Analysis of luminescence of Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ powders with Judd-Ofelt theory

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Abstract
Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ particles of 6 to 10 nm in diameter are prepared by Pechini-type polymerized complex route based on polyesterification between citric acid (CA) and ethylene glycol. X-ray diffraction measurements confirmed that Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ powders crystallized in the face-centered cubic lattice (Fd3m). Emission spectra displayed characteristic $5D_0 \rightarrow 7F_J$ ($J = 0, 1, 2, 3$ and $4$) spin forbidden f-f electronic transitions of the Eu$^{3+}$ ions with the most pronounced emission coming from $5D_0 \rightarrow 7F_2$ and with the emission decays varying between 0.75 and 0.60 ms for samples doped with different concentration of Eu$^{3+}$. The Judd-Ofelt theory was applied to the experimental data for the quantitative determination of optical parameters such as $\Omega_2$, $\Omega_4$, Judd-Ofelt parameters, radiative and nonradiative transition rates and emission quantum efficiency. It was observed that, for all the samples, $\Omega_2 >> \Omega_4$. The luminescence quantum yields were calculated by means of the Judd-Ofelt theory and the highest value 60.83 % is obtained for particles doped with concentration of 3 % Eu$^{3+}$.

Key words: Judd-Ofelt analyses, Eu$^{3+}$, luminescence, lanthanides.

1. Introduction
In the last decades, much research has been focused on luminescent materials containing trivalent lanthanide ions, Ln$^{3+}$ [1]. Rare earth compounds have been widely used in high performance luminescent devices, magnets, catalysts, and other functional materials. Materials containing RE ions as activators show a series of sharp absorption and emission lines from the infrared up to the ultraviolet region [2]. Pyrochlore compounds are inherent ionic conductors whose properties may be altered by changing the processing conditions and doping of different elements on various sites. These materials can also be used as solid electrolyte in solid oxide fuel cell [3]. Structurally, pyrochlore exhibits fluorite type structure. The Lu$_2$Ti$_2$O$_7$ phase is known to have the cubic (Fd3m) pyrochlore structure.
with a large unit cell constant of about 10 Å. [4-5]. Pyrochlore oxides have attracted much attention because, depending on the chemical elements involved, they display a large variety of physical and chemical properties and therefore, potential applications in many areas of technological interest [6]. In the present work, we propose a Pechini method to synthesize Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ with a pyrochlore type structure. Also, we present structural, morphological and optical characterization of Eu$^{3+}$ doped pure phase Lu$_2$Ti$_2$O$_7$ powders, and discuss obtained results. Photoluminescence measurements are performed to analyze emission and emission decay characteristics of powders. The Judd-Ofelt analysis of the emission spectra of Eu$^{3+}$ ions was performed, which allowed to calculate radiative and non-radiative transition probabilities, Judd-Ofelt intensity parameters and the quantum efficiency of the Eu$^{3+}$ emission in the Lu$_2$Ti$_2$O$_7$ particles. Therefore, the analysis provides the best concentration of Eu$^{3+}$ ions that delivers Lu$_2$Ti$_2$O$_7$ particles with the best luminescence properties. So far no data on the radiative and non-radiative transition probabilities and quantum efficiencies of emission of RE impurities in Lu$_2$Ti$_2$O$_7$ particles have been reported.

2. Materials and methods

2.1. Synthesis of Lu$_2$Ti$_2$O$_7$:Eu$^{3+}$ powder

A set of six samples were prepared with different Eu$^{3+}$ concentrations (1; 3; 5; 7; 10 and 15 at.%) by Pechini-type polymerized complex route based on polyestefication between citric acid (CA) and ethylene glycol. In brief, for synthesis of rare earth doped Lu$_2$Ti$_2$O$_7$ particles, titanium (IV)-isopropoxide, lutetium (III)-nitrate, citric acid and ethylene glycol were mixed in 1:1:5:20 molar ratio. In the first step, titanium (IV)-isopropoxide (Alfa Aesar, 97%) was dissolved in ethylene glycol (Lach-Ner, 99%). Then citric acid (Kemika, 99.5%) was added to the solutions. Appropriate amounts of Lu$_2$O$_3$ (Alfa Aesar, 99.9%) and Eu$_2$O$_3$ (Alfa Aesar, 99.9%) were dissolved in hot, concentrated nitric acid, evaporated to dryness and joined with titanium (IV)-isopropoxide/EG/CA mixture. The mixtures were stirred for 1h at 60°C until they became transparent and further heated at 130°C for few hours to promote polymerization and transform to resin like form. Black, amorphous resins were fired at 350°C for 30 minutes and grounded to a powder. In order to obtain pure phase Lu$_2$Ti$_2$O$_7$ the particles were calcined at 820°C for 4 hours.

