Morphological Characterisation

The XRD pattern of the CeF₃:Tb nanocrystalline powder calcinated at 400 °C is depicted in Figure 1; the results of the Rietveld analysis are presented in Figure 1 and Tables 1 and 2. The analysis showed the presence of a dominant Ce_{0.75}F₃ crystalline phase (of about 98.7%), accompanied by a much smaller CeO_{1.66} crystalline fraction (of about 1.2%), both stable at room temperature. The formation of Ce_{0.75}F₃ as a dominant crystalline phase is the consequence of the synthesis and processing conditions that result in a material with defects and multiple fraction valencies of cerium ions [17]. The lattice parameters are very close to those from the ICDD database (Table 1), and the nanocrystallite's size agrees very well with SEM microscopy data (see below).



Figure 1. XRD pattern (black curve) and Rietveld refinement plot (red curve) of CeF₃:Tb nanocrystalline powder calcinated at 400 °C, with the Bragg reflections for Ce_{0.75}F₃ and CeO_{1.66} crystalline phases indicated by vertical bars; the lower trace represents the difference curve between observed and calculated patterns.

From Table 2, it can be observed that the positions of the Ce³⁺ ions and their first neighbor (F₁ ions) are slightly shifted compared to the reference. As the Tb³⁺ ions ionic radius (R = 1.095A) is smaller than that of Ce³⁺ ions (R = 1.196A), a substitutional incorporation is very likely; the photoluminescence spectra showed a crystal-field structure of the Tb³⁺ luminescence bands (see below). However, the XRD pattern analysis has shown small changes in the cell parameters (Table 1), and therefore, a partial interstitial incorporation of Tb³⁺ ions cannot be completely rejected. The microstrain values for both phases indicated different values of the distances between the crystallographic planes, which can be related to the lattice defects produced during the synthesis and lattice distortion induced by the Tb³⁺ ions' incorporation into the Ce_{0.75}F₃ crystalline lattice.

Crystalline Phase	Cerium Fluoride (Ce0.75F3)	Cerium Oxide (CeO _{1.66})	R Factors (%)
Weight fraction (%)	98.798 ± 0.001	1.2017 ± 0.002	
Crystal size (nm)		13.985(2)	
Crystal system	Hexagonal	Cubic	
Space group	P-3c1	Fm-3m	
	a = b = 7.1053(3)	a = 5.415(1)(2)	
Calculated Offit Cell (A)	c = 7.2614(1)		$D_{(0/)} =$
Cell_angle_alpha	90°	90°	$K_{wp}(7_0) =$
Cell_angle_beta	90°	90°	2.994 R _B (%) = 2.358
Cell_angle_gamma	120°	90°	
Unit Cell according PDF (Å) (ref.	a = b = 7.1 $a = b = 5.4112(10)$		$K_{exp.} = 1.015$
[21])	c = 7.27		$\chi^2 = 2.049$
Cell Volume (Å ³)	317.38 (3)	158.45(1)	
Microstrain	$1.7 \times 10^{-5} \pm 0.002$	$2.3 \times 10^{-6} \pm 0.001$	

Table 1. Rietveld refinement results for Tb3+doped CeF3 nanocrystalline powders calcinated at 400 °C.

Table 2. Atomic site occupancy for Tb³⁺doped CeF₃ nanocrystalline powders.

Atoms	Ce0.75F3 (calc.)	Ce0.75F3 (theor.)	Ce0.75F3 (calc.)	Ce0.75F3 (theor.)	Ce0.75F3 (calc.)	Ce0.75F3 (theor.)	Wyckoff Site	Atom Site Occupancy (theor/calc)
	x		у		Z			
\mathbf{F}_1	0.3862(3)	0.356	0.3610(4)	0.328	0.0712(3)	0.096	12g	1/0.8393(5)
Ce	0.3394(5)	0.3333	0	0	0.2504(1)	0.25	6f	0.75/0.7503(2)
F3	0.3334(2)	0.3333	0.6671(5)	0.6666	0.2267(3)	0.167	4d	1/0.9851(5)
F_4	0	0	0	0	0.2497(2)	0.25	2a	1/0.9877(4)

The SEM image analysis has shown a distribution of round-shaped nanoparticles of about 15 nm in size (Figures 2 and 3). Chemical composition analysis resulting from the EDX spectra (Figure 3) has shown a relative agreement (within the experimental errors) between the atoms' concentrations in the precursor chemicals and in the annealed samples: 14 at%(Ce), 79 at%(F), 1.5 at%(O), and 1.5 at%(Tb).



