

Upconversion luminescent property and EPR study of NaGdF₄:Yb³⁺/Tm³⁺ synthesized by the hydrothermal method

Jing LIU, Jing-Ying ZHANG, Kai LIU, Hong-Jian GAO, Xiao-Long YU, Yang CAO, and Zhong-Xin LIU (✉)

Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan University, Haikou 570228, China

© Higher Education Press and Springer-Verlag Berlin Heidelberg 2015

ABSTRACT: Water soluble upconversion (UC) luminescence hexagonal-phase NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles have been successfully synthesized by the hydrothermal method. XRD, SEM, UC photoluminescence spectra and electron paramagnetic resonance (EPR) spectrum were used to characterize the nanoparticles. The intensity of UC emission region could be controlled through different sodium source and the fluorine source, ⁶P_J→⁸S_{7/2} emission of Gd³⁺ is also observed at 310 nm. A broad spectrum with a dominant resonance at *g* of about 2 was observed by the EPR spectrum of the NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles. The transparent NaGdF₄:Yb³⁺/Tm³⁺ solution presented naked eye-visible violet-blue light under the 980 nm LD excitation. The current work paves the way for their potential application in infrared tomography and magnetic resonance imaging (MRI).

KEYWORDS: hydrothermal method; sodium source; fluorine source; electron paramagnetic resonance (EPR); magnetic resonance imaging (MRI)

Contents

- 1 Introduction
- 2 Experimental
 - 2.1 Chemical and synthesis
 - 2.2 Characterizations and performance measurements
- 3 Results and discussion
 - 3.1 XRD patterns of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors
 - 3.2 The morphology of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors
 - 3.3 Energy-dispersive X-ray spectroscopy (EDS) analysis of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors

- 3.4 PL spectra of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors
- 3.5 Energy level diagrams of Gd³⁺, Tm³⁺ and Yb³⁺
- 3.6 EPR spectrum of NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles
- 3.7 The image of water soluble NaGdF₄:Yb³⁺/Tm³⁺
- 4 Conclusions
- Abbreviations
- Acknowledgements
- References

1 Introduction

Lanthanide-based upconversion nanoparticles (Ln-UCNPs) have received considerable attention for their favorable luminescent properties, such as photostability, low toxicity, narrow emission peaks, and large anti-stokes shifts, which lead to their potential applications in drug

targeting or carrier [1], magnetic resonance imaging (MRI), near-infrared (NIR) optical imaging [2]. Among these materials, most of the attention has been focused on NaYF₄ because it is a particularly important host material for green and blue upconversion (UC) phosphors [3]. It is well known that hexagonal NaYF₄ is the most efficient UC host material known to date, and Y³⁺ can be replaced in any ratio by rare-earth (RE) ions, for example, by Yb³⁺, Tm³⁺, Er³⁺, and Eu³⁺. Among all RE ions, complex containing Gd³⁺ ions can be considered as the most perspective ones for the intrinsic magnetic and efficient UC properties [4–5]. UC phosphors with good water solubility can be better applied into biological field. These magnetic-optical nanoparticles have wide application in biological field, especially in infrared tomography and MRI.

NaYF₄ inorganic luminescent materials doped with different lanthanide ions or ion pairs have been synthesized by the hydrothermal method [6–7]. Wang and other workers had suggested that the cations coming from different fluoride sources XF (X = K⁺, H⁺, NH₄⁺, Na⁺, Rb⁺, Cs⁺) selectively adsorbed on the different crystals facets of EuF₃ nanoparticles, resulting in the formation of various shapes [8].

There are only a few reports on the magnetic-optical nanoparticles and their magnetic properties. In this work, we have prepared water soluble NaGdF₄:Yb³⁺/Tm³⁺ UCNPs using hydrothermal method. In this process, polyethylenimine (PEI) ligands play a key role in the formation of NaGdF₄ nanorods and PEI is also a macromolecular surface modifier to improve the hydrophilicity [9]. The effects of different sodium sources and fluorine sources on the UC luminescent spectra have been studied.