2.2. Instruments and measurements

X-ray diffraction (XRD) measurements were performed using Rigaku SmartLab diffractometer. Diffraction data were recorded in a 2θ range from 10° to 90°, counting 0.7°/minute in 0.02° steps. Relevant results of structural analysis (unit cell parameter, crystal coherence size, microstrain values and data fit parameters) were obtained using built-in package software. Microstructural characterization was done using a JEOL JSM-6610LV scanning electron microscope (SEM). An acceleration voltage of 20kV was used for the analyses. Photoluminescence (PL) measurements were done on Fluorolog-3 Model FL3-221 spectroflurometer system (Horiba Jobin-Yvon), utilizing 450 W Xenon lamp as the excitation source for emission measurements and Xenon-Mercury pulsed lamp for lifetime measurements. TBX-04-D PMT detector is used for lifetime and steady state acquisitions.
3. Results and discussion

3.1. XRD analysis

Lu$_2$Ti$_2$O$_7$ crystallizes in the face centered cubic structure, space group Fd3m, No. 227, which was confirmed by XRD analyses after calcination at 820°C for 4h. XRD patterns of Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ are presented in Fig. 1. The main diffraction peaks are indexed according to the ICDD card No. 01-074-9562 [7].

![Figure 1. XRD patterns of Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ powder samples.](image)

Relevant results of structural analysis (unit cell parameter, crystal coherence size and microstrain values) are presented in Table 1. Microstrain values are low suggesting good ion ordering in the crystals.

| Lu$_2$Ti$_2$O$_7$ | Crystallite size | $a$ (Å) | Microstrain (%) | Rwp (%) | Rp (%) | GOF (%) |
|------------------|-----------------|---------|-----------------|---------|--------|---------|
| 1 at.% Eu$^{3+}$ | 9.7(12)         | 10.0631(5) | 0.44(12)      | 5.08    | 3.43   | 2.5240  |
| 3 at.% Eu$^{3+}$ | 6.2(6)          | 10.0874(11) | 0.38(3)       | 5.17    | 3.69   | 2.6836  |
| 5 at.% Eu$^{3+}$ | 8.5(9)          | 10.0775(13) | 0.52(11)      | 5.29    | 3.54   | 2.6466  |
| 7 at.% Eu$^{3+}$ | 8.9(10)         | 10.0779(6)  | 0.48(12)      | 5.20    | 3.60   | 2.6328  |
| 10 at.% Eu$^{3+}$| 7.3(5)          | 10.0862(8)  | 0.49(9)       | 4.85    | 3.39   | 2.4379  |
| 15 at.% Eu$^{3+}$| 7.9(8)          | 10.0877(8)  | 0.48(14)      | 4.50    | 3.24   | 2.2744  |
3.2. SEM analysis

Morphology of the representative sample Lu₂Ti₂O₇:1 at.% Eu³⁺ obtained through Pechini-type polymerized complex route is shown in Fig. 2. The micrograph provided by SEM analysis, indicated that Lu₂Ti₂O₇:1 at.% Eu³⁺ consists of large chunks, up to several microns in size, formed wholly of smaller particles.

