The morphological changes induced by the thermal treatments of YAG: Eu crystals synthesized by a sol-gel method have investigated using the Mössbauer and optical techniques. Both methods exhibit a drastic change of the spectral parameters at amorphous – garnet phase transition, followed by a slow evolution of these parameters with the increase of the annealing temperature. This slow evolution is due to the increase in size of the nanocrystals.

Key words: Mössbauer spectroscopy, nanocrystals, YAG, Eu$^{3+}$, sol-gel method.

INTRODUCTION

Yttrium aluminates based on the system $Y_2O_3$–$Al_2O_3$ are promising materials with regard to their optical, mechanical, chemical, and thermal properties. The yttrium aluminum garnet ($YAG$–$Y_3Al_5O_{12}$) crystallizes in the cubic form and exhibits outstanding properties when doped with lanthanide or transition elements. Usual applications include laser active media and phosphors. Nd:YAG is the most widely used solid-state active medium and, recently, highly efficient ceramic Nd:YAG active media were produced [1]. YAG:Eu$^{3+}$ and YAG:Tb$^{3+}$ are, respectively, well-known red and green phosphors [2, 3], while YAG:Er$^{3+}$ (co-doped with Tb$^{3+}$) is used as upconversion phosphor [4].

The solid-state synthesis of YAG ceramics from aluminum and yttrium oxides requires high sintering temperatures ($>1600^\circ$C) [5]. In such conditions, it is difficult to control the homogeneity and purity of YAG powders. An alternative synthesis approach is the sol-gel method [6]. This method allows for preparation of high purity single-phase YAG at significantly lowers temperature.
Generally, the Mössbauer (known as the nuclear $\gamma$ resonance, NGR) and optical spectroscopies can detect the structural changes during the phase transition or/and in process of crystallization, by the changes in the spectrum shape and/or spectral parameters. One of the promising applications of them is the controlling investigation on different steps in the technological procedures of optical advanced materials, containing as constituent and or dopant the optical and/or Mössbauer probes.

In this paper we report the Mössbauer and optical investigations monitoring the transition from the amorphous to the garnet phase and the change of the crystallite size induced by the thermal (annealing) treatment.

**EXPERIMENTAL**

The YAG:Eu nanocrystals were obtained by a nitrate-citrate sol-gel method [7, 8]. Aqueous solutions of Y(NO$_3$)$_3$·5H$_2$O 1.93 M, Al(NO$_3$)$_3$·9H$_2$O 2.12 M, and Eu(NO$_3$)$_3$·5H$_2$O 1.93 M are mixed in a molar ratio Y:Eu:Al of 2.97:0.03:5 according to formula (Y$_{2.97}$Eu$_{0.03}$Al$_5$O$_{12}$). The mixture was added to a citric acid solution (C$_6$H$_8$O$_7$·H$_2$O) 2 M, in a molar ratio citric acid: nitrates of 3:1. The mixture was evaporated at 80$^\circ$C until a transparent viscous gel was obtained. The gel was decomposed at 600$^\circ$C for 6 h obtaining a black fluffy powder in an amorphous state. The powder was calcinated at 850$^\circ$C for 4 hours in air to obtain a white powder, by burning away the organic compounds. Thermal treatments were applied at successively increasing temperatures in the interval (900–1400$^\circ$C), for 4 hours each. After a thermal treatment at 930$^\circ$C, pure crystalline YAG phase was obtained.

XRD measurements (see Fig. 1) were performed at room temperatures (RT) on TUR M-62 diffractometer, on line with a PC, using CoK$_\alpha$ radiation ($\lambda = 1.7902$ Å) [9]. Mössbauer and optical measurements were performed on powder samples annealed at 900, 930, 1000, 1100, 1200, 1300 for 4 hours and 1400$^\circ$C a longer time (20 hours). All the measurements were performed at room temperature (RT). The Mössbauer spectra (MS) were measured in the standard transmission geometry experiment, using $^{151}$Eu isotope in Sm$_2$O$_3$-matrix as Mössbauer source. The main characteristics of the source are:

- the isotopic abundance, $a_{^{151}Eu} = 47.8\%$;
- the $\gamma$-ray and recoil energies, $E_\gamma (= 21.5418$ KeV), $E_R (= 1.6404\cdot10^{-3}$ eV) of the nuclear $\gamma$-ray transition, $7/2^+ \rightarrow 5/2^+ > (\text{M1 + E2})$;
- the cross-section $\sigma_0 = 2.377 \times 10^{-19}$ cm$^2$;
Mössbauer and optical investigation of Eu:YAG nanocrystals