2 Experimental

2.1 Chemical and synthesis

All reagents were analytical grade. RECl₃·6H₂O (RE = Gd, Yb and Tm) salt was freshly prepared by the reaction of RE₂O₃ with hydrochloric acid. For a typical synthesis, 79.8 mmol/mL of GdCl₃, 20 mmol/mL of YbCl₃, 0.2 mmol/mL of TmCl₃ were added into aqueous solution containing 0.1 g/mL PEI. After vigorous stirring for 15 min, appropriate stoichiometric amounts of NaCl, NH₄F and NaF were added into the above solution. The experimental conditions and sample symbolisms are shown in Table 1. After additional agitation for 15 min, the as-obtained

Table 1 Experimental conditions and sample symbolisms

Sample	Mol ratio of <i>x</i> (Na): <i>x</i> (RE): <i>x</i> (F)	<i>x</i> (NaCl) /mmol	<i>x</i> (NH ₄ F) /mmol	<i>x</i> (NaF) /mmol
S1	4:1:4	–	–	5.6
S2	4:1:4	5.6	5.6	–
S3	1:1:4	–	4.2	1.4
S4	1:1:4	1.4	5.6	–

mixing solution was transferred into a Teflon-lined stainless-steel autoclave, which was sealed and maintained at 170°C for 10 h. After the autoclave was cooled, the final powder products were collected by centrifugation, washed with distilled water and dried in a desiccator at ambient temperature. The final powders were calcined in air at 350°C for 4 h.

2.2 Characterizations and performance measurements

The phase analysis of the samples was characterized by power X-ray diffraction (XRD) using a Bruker D8 Advance with Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and microstructure was observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The UC luminescent spectra were evaluated using photoluminescence (PL) spectroscopy (Hitachi, F-7000, Japan) under the 980 nm laser excitation. The electron paramagnetic resonance (EPR) measurement was obtained by EPR spectroscopy (Bruker, A320, Germany) operating at room temperature.

3 Results and discussion

3.1 XRD patterns of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors

XRD patterns of NaGdF₄:Yb³⁺/Tm³⁺ composites are presented in Fig. 1. The sample S1 without sintered (Curve a in Fig. 1) existed in two phases, namely, cubic (α -phase) and hexagonal (β -phase), corresponding to the standard values (JCPDS Card Nos. 26-0697 and 26-0699). All of the strong and sharp diffraction peaks of the sample S1 after sintering at 350°C could be readily assigned as hexagonal NaGdF₄ based on the standard XRD pattern (JCPDS Card No. 26-0699). It may be described that the amount of Yb³⁺ and Tm³⁺ was very few, so XRD patterns only showed the standard values of NaGdF₄. The sample experienced phase transition (cubic to hexagonal) after heat treatment, so the sample S1 after sintering at 350°C (Curve b in Fig. 1) only showed the hexagonal phase.

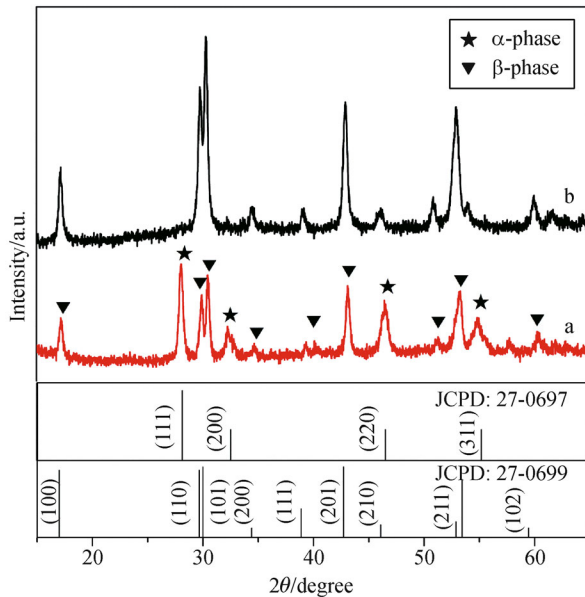


Fig. 1 XRD patterns of the obtained samples: S1 unsintered (a); S1 sintered at 350°C (b).