![SEM image taken from Lu₂Ti₂O₇:1 at.% Eu³⁺ powder.](image)

3.3. Photoluminescence emission spectra and lifetime measurements

Emission spectra of Lu₂Ti₂O₇ samples doped with 1 at.%, 3 at.%, 5 at.%, 7 at.%, 10 at.%, 15 at.% of Eu are measured, and the representative spectrum is presented in Fig 3. Due to the even number of electrons in the 4f shell (4f⁶ configuration), the crystal-field perturbation by the crystalline host matrix lifts partly or completely the degeneracies of the Eu³⁺ levels [8]. Therefore, emission spectra show five characteristic bands centered around 17287, 16896, 15333 and 14257 cm⁻¹ that origin from ⁵D₀ → ⁷Fᵢ (ᵢ = 0, 1, 2, 3 and 4) spin forbidden f-f electronic transitions of the Eu³⁺ ions. The ⁵D₀ → ⁷F₁ transition is magnetic dipole in nature and follows the selection rule ΔJ = 1. Its intensity is independent of the host matrix. On the other hand, the ⁵D₀ → ⁷Fᵢ (ᵢ = 2, 4, 6) are “the forced” electric dipole transitions, known to be forbidden by the Laporte selection rule, and may occur due to the mixing of the 4f orbitals with opposite parity at the low symmetry sites. The ⁵D₀ → ⁷F₂ is known as a hypersensitive transition because it is easily affected by the local environment around the europium ion, and its intensity depends on the symmetry of the crystal field around the europium ion. The intensity of ⁵D₀ → ⁷F₂ transition is the most intense across the emission spectra. The ⁵D₀ → ⁷F₀ transition is not allowed since 0 − 0 transitions are forbidden by the selection rule J = 0 → J' = 0. The appearance of this transition is mainly due to the J-mixing effect [9] and indicates that the Eu³⁺ ion is located in a site without an inversion center. Low energy transitions, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄, are also clearly visible. Emissions from ⁵D₀ → ⁷F₅ (12990-13510 cm⁻¹) and ⁵D₀ → ⁷F₅ (11900-12350 cm⁻¹) transitions could not be detected due to the instrument limitations.
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Figure 3. Representative emission spectrum (left) and emission decay (right) of Lu$_2$Ti$_2$O$_7$:Eu$^{3+}$ powder.

The emission decays of the $^5D_0$ emitting level of Lu$_2$Ti$_2$O$_7$:Eu$^{3+}$ powder are obtained under 394 nm excitation. Average lifetime values are calculated using the following equation:

$$\tau_{\text{avg}} = \frac{\int_0^\infty t l(t) dt}{\int_0^\infty l(t) dt}$$

(1)

where $l(t)$ represents the luminescence intensity at time $t$, corrected for the background. The results of the calculations are presented in Table 2.

Table 2. Lifetimes of the $^5D_0$ emission level of Eu$^{3+}$ in Lu$_2$Ti$_2$O$_7$ particles doped with different concentration of Eu$^{3+}$.

| Eu$^{3+}$ doped Lu$_2$Ti$_2$O$_7$ concentration (at. %) | Lifetime constant (ms) |
|------------------------------------------------------|------------------------|
| 1                                                    | 0.70                   |
| 3                                                    | 0.74                   |
| 5                                                    | 0.71                   |
| 7                                                    | 0.75                   |
| 10                                                   | 0.66                   |
| 15                                                   | 0.60                   |

In all samples the highest integral emission intensity is observed for the $^5D_0 \rightarrow ^7F_2$ transition. The intensity of this transition is shown in Figure 3, and the lifetime values in Table 2. The lifetime values of the $^5D_0$ level are similar up to 7 at. % Eu$^{3+}$ ($\approx 0.70 - 0.75$ ms), but they experience a decrease at 10 at. % Eu$^{3+}$ ($\approx 0.66$ ms).

3.4. Judd-Ofelt calculations and results

The Judd-Ofelt theory [10,11] describes intensities of transitions of lanthanides and actinides in solids and solutions, whereas the Judd-Ofelt parameters characterize the local structure and bonding in the vicinity of rare earth ions. This theory provides information
about oscillator strengths, radiative lifetime ($\tau_R$) and transition probability ($A$). The analysis also provides values of quantum efficiency and estimates of the degree of Eu ligand covalency. According to J-O theory [10,11] the theoretical expression for oscillator strength for an induced electric dipole transition from the ground state to an excited state is:

$$f = \frac{8\pi^2 mc\nu}{3h(2J + 1)} \frac{(n^2 + 2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda}(\Psi_J\|U^\lambda\|\Psi_{J'}^2)$$