Figure 2. SEM image of CeF3:Tb nanocrystalline powder calcinated at 400 °C.

It can be seen that the F to Ce ratio (of about 5.5) is relatively close to the four expected for $Ce_{0.75}F_3$ phase (Table 1), but higher than the three expected for CeF₃, indicating Ce³⁺ ion deficiency and lower Tb³⁺ ion concentration than expected; XRD analysis has shown Ce_{0.75}F₃ phase, i.e., Ce³⁺ ion deficiency. We suppose that the reason is related to the NH₄F amount used for the synthesis, since it plays a critical role in controlling the final morphology and size of the product [11]. In the present case, for

size (Figure 2) with Ce³⁺ ion deficiency as resulting from the EDX and XRD analyses (Table 1 and Figure 3), this aspect having been overlooked by previous studies. The Ce³⁺ ion deficiency suggested that a higher NH₄F amount is required to accomplish the reaction and the Tb³⁺-doping process. However, for higher NH₄F content, different nanocrystals morphologies were obtained with hundreds of nm in size, accompanied by crystallinity and luminescence signal improvement [11]. Therefore, by using a stoichiometric NH₄F amount, we obtained nanocrystals "with defects", i.e., a Ce_{0.75}F₃ nanocrystalline phase with lower "effective" Tb³⁺ ions' dopant concentration.



Figure 3. Nanocrystals size distribution (**left**) and the corresponding energy dispersive X-ray (EDX) analysis with the characteristic X-ray lines assignment (**right**); the dotted curve is just a guide for the eyes.

3.2. X-ray Photoelectron Spectroscopy (XPS) Characterization

For the investigation of the nanocrystals' surface, we used the XPS technique, which is recognized as a valuable investigation tool for the chemistry associated to different bonds and related compounds ([22] and references therein).

Figure 4 shows different spectral lines of the XPS spectrum of CeF3:Tb nanocrystalline powder annealed at 400 °C. The region between 880 and 925 eV was assigned to the Ce3d line of the Ce³⁺ ion species, and the energies indicate Ce-F bonds [23]. The XPS spectrum is composed of several convoluted peaks that correspond to the Ce 3d^{5/2} and 3d^{3/2} lines, and each of them is split into two lines due to the multiplet splitting effect arising from the two possible states after photoionization: 4f¹ and 4f². The 884.57 and 902.97 eV peaks were due to the 4f² final state, whereas the others at 888.12 and 906.38 eV were due to the 4f1 final state. The 899.05 and 918.11 eV peaks were assigned to the "loss" type peaks due to the energy transfer from the F2p orbitals to the conduction band orbitals of Ce (4d,5d,6s) [24,25]. The CeF₃ nanocrystalline phase was revealed by the strong single F1s peak at 685.20 eV, in connection to the Ce 3d peaks. The oxygen species' characteristic peaks are observable in the energy region at around 530-532 eV. The 529.07 eV peak was assigned to the oxidized metal, whereas the 531.99 eV peak was assigned to the adsorbed species and carbon bonds; low signal of the oxygen indicates low oxygen concentration. The oxidized metal species were observed in LaF₃ nanoparticles within a nanometric layer at their surfaces [18] and are related to the calcination process. Regarding the Tb³⁺-ion dopant, its characteristic spectrum in the 4d region between 140 and 160 eV showed a complex multiplet splitting (not presented), which is difficult to analyze. However, the values of the energy bonds and the spectrum shape attribute the observed features to Tb^{3+} ion species. In the 3d region, the Tb3d^{3/2} peak overlaps with the Ce3p^{1/2} peak, and the two 1241.96 and 1245.19 eV energy peaks were assigned to the Tb3d^{5/2} multiplet splitting, corresponding to the 3d⁹4f⁹ and 3d104f8 final states. As the bond energies are slightly higher than for corresponding metal or oxides [26,27], and fluorine electronegativity is higher than for oxides, the peaks were assigned to the Tb-F bonds, due to the Tb³⁺ incorporation in the CeF₃ matrix.