3.2 The morphology of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors

Figure 2 shows SEM images of the S1 unsintered sample and the S1 sintered sample at 350°C. As shown in Fig. 2, average particle sizes barely increased after heat treatment. It shows that 350°C is a suitable temperature to improve the purity of samples. The forming particles were rod-like and homogeneous, and the diameter and length of the rod were about 120 and 50 nm, respectively.

3.3 Energy-dispersive X-ray spectroscopy (EDS) analysis of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors

The EDS result was shown in Fig. 3. We can see that NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors mainly contained the

element of Na, Gd, F and Yb. Since the content of Tm is negligible, the EDS result was not composed of it.

3.4 PL spectra of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors

Figure 4 displays room temperature PL spectra of NaGdF₄:Yb³⁺/Tm³⁺ UC phosphors: S1, S2, S3 and S4 under excitation at 980 nm. It is seen that at 310, 346 and 362 nm, relatively intense ultraviolet (UV) emission was displayed, and blue UC luminescence was observed centered at 450 and 475 nm. These UV and blue UC luminescence were corresponding to the emission ${}^6P_1 \rightarrow {}^8S_{7/2}$, ${}^1I_6 \rightarrow {}^3F_4$, ${}^1D_2 \rightarrow {}^3H_6$, ${}^1D_2 \rightarrow {}^3F_4$, and ${}^1G_4 \rightarrow {}^3H_6$, respectively. The different spectral distributions in PL spectra for different samples may result from different crystallinities [10]. NaF as the sodium source and the fluorine source, the sample was conducive to the visible light; NaCl and NH₄F as the sodium source and the fluorine source, the sample was conducive to the UV light.

3.5 Energy level diagrams of Gd³⁺, Tm³⁺ and Yb³⁺

Figure 5 shows energy level diagrams of Gd³⁺, Tm³⁺ and Yb³⁺ as well as the proposed mechanisms of UC emissions. It is known that Gd³⁺ ions cannot be excited by 980 nm directly, but the ${}^6P_1 \rightarrow {}^8S_{7/2}$ emission of Gd³⁺ is observed at 310 nm, so there should be energy transfer from Tm³⁺ to Gd³⁺ [11]. The Yb³⁺ ions firstly absorb laser photons at 980 nm, and are excited from the ground state ${}^2F_{7/2}$ to the ${}^2F_{5/2}$ state. The subsequent step involves an energy transfer (ET) process, by which the energy levels of Tm³⁺ 3H_5 were excited. Once the state is populated, a subsequent incoming pump photon or a second or multiple ET from a neighboring Yb³⁺ ion may result in the population of the 3F_2 , 1G_4 and 3P_2 states of these ions.

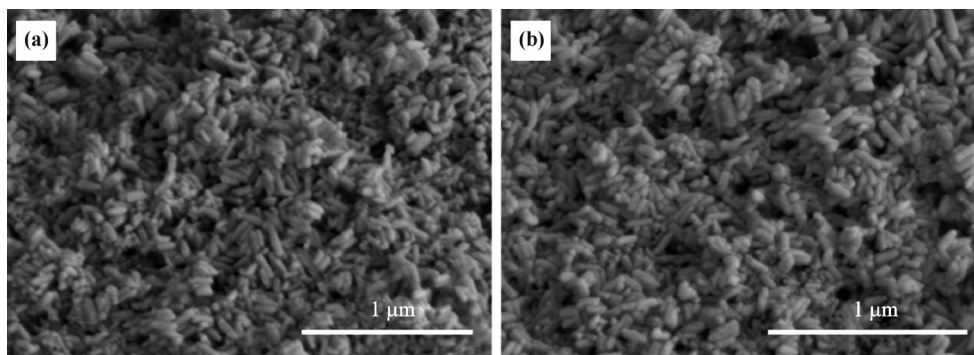


Fig. 2 SEM images of the samples: (a) S1 unsintered; (b) S1 sintered at 350°C.