3. RESULTS AND DISCUSSION

Generally, the Mössbauer spectroscopy can detect the structural changes during the phase transition or/and in process of crystallization, by dramatic changes of the Mössbauer spectrum (MS) shape and of its parameters (of recoilless fraction \( f \) and/or full line-widths \( \Gamma_{\text{obs}} \) observed in spectrum area \( A_{\text{obs}} \sim C \cdot f \cdot \Gamma_{\text{obs}} \), isomer shift \( \delta \) and quadrupole shift parameter \( \epsilon_Q \), in our case). One of the promising applications of NGR is the controlling investigation on different steps in the technological procedures of optical advanced materials,

\[ 1 \text{ mm/s} = 7.18544 \times 10^{-8} \text{ eV}; \quad 1 \text{ mm/s} = 17.3743 \text{ MHz} \]
containing as constituent and or dopant the Mössbauer probes. So, RT Mössbauer spectroscopy technique of powder-samples, with different annealing temperature $T_{an}$ during the YAG crystallization process, have carried out, using $^{151}$Eu as Mössbauer dopant (see Fig. 2).

As one can see, the different shapes have revealed in the MS of samples annealed at 900°C and 930°C. RTMS of the sample annealed at 900°C shows a very noised background (15-20% of the central peak-gap), a central peak and an additional one at ~ + 7mm/s, which has not found in the other spectra. The most probably, the additional peak is either a strong component of a $^{151}$Eu large quadrupole splitting pattern or more probably a signal of Mössbauer probe in primary chemical ingredients, Eu(NO$_3$)$_3$. MS evidence a very large and slightly asymmetric transmission peak closed to center for the samples annealed at $T_{an} \geq 930°C$. That means the presence of trivalent state of the Mössbauer hosting ion in a neighborhood with a very slight distortion of oxygen polyhedrons, corresponding to a high symmetric location of the Mössbauer probe. Taking into account the geometrical aspects the electric charge balance and the chemical similarity of the Y and Eu properties, the ionic host of Mössbauer probe is substituting the Y in the Thompson cube of YAG crystal.

Fig. 2 – RTMS of the YAG:Eu sample annealed at specified annealed temperatures.
The every MS of the sample obtained at $T_{an} > 930{^\circ}C$ revealed only a single absorption lines with slight asymmetry change, and slow changes of $A_{obs}$ and shift vs. to increasing $T_{an}$.

Taking into account the slight asymmetry of the central peak, the MS have fitted using one quadrupole splitting pattern, as a sum of Lorentz functions with the same line-width and the intensities and positions corresponding to the nuclear $\gamma$ ray transition of $^{151}$Eu [16]. In Table 1 are given the parameters of the fitted spectra. In Fig. 3 are plotted the Mössbauer spectral parameters vs. $T_{an}$. As one can see, the plotted parameters are showing abrupt changes from $T_{an} = 900{^\circ}C$ to $T_{an} = 930{^\circ}C$ (known as amorphous-crystalline temperature of YAG).

The abrupt change of isomer shift shows an increasing Eu-ns-electron density at Mössbauer probe and a decreasing of the $s, p, d$ and $f$-electron shielding. That corresponds to an increasing of the Eu-O bonding ionicity.

$$\delta = cst \cdot \sum_n |\Psi_{ns}(0)|^2_{\text{YAG}:^{151}\text{Eu}} - \delta_{\text{SmO}:^{151}\text{Eu}}$$

$$cst > 0$$

On the other hand the sudden magnitude increasing of the quadrupolar shift denotes new arrangements both of the Eu electron shells and Eu-surrounding anions. That corresponds to a more distortion of oxygen polyhedron, which accompanies the structural transformations.