Figure 4. The XPS spectrum of the CeF3:Tb nanocrystalline powder calcinated at 400 °C.

3.3. Magnetic Properties

The paramagnetic properties of the CeF₃:Tb³⁺ nanocrystalline powder calcinated at 400 °C are confirmed by the magnetization vs. magnetic field dependencies (at low and high temperatures) of the magnetization curves (Figure 5).



Figure 5. Magnetization vs. magnetic field dependence measured at T = 300 K and T = 5 K recorded on CeF₃:Tb nanocrystalline powder calcinated at 400 $^{\circ}$ C.

Temperature dependence of both magnetization and the inverse magnetic susceptibility (computed from the experimental data) are depicted in Figure 6. In both cases (for applied magnetic

fields of 0.1 and 5 T), the magnetic susceptibility shows a typical paramagnetic behavior with small inflection at around 150 K that can be attributed to the Ce³⁺ ions' crystal field splitting. Tb³⁺ contribution is very weak considering the small percentage of Ce³⁺ substitution. It is known that cerium is a Kramer's ion, having an odd number of 4f electrons, and the maximum possible splitting of the ${}^{2}F_{5/2}$ state is in three doublets. When Ce³⁺ ions are placed in a hexagonal symmetry, the maximum splitting of levels will occur [28]. Energy splitting calculations showed that, for a hexagonal crystal field in cerium, the doublets were excited to 30 and 150 K above the ground state [29]. These values are comparable to those reported at 89 and 206 K for Ce³⁺ ions in hexagonal yttrium [30].



Figure 6. Temperature dependencies of the magnetization at an applied magnetic field of 5 T (inset) and 0.1 T, respectively, (**a**) and the inverse magnetic susceptibility at a perpendicularly applied magnetic field of 5 T (in inset) and 0.1 T, respectively (**b**).

3.4. Photoluminescence Properties

The photoluminescence properties and energy transfer mechanism for Tb³⁺-doped CeF₃ have been extensively investigated in CeF₃ [9–12], and therefore, we do not address them in detail here. The energy levels of Tb³⁺ allow an efficient energy transfer (ET) from the 5d-4f emission of the Ce³⁺ ions, resulting in high light output (Figure 6–left). Under 250 nm UV light pumping, Ce³⁺ ions are excited from $^{7}F_{7/2,5/2}$ ground state levels to the 4f5d excited energy levels. Then, a radiative energy transfer to the Tb³⁺ excited levels occurs, followed by radiative deexcitation from the green emitting levels of Tb³⁺ ($^{5}D_{4} \rightarrow ^{7}F_{j}$; J = 5, 4, 3)—Figure 6. The maximal ET rate is about 89% for 7.5 mol% Tb³⁺ doping [5], or 79.7% for 10mol% Tb³⁺-doping [10]. In the present case, we computed the ET efficiency (η_{ETE}) from Ce³⁺ to the Tb³⁺ activator ions using the Ce³⁺ luminescence signal intensities in the absence (I₀) and presence (I) of Tb³⁺-activator ions [31]: "η_{ETE} = 1–I/I₀", and we obtained an ET efficiency value of about 92%.

The luminescence and excitation spectra recorded on undoped and Tb-doped CeF₃ nanocrystalline powders calcinated at 400 °C are depicted in Figure 7. Under 250 nm UV light excitation, the undoped nanoparticles showed weak 375 nm luminescence assigned to the 5d-4f radiative deexcitation (Figure 7—dotted curve) [9]. This luminescence cannot be seen in the doped nanocrystal sample, where we observed only the Tb³⁺-related luminescence peaks at 542, 585, and 620 nm ($^{5}D_{4} \rightarrow ^{7}F_{17}$; J = 5, 4, 3). The PL bands showed a crystal field structure associated to Ce³⁺ substitution by the Tb³⁺ in the CeF₃ crystalline lattice. The excitation spectrum of the green 545 nm Tb³⁺-luminescence showed the characteristic 4f-4f transitions of the Tb³⁺ ions, accompanied by a broad and intense peak at 250 nm assigned to the Ce³⁺ transitions ⁷F_{7/2,5/2} to 4f5d excited states.