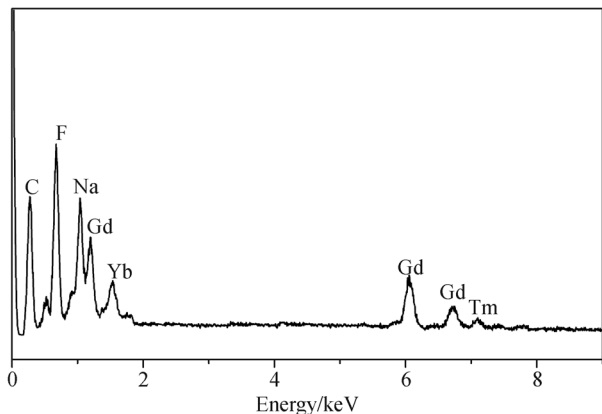


Fig. 3 EDS result of NaGdF₄:Yb³⁺/Tm³⁺ nanocrystals.

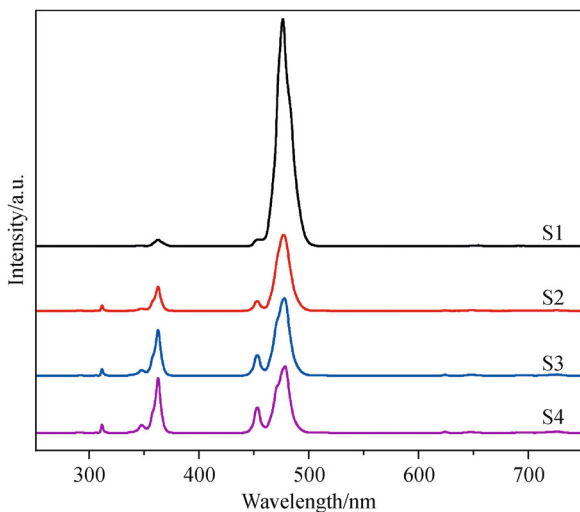


Fig. 4 PL spectra of NaGdF₄:Yb³⁺/Tm³⁺ nanocrystals under the 980 nm laser diode (LD) excitation.

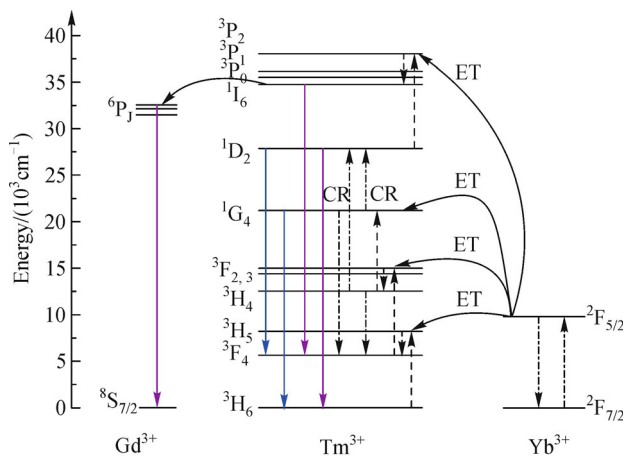


Fig. 5 Energy level diagrams of Gd³⁺, Tm³⁺ and Yb³⁺ and the proposed mechanism of UC emissions.

The population of these states may also occur via a nonradiative decay to the low-lying ³H₅, ³H₄ and ³P₀. Besides, there are primarily two cross-relaxation processes in populating the ¹D₂ level: ³H₄ + ¹G₄ → ³F₄ + ¹D₂ and ¹G₄ + ³H₄ → ³F₄ + ¹D₂. At last, the UV emission band at 310, 346 and 362 nm were considered to the radiative transition of ⁶P_J → ⁸S_{7/2}, ¹I₆ → ³F₄ and ¹D₂ → ³H₆, respectively; the strong blue emission band at 450 and 475 nm are considered to the radiative transition of ¹D₂ → ³F₄ and ¹G₄ → ³H₆, respectively.