where $h$ denotes the Planck constant ($6.63 \times 10^{-27}$ erg·s), $2J + 1$ is the degeneracy of the initial state, $n$ is the refractive index, $\Omega_{\lambda}$ are the Judd-Ofelt parameters and $\|U^\lambda\|$ the double reduced matrix elements of unit tensor operators whose values are independent of the local environment of the ion. According to the Judd-Ofelt theory the spontaneous transition probability, $A$, is related to its dipole strength according to the following equation:

$$A(\Psi_{J'}; \Psi_J) = \frac{64\pi^4 e^2}{3h(2J + 1)\lambda^3} \left[ n \left( \frac{n^2 + 2}{9} \right)^2 D_{\text{ed}} + n^2 D_{\text{md}} \right]$$

where $D_{\text{ed}}$ and $D_{\text{md}}$ are the electric and magnetic dipole strengths (in esu$^2$ cm$^2$), respectively. Transition probabilities of the rare earths are composed mainly of the electric dipole contribution $^5D_0 \rightarrow ^7F_i$ $(i = 2, 4)$ and to a much lesser extent by the magnetic-dipole contribution $^5D_0 \rightarrow ^7F_1$. The $^5D_0 \rightarrow ^7F_3$ transition is forbidden according to Judd-Ofelt theory both in magnetic and induced electric dipole scheme, and this transition can only gain intensity via J-mixing [12,13]. Also, the $^5D_0 \rightarrow ^7F_0$ transition is strictly forbidden according to the standard Judd-Ofelt theory. Due to the above mentioned, these two transitions will not be considered in the determination of transition probabilities. The intensity of $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition is largely independent of the environment and can be considered in a first approximation to be constant [14]. The magnetic dipole transition can be calculated by theory [12,15] as:

$$D_{\text{md}} = 9.6 \times 10^{-42} \text{esu}^2 \text{cm}^2.$$ (4)

The strength of all induced electric dipole transitions is:

$$D_{\text{ed}}(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda}(\Psi_J\|U^\lambda\|\Psi_{J'})^2$$

where $|\langle \Psi_J\|U^\lambda\|\Psi_{J'}^2|$ are squared reduced matrix elements whose values are independent of the host matrix. For the case of Eu$^{3+}$ these values are given in Ref. [15-17]. In the case of Eu$^{3+}$ emission, Judd-Ofelt intensity parameters can be evaluated solely from the emission spectrum because non-diagonal elements of the $|\langle \Psi_J\|U^\lambda\|\Psi_{J'}^2|$ matrix have zero values:

$$\Omega_{\lambda} = \frac{D_{\text{md}}\nu_3^3}{e^2\nu_\lambda^3} \frac{9n^3}{n(n^2 + 2)^2} \frac{9n^3}{f_{\lambda}(\nu_3) f_{\lambda}(\nu_1)}$$

(6)

For the J-O calculations the value of refraction index of 2.12 is taken from the literature [18]. Then, it is possible to calculate the ratio of the radiative transition probabilities $A$
of different transitions from the ratios of areas $S$ under the corresponding emission bands [17,19]:

$$A(5D_0 \rightarrow 7F_{2,4}) = A(5D_0 \rightarrow 7F_1) \times \frac{S(5D_0 \rightarrow 7F_{2,4})}{S(5D_0 \rightarrow 7F_1)} \quad (7)$$

The total radiative rate, $A_R$, defined as the sum of all radiative rates, can be further used to evaluate the non radiative rate, $A_{NR}$, the value of luminescence intensity ratio $R$ and the emission quantum efficiency, $\eta$ (ratio between number of photons emitted by the $\text{Eu}^{3+}$ ion to those absorbed by the $\text{Eu}^{3+}$ ion).