Figure 7. Energy level scheme of the Ce³⁺ and Tb³⁺ ions (**left**) and the photoluminescence excited at 250 nm with the excitation spectrum of the 545 nm luminescence recorded on CeF₃:Tb nanocrystalline powder calcinated at 400 °C (**right**); photoluminescence of undoped CeF₃ nanocrystalline sample is shown for comparison (dotted curve).

Figure 8 shows the Commission Internationale de l'Eclairage (CIE) chromaticity diagram of CeF₃:Tb³⁺ nanocrystalline powder with the coordinates x = 0.252 and y = 0.725 in the region of green light characteristic to the Tb³⁺ luminescence region. In the present case, the quantum yield (QY) of the Tb³⁺ ions green-related luminescence is about 20% (for 250 nm excitation wavelength) and is smaller than for YAG:Ce phosphor nanoparticles (of about 130 to 270 nm size), where a QY of 70–72% was reported [32]. On the other hand, the QY is influenced by the nanocrystals' size: the QY of Ca₃Sc₂Si₃O₁₂:Ce³⁺ nanopowders is about 50% and increases to 70–72% for microparticles [33].



Figure 8. The chromaticity coordinates of the Commission Internationale de l'Eclairage (CIE) chromaticity diagram of CeF₃:Tb nanocrystalline powder calcinated at 400 °C.

4. Conclusions

In this study, Tb^{3+} -doped CeF₃ nanocrystals showing both magnetic and photoluminescence properties were prepared at room temperature via a polyol mediated route followed by calcination.

X-ray diffraction analysis has shown a dominant $Ce_{0.75}F_3$ nanocrystalline phase (of about 99%), in which Tb^{3+} ions are substitutionally and interstitially incorporated, accompanied by traces of $CeO_{1.66}$ (of about 1%). Electron microscopy investigations have shown a relatively uniform

The combination of fluorescent alongside magnetism-integrated functions of multifunctional nanoparticles could lead to new opportunities in nano-bio related applications.