3.6 EPR spectrum of NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles

EPR spectrum of NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles S1 after sintering at 350°C is shown in Fig. 6. According to previous studies, the EPR spectrum of Gd³⁺ (S = 7/2) ions in a crystalline electric field is characterized by the Zeeman interaction with a g value close to 2. And the broad resonance encompassing the g of about 2.0 feature has been attributed to two different sources: clustered and isolated RE ions [12]. The paramagnetic Gd³⁺ ion exhibits a strong EPR response even at room temperature, and for weak crystal fields the corresponding X-band (9.7749 GHz) EPR powder signal consists of a broad spectrum with a dominant resonance at g of about 2.0 as observed for the NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles (Fig. 5).

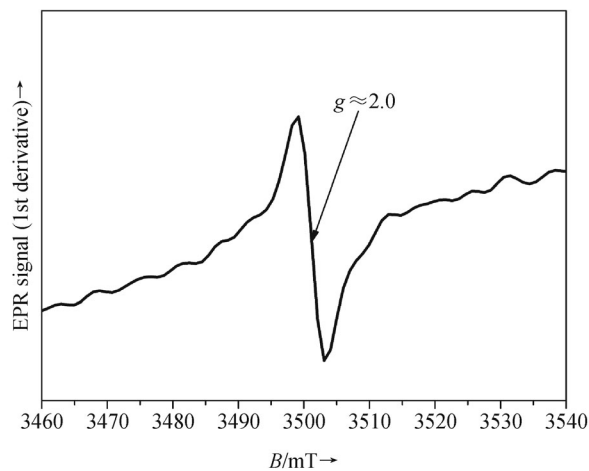


Fig. 6 EPR spectrum of NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles.

3.7 The image of water soluble NaGdF₄:Yb³⁺/Tm³⁺

In order to investigate water soluble of NaGdF₄:Yb³⁺/Tm³⁺, we disperse the NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles

(S4) in the water for 2 d, and Fig. 7(a) shows the image of NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles (2 mg/mL). The solution was transparent and it did not have obvious precipitation. Figure 7(b) shows the image of luminescence from NaGdF₄:Yb³⁺/Er³⁺ solution under 980 nm LD excitation, which presented naked eye-visible violet-blue light. NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles with good water solubility can be better applied into biological field.

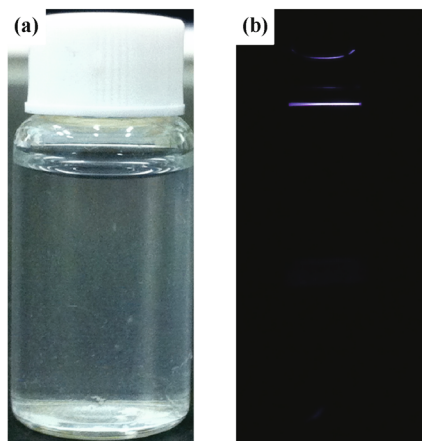


Fig. 7 (a) Image of NaGdF₄:Yb³⁺/Tm³⁺ nanocrystals dispersed in water. (b) Image of luminescence from NaGdF₄:Yb³⁺/Er³⁺ solution under the 980 nm LD excitation.

4 Conclusions

In conclusion, we have prepared UC luminescence NaGdF₄:Yb³⁺/Tm³⁺ nanorods with about 120 nm in diameter and 50 nm in length by the hydrothermal method. The samples showed UV emission bands at 310, 346 and 362 nm, considered to be the radiative transition of ⁶P_J → ⁸S_{7/2}, ¹I₆ → ³F₄ and ¹D₂ → ³H₆, respectively; the strong blue emission bands at 450 and 475 nm were considered to be the radiative transition of ¹D₂ → ³F₄ and ¹G₄ → ³H₆, respectively. NaF as the sodium source and the fluorine source, the sample was conducive to the visible light; NaCl and NH₄F as the sodium source and the fluorine source, the sample was conducive to the UV light. The paramagnetic Gd³⁺ ion exhibits a strong EPR response at room temperature. NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles with good water solubility exhibited naked eye-visible violet-blue light under the 980 nm LD excitation. Possible exploiting NaGdF₄:Yb³⁺/Tm³⁺ nanoparticles will lead to infrared tomography and MRI.