The $\Omega_2$ intensity parameter depends on the symmetry of the local surrounding around the $\text{Eu}^{3+}$ site and is strongly affected by the degree of the covalence bond between $\text{Eu}^{3+}$ and ligands. $\Omega_4$ and $\Omega_6$ parameters are associated to the viscosity and rigidity of the host material. The stronger the covalence the higher the value of $\Omega_2$ [20,21]. Luminescence intensity ratio $R = \frac{5D_0 \rightarrow 7F_2}{5D_0 \rightarrow 7F_1}$, also known as asymmetry ratio [22], represents the measure of degree of Eu-O covalency [23]. As the value of $R$ increases, the symmetry around the trivalent europium reduces [24]. $\Omega_2$ and $R$ reveal complementary physical information on the bonding nature between the $\text{Eu}^{3+}$ ion and the surrounding anions. Furthermore, the $R$ value depends on the J-O parameter $\Omega_2$ which is used to explain the short range effects in the local structure around the $\text{Eu}^{3+}$ ions and Eu-O covalence [25]. The $\Omega_6$ intensity parameter could not be determined because the $5D_0 \rightarrow 7F_6$ emission in this sample couldn’t be detected due to the instrumental limitations.

Calculated Judd-Ofelt parameters show variations with different concentrations of $\text{Eu}^{3+}$, and their values are presented in Table 3.

### Table 3. Intensity parameters, radiative and non-radiative transition rates, quantum efficiencies and asymmetry ratios of $\text{Eu}^{3+}$ emission from $\text{Lu}_2\text{Ti}_2\text{O}_7$ particles prepared with different concentration of $\text{Eu}^{3+}$.

| $n$ (%) | $\Omega_2 \times 10^{-20} \text{ cm}^{-1}$ | $\Omega_4 \times 10^{-20} \text{ cm}^{-1}$ | $A \text{ (s}^{-1})$ | $A_{NR} \text{ (s}^{-1})$ | $\eta \text{ (%)}$ | $R$ |
|------|----------------------------------------|----------------------------------------|-----------------|-----------------|----------------|---|
| 1    | 4.68                                   | 2.53                                   | 717.30          | 711.27          | 50.2           | 3.23 |
| 3    | 5.52                                   | 3.02                                   | 822.15          | 529.22          | 60.8           | 3.91 |
| 5    | 5.02                                   | 2.58                                   | 752.51          | 655.94          | 53.4           | 3.56 |
| 7    | 4.83                                   | 2.46                                   | 728.60          | 604.77          | 54.6           | 3.43 |
| 10   | 5.25                                   | 2.62                                   | 777.34          | 737.80          | 51.3           | 3.72 |
| 15   | 4.97                                   | 2.48                                   | 743.17          | 923.51          | 44.6           | 3.53 |

Calculated values of the $\Omega_2$ and $\Omega_4$ parameter are similar for all $\text{Eu}^{3+}$ concentrations. This trend is displayed in Figure 4(a). The $\Omega_2 > \Omega_4$ trend confirms the existence of covalence between the $\text{Eu}^{3+}$ ion and ligands as well as the asymmetry around the metal ion site [26]. The obtained results for $\Omega_2$ and $\Omega_4$ are similar and no significant changes are observed. Likewise, calculated values of asymmetric ratio $R$ are also close. The asymmetric ratio $R$ in dependence of different atomic percentage of $\text{Eu}^{3+}$ (1, 3, 5, 7, 10 and 15 %) is presented in Figure 4(b). These results indicates that the local environment of the ion was stable and does not change with concentrations in this range [27].
Figure 4. (a) $\Omega_2$ (black squares) and $\Omega_4$ (red circles) intensity parameters, and (b) asymmetric ratio as a function of Eu$^{3+}$ (1, 2, 4, 8 and 12 %) concentration.

Figure 5(a) shows changes of the radiative and non-radiative transition rates of Eu$^{3+}$ emissions in samples doped with different concentration of Eu$^{3+}$. The results for quantum efficiency are displayed in Figure 5(b). The highest value of the quantum efficiency is obtained for concentration of 3% and it is 60.83%, and the lowest value is obtained for the 15% and it is 44.58%. The decrease of the quantum efficiency with the increase of the dopant concentration above 10% is the consequence of high cross-relaxation processes.

It is acknowledged that Judd-Ofelt theory estimates transition probabilities with accuracy generally not worse than 10% [28].

4. Conclusion

To conclude, a set of samples with different Eu$^{3+}$ concentrations (1; 3; 5; 7; 10 and 15 at. %) doped Lu$_2$Ti$_2$O$_7$ particles has been prepared with Pechini-type polymerized com-
plex route. Particles doped with 3 % of Eu$^{3+}$, exhibiting quantum efficiency of emission of 60.9 %, showed the best luminescence properties. In all samples the Judd-Ofelt intensity parameter $\Omega_2$ was larger than $\Omega_4$ parameter showing existence of covalence between the Eu$^{3+}$ ion and ligands as well as the asymmetry around the metal ion sites.