Author Contributions: The samples were prepared by C.S., and C.B., E.M., C.N., and M.S. cooperated carefully together on the physical characterization and analysis of the data: A.L. was involved specifically with magnetic measurements, C.B. with magnetic measurement analysis and structural analysis with XRD, E.M. with electron microscopy characterization by SEM, C.N. with X-ray spectroscopy, and C.S. and M.S. with photoluminescence and quantum yield characterization. The manuscript was written by M.S. in collaboration with C.B. and C.N. and approved by all authors. All authors contributed to discussions and reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the Romanian Ministry of Research and Innovation through Core Program (2020). M.S. and C.B. acknowledges the POC (European Regional Development Fund, Operational Fund Competitiveness) Projects number 54/05.09.2016, 28/01.09.2016 and PCCDI no. 47/2018 for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Escudero, A.; Becerro, A.I.; Carrillo-Carrion, C.; Núñez, N.O.; Zyuzin, M.V.; Laguna, M.; González, D.; Ocaña, M.; Parak, W.J. Rare earth based nanostructured materials: Synthesis, functionalization, properties and bioimaging and biosensing applications. *Nanophotonics* 2017, *6*, 881–921.
- 2. Sharma, R.K.; Mudring, A.V.; Ghosh, P. Recent trends in binary and ternary rare-earth fluoride nanophosphors: How structural and physical properties influence optical behavior. *J. Lumin.* **2017**, *189*, 44–63.
- 3. Fedorov, P.; Luginina, A.A.; Kuznetsov, S.V.; Osiko, V.V. Nanofluorides. J. Fluor. Chem. 2011, 132, 1012–1039.
- 4. Lee, G.H.; Chang, Y.; Kim, T.J. *Ultrasmall Lanthanide Oxide Nanoparticles for Biomedical Imaging and Therapy*; Woodhead Publishing Series in Biomaterial; Woodhead Publishing: Cambridge, MA, UK, 2004.
- 5. Cheetham, A.K.; Fender, B.E.F.; Fuess, H. and Wright, A.F. A powder neutron diffraction study of lanthanum and cerium trifluorides. *Acta Crystallogr.* **1976**, *B32*, 94–97.
- Samanta, T.; Sarkar, S.; Adusumalli, V.N.K.B.; Praveen, A.E.; Mahalingam, V. Enhanced visible and near infrared emissions via Ce³⁺ to Ln³⁺ energy transfer in Ln³⁺-doped CeF₃ nanocrystals (Ln = Nd, Sm). *Dalton Trans.* 2016, 45, 78–84.
- Li, C.; Li, F.; Li, T.; Bai, T.; Wang, L.; Shi, Z.; Feng, S. A facile synthesis and photoluminescence properties of water-dispersible RE³⁺ doped CeF₃ nanocrystals and solid nanocomposites with polymers. *Dalton Trans.* 2012, 41, 4890–4895.
- 8. Sayed, F.N.; Grover, V.; Dubey, K.A.; Sudarsan, V.; Tyagi, A.K. Solid state white light emitting systems based on CeF₃:RE³⁺ nanoparticles and their composites with polymers. *J. Colloid Interface Sci.* **2011**, *353*, 445–453.
- 9. Li, X.; Zhang, W.; Dong, L.; Liu, D.; Qi, Z. Low temperature molten salt synthesis of CeF₃ and CeF₃:Tb³⁺ phosphors with efficient luminescence properties. *J. Lumin.* **2019**, 205, 122–128.
- 10. Sun, Z.; Li, Y.; Zhang, X.; Yao, M.; Ma, L.; Chen, W. Luminescence and energy transfer in water soluble CeF₃ and CeF₃:Tb³⁺ nanoparticles. *J. Nanosci. Nanotechnol.* **2009**, *9*, 6283–6291.
- Qu, X.; Yang, H.K.; Chung, J.W.; Moon, B.K.; Choi, B.C.; Jeong, J.H.; Kim, K.H. Polyol-mediated solvothermal synthesis and luminescence properties of CeF₃, and CeF₃:Tb³⁺ nanocrystals. *J. Solid State Chem.* 2011, 184, 246–251.
- 12. Wang, Z.L.; Quan, Z.W.; Jia, P.Y.; Lin, C.K.; Luo, Y.; Chen, Y.; Fang, J.; Zhou, W.; O'Connor, C.J.; Lin, J. A facile synthesis and photoluminescent properties of redispersible CeF₃, CeF₃:Tb³⁺ and CeF₃:Tb³⁺/LaF₃ (core/shell) nanoparticles. *Chem. Mater.* **2006**, *18*, 2030–2037.
- 13. Savinkov, A.V.; Korableva, S.L.; Tagirov, M.S.; Suzuki, H.; Matsumoto, K.; Abe, S. Revised measurements and interpretation of magnetic properties of oriented CeF₃ single crystals. *J. Low Temp. Phys.* **2016**, *185*, 603–608.