Abbreviations

EDS	energy-dispersive X-ray spectroscopy
EPR	electron paramagnetic resonance
ET	energy transfer
LD	laser diode
MRI	magnetic resonance imaging
NIR	near-infrared
PEI	polyethylenimine
PL	photoluminescence
RE	rare-earth
SEM	scanning electron microscopy
UC	upconversion
UCNP	upconversion nanoparticle
UV	ultraviolet
XRD	X-ray diffraction

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 51361009), Key Program for International S&T Cooperation Projects of Hainan Province, China (GJXM201103), Science and Technology Department of Hainan Province, China (Grant No. 090401), and the Natural Science Foundation of Hainan Province, China (Grant No. 513136).

References

- [1] Gnach A, Bednarkiewicz A. Lanthanide-doped up-converting nanoparticles: merits and challenges. *Nano Today*, 2012, 7(6): 532–563
- [2] He M, Huang P, Zhang C, et al. Dual phase-controlled synthesis of uniform lanthanide-doped NaGdF₄ upconversion nanocrystals via an OA/ionic liquid two-phase system for *in vivo* dual-modality imaging. *Advanced Functional Materials*, 2011, 21(23): 4470–4477
- [3] Krämer K W, Biner D, Frei G, et al. Hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors. *Chemistry of Materials*, 2004, 16(7): 1244–1251
- [4] Wong H-T, Chan H L W, Hao J H. Magnetic and luminescent properties of multifunctional GdF₃:Eu³⁺ nanoparticles. *Applied Physics Letters*, 2009, 95(2): 022512 (3 pages)
- [5] Singh S K, Kumar K, Srivastava M K, et al. Magnetic-field-induced optical bistability in multifunctional Gd₂O₃:Er³⁺/Yb³⁺ upconversion nanophosphor. *Optics Letters*, 2010, 35(10): 1575–1577
- [6] Zeng J H, Su J, Li Z H, et al. Synthesis and upconversion luminescence of hexagonal-phase NaYF₄: Yb, Er³⁺ phosphors of controlled size and morphology. *Advanced Materials*, 2005, 17(17): 2119–2123
- [7] Li C, Quan Z, Yang J, et al. Highly uniform and monodisperse β-

- NaYF₄:Ln³⁺ (Ln = Eu, Tb, Yb/Er, and Yb/Tm) hexagonal microprism crystals: hydrothermal synthesis and luminescent properties. *Inorganic Chemistry*, 2007, 46(16): 6329–6337
- [8] Wang M, Huang Q L, Hong J M, et al. Controlled synthesis and characterization of nanostructured EuF₃ with different crystalline phases and morphologies. *Crystal Growth & Design*, 2006, 6(9): 2169–2173
- [9] Zeng S, Tsang M K, Chan C F, et al. Dual-modal fluorescent/magnetic bioprobes based on small sized upconversion nanoparticles of amine-functionalized BaGdF₅:Yb/Er. *Nanoscale*, 2012, 4(16): 5118–5124
- [10] Zhao J, Sun Y, Kong X, et al. Controlled synthesis, formation mechanism, and great enhancement of red upconversion luminescence of NaYF₄:Yb³⁺, Er³⁺ nanocrystals/submicroplates at low doping level. *The Journal of Physical Chemistry B*, 2008, 112(49): 15666–15672
- [11] Li J, Hao Z, Zhang X, et al. Hydrothermal synthesis and upconversion luminescence properties of β-NaGdF₄:Yb³⁺/Tm³⁺ and β-NaGdF₄:Yb³⁺/Ho³⁺ submicron crystals with regular morphologies. *Journal of Colloid and Interface Science*, 2013, 392: 206–212
- [12] Brodbeck C M, Iton L E. The EPR spectra of Gd³⁺ and Eu²⁺ in glassy systems. *The Journal of Chemical Physics*, 1985, 83(9): 4285–4299