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References

[1] T. Justel, H. Nikol and C. Ronda, Angew. Chem. Int. Ed. 37, 3084 (1998).
[2] A. J. Kenyon, C. E. Chryssou and C. W. Pitt, J. Appl. Phys. 91, 367 (2002).
[3] S. A. Kramer, H. L. Tuller, Solid State Ion. 82, 15 (1995).
[4] E. Aleshin and R. Roy, J. Am. Ceram. Sot. 45, 18 (1962).
[5] D. D. Hogarth, Am. Mineral. 62, 403 (1977).
[6] M. Subramanian, G. Aravamudan, G. V. Subba Rao, Prog. Solid State Chem. 15, 55 (1983).
[7] A. V. Shlyakhtina, A. V. Knotko, M. V. Boguslavskii, S. Yu. Stefanovich, D. V. Peryshkov, I. V. Kolbanev, L. G. Shcherbakova, Solid State Ion. 176, 2297 (2005).
[8] K. Binnemans, Coord. Chem. Rev. 295, 1 (2015).
[9] P. A. Tanner, Y. Y. Yeung, and L. Ning, J. Phys. Chem. A 117, 2771 (2013).
[10] B. R. Judd, Phys. Rev. 127, 750 (1962).
[11] G. S. Ofelt, J. Chem. Phys. 37, 511 (1962).
[12] M. J. Weber, T. E. Varitimos, and B. H. Matsinger, Phys. Rev. B 8, 47 (1973).
[13] J. E. Lowther, J. Phys. C 7, 4393 (1974).
[14] C. Görller-Walrand, L. Fluyt, A. Ceulemans, and W.T. Carnall, J. Chem. Phys. 95 (1991).
[15] M. H. V. Werts, R. T. F. Jukes, and J. W. Verhoeven, Phys. Chem. Chem. Phys. 4, 1542 (2002).
[16] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. 49, 4412 (1968).
[17] L. Dacanin, S. R. Lukić, D. M. Petrović, M. Nikolić, and M. D. Dramićanin, Physica B 406, 2319 (2011).
[18] D. D. Gulamova, Geliotekhnika 2009(1), P55-66 CAPLUS.

[19] D. Uma Maheswari, J. Suresh Kumar, L. R. Moorthy, K. Jang, and M. Jayasimhadri, Physica B 403, 1690 (2008).

[20] C. Koeppen, S. Yamada, G. Jiang, A. F. Garito, and L. R. Dalton, J. Opt. Soc. Am. B: Opt. Phys. 14, 155 (1997).

[21] S. S. Braga, R. A. Sá Ferreira, I. S. Gonçalves, M. Pillinger, J. Rocha, J. J. C. Teixeira-Dias, and L. D. Carlos, J. Phys. Chem. B 106, 11430 (2002).

[22] A. Patra, E. Sominska, S. Ramesh, Y. Koltypin, Z. Zhong, H. Minti, R. Reisfeld, and A. Gedanken, J. Phys. Chem. B 103, 3361 (1999).

[23] G. Ehrhart, M. Bouazaoui, B. Capoen, V. Ferreiro, R. Mahiou, O. Robbe, and S. Turrell, Opt. Mater. 29, 1723 (2007).

[24] K. Binnemans, K. Van Herck, and C. Görller-Walrand, Chem. Phys. Lett. 266, 297 (1997).

[25] P. Babu, and C. K. Jayasankar, Physica B 279, 262 (2000).

[26] M. Kumar, T. K. Seshagiri, and S. V. Godbole, Physica B 410, 141 (2013).

[27] G. Zhou, Z. Wang, B. Zhou, Y. Zhao, G. Zhang, S. Wang, Opt. Mater. 35, 774 (2013).

[28] R. Rolli, K. Gatterer, M. Wachtler, M. Bettinelli, A. Speghini, D. Ajó, Spectrochim. Acta Mol. Biomol. Spectrosc. 57, 2009 (2001).