- 14. Xu, Y.; Duan, M. Theory of Faraday rotation and susceptibility of rare-earth trifluorides. *Phys. Rev. B* **1992**, 46, 11636–11641.
- 15. Gong-Qiang, L.; Wen-Kang, Z.; Xing, Z. Quantitative analyses of magnetic and magneto-optical properties in cerium trifluoride. *Phys. Rev. B* **1993**, *48*, 16091–16094.
- Chaput, F.; Lerouge, F.; Bulin, A.L.; Amans, D.; Odziomek, M.; Faure, A.-C.; Monteil, M.; Dozov, I.; Parola, S.; Bouquet, F.; et al. Liquid-crystalline suspensions of photosensitive paramagnetic CeF³ nanodiscs. *Langmuir* 2019, *35*, 16256–16265.
- 17. Shoko, E.; Smith, M.F.; McKenzie, R.H. Mixed valency in cerium oxide crystallographic phases: Determination of valence of the different cerium sites by the bond valence method. *Phys. Rev. B* **2009**, *79*, 134108.
- 18. Secu, C.E.; Matei, E.; Negrila, C.; Secu, M. The influence of the nanocrystals size and surface on the Yb/Er doped LaF₃ luminescence properties. *J. Alloy. Compd.* **2019**, *791*, 1098–1104.
- 19. Rietveld, H.M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **1969**, 2, 65–71.
- 20. Lutterotti, L.; Matthies, S.; Wenk, H.-R. MAUD (material analysis using diffraction): A user friendly Java program for Rietveld texture analysis and more. In Proceedings of the Twelfth International Conference on Textures of Materials (ICOTOM-12), Montreal, Canada, 9–13 August 1999.
- 21. PDF-ICDD. *Powder Diffraction File (PDF-4+ 2018 Software 4.18.0.2),* International Centre for Diffraction Data, 12 Campus Boulevard: Newtown Square, PA, USA, 2011.
- 22. Baer, D.R.; Engelhard, M.; Johnson, G.E.; Laskin, J.; Lai, J.; Mueller, K.; Munusamy, P.; Thevuthasan, S.; Wang, H.-F.; Washton, N.; et al. Surface characterization of nanomaterials and nanoparticles: Important needs and challenging opportunities. *J. Vac. Sci. Technol. A: Vac. Surf. Films* **2013**, *31*, 050820.
- 23. Barreca, D.; Gasparotto, A.; Maccato, C.; Maragno, C.; Tondello, E. Cerium (III) Fluoride Thin Films by XPS. *Surf. Sci. Spectra* **2006**, *13*, 87.
- 24. Kalkowski, G.; Kaindl, G.; Wortman, G.; Lentz, D.; Krause, S. 4f-ligand hybridization in CeF₄ and TbF₄ probed by core-level spectroscopies. *Phys. Rev.B* **1988**, *37*, 1376–1382.
- Bossche, J.V.D.; Neyts, K.; De Visschere, P.; Corlatan, D.; Pauwels, H.; Vercaemst, R.; Fiermans, L.; Poelman, D.; Van Meirhaeghe, R.L.; Laflére, W.H.; et al. XPS Study of TbF, and TbOF Centres in ZnS. *Phys. Stat. Sol.* (A) **1994**, 146, K67.
- 26. Lee, C.J.; Vashishtha, S.; Sayal, A.; Weaver, J.F. Oxidation of a c-Tb₂O₃(111) thin film by the sequential formation of stoichiometric phases. *Surf. Sci.* **2020**, *694*, 121555.
- 27. Sarma, D.D.; Rao, C.N.R. XPES studies of oxides of second-and third-row transition metals including rare earths. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 25–45.
- 28. Segal, E.; Wallace, W. Rare earth ions in a hexagonal field III. J. Solid State Chem. 1974, 6, 203–213.
- 29. Bleaney B. Rare Earth Research II: proceedings of the Third Conference on Rare Earth Research, Ed. K. Vorres, p. 417, Gordon and Breach, New York (1964).
- 30. Yoshida, S.; Sugawara, T. Kondo effect in single crystals of Y-Ce alloys. Phys. Lett. A 1969, 30, 422-423.
- 31. Bourcet, J.C.; Fong, F.K. Quantum efficiency of diffusion limited energy transfer in La_{1-x-y}Ce_xTb_yPO₄. *J. Chem. Phys.* **1974**, *60*, 34–39.
- 32. Borlaf, M.; Kubrin, R.; Aseev, V.; Petrov, A.Y.; Nikonorov, N.; Graule, T. Deep submicrometer YAG:Ce phosphor particles with high photoluminescent quantum yield prepared by flame spray synthesis. *J. Am. Ceram. Soc.* **2017**, *100*, 3784–3793.
- Batentschuk, M.; Brabec, C.J.; Khaidukov, N.; Levchuk, I.; Osvet, A.; Römling, L.; Schröppel F., Van Deun, R.; Zorenko, Y. Highly Luminescent Ca₃Sc₂Si₃O₁₂:Ce³⁺ Silicate Garnet Nano- and Microparticles with 50– 70% Photoluminescence Quantum Yields as Efficient Phosphor Converters for White LEDs. *TechConnect Briefs*, Volume: 4, Informatics, Electronics and Microsystems, **2017**, 194–197.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).