Generally, the change of the spectrum area $A_{obs}$ is raising from the changes of the $^{151}$Eu concentration, the full line-width $\Gamma_{obs}$ and/or of the recoilless factor $f$. All investigated samples have the same precursor, so there is no reason of the $^{151}$Eu concentration changes. The substitutional disorder, dynamics of hyperfine

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{an}$ [°C]</th>
<th>$\Delta t$ [h]</th>
<th>$\delta$ [mm/s]</th>
<th>$\epsilon_{Q}$ [mm/s]</th>
<th>$\Gamma_{obs}$ [mm/s]</th>
<th>$A_{obs}$</th>
<th>$r^2$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>900</td>
<td>6</td>
<td>7.725</td>
<td>-6.57</td>
<td>1.35</td>
<td>0.078</td>
<td>0.4935</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.114</td>
<td>-0.25</td>
<td>2.24</td>
<td>0.337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>930</td>
<td>4</td>
<td>0.486</td>
<td>-7.70</td>
<td>1.53</td>
<td>0.603</td>
<td>0.9330</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>1000</td>
<td>4</td>
<td>0.505</td>
<td>-8.56</td>
<td>1.37</td>
<td>0.595</td>
<td>0.8991</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1100</td>
<td>4</td>
<td>0.468</td>
<td>-10.25</td>
<td>1.38</td>
<td>0.675</td>
<td>0.9569</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>1300</td>
<td>4</td>
<td>0.403</td>
<td>-10.57</td>
<td>1.36</td>
<td>0.786</td>
<td>0.9520</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>1400</td>
<td>24</td>
<td>0.501</td>
<td>-9.80</td>
<td>1.45</td>
<td>0.821</td>
<td>0.9672</td>
<td></td>
</tr>
<tr>
<td>Errors</td>
<td>±10</td>
<td>±0.075</td>
<td>±0.15</td>
<td>±0.08</td>
<td>±0.105</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\epsilon_{Q} = eQ_{1/2}V_{ZZ}/4.$
Fig. 3 – The Mössbauer parameters of the $^{151}$Eu:YAG samples annealed at different temperatures. The dashed areas correspond to zones of amorphous-crystalline temperature range.

fields and/or disorder-order phase transition generates the change of $\Gamma_{obs}$. On the other hand the changes of $f$-factor of RTMS reveals the change in parameters characterizing the lattice dynamics. In deed, the $f$ is depending of the density $\rho(\nu)$ and the limits $\nu_{\min}$, $\nu_{\max}$ of the normal mode frequencies $\nu$. In the approximation of Debye model of lattice vibrations $f$ factor is given by:

$$f = \exp \left\{ -\frac{3E_R}{2k_B\theta_D} \left[ 1 + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\nu_{\max}/T} \frac{xdx}{e^x - 1} \right] \right\}$$

where $x = \frac{h\nu}{k_BT}$.

$$f = \exp \left\{ -\frac{3E_R}{2k_B\theta_D} \left[ 1 + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\nu_{\max}/T} \frac{xdx}{e^x - 1} \right] \right\}; \quad x = \frac{h\nu}{k_BT}$$  \hspace{1cm} (2)
The recoilless factor increases, when the ratio \( E_R/k_B\theta_D \) decreases and that correspond to the increasing of the Debye energy \( k_B\theta_D \). That suggest the more intense elastic forces of in solids.

So, the sudden changes of MS observed parameters of the samples annealed at 900°C and 930°C most probably correspond to the amorphous-crystalline transformation of YAG.

The MS of samples annealed at \( T_{an} > 930°C \) revealed slower changes of spectral parameters vs. increasing \( T_{an} \). Probably, that is given by the sensibility of MS parameters to the size increasing of YAG crystallite [9] vs. \( T_{an} \). Moreover empirical dependencies of the spectral parameters, parameters \( \delta(T_{an}) \), \( \varepsilon_Q(T_{an}) \) and \( A_{obs}(T_{an}) \) for \( T_{an} \geq 930°C \) can be obtained by the simple polynomial fits (see Fig. 3).

\[
\begin{align*}
\langle D \rangle_V(T_{an}) &= 30.3(3.5) + 3.17(1.8)\exp \left[ \frac{T_{an} - 900}{142.6(27.3)} \right] \\
T_{an} &= \text{Inv}[\langle D \rangle_V(T_{an})] = 900 + 142.6 \cdot \ln \frac{\langle D \rangle_V - 30.3}{3.17}
\end{align*}
\]

An acceptable simulation of the apparent average size data [9] vs. \( T_{an} \) corresponds to an exponential growth:

\[
\langle D \rangle_V(T_{an}) = 30.3(3.5) + 3.17(1.8)\exp \left[ \frac{T_{an} - 900}{142.6(27.3)} \right]
\]

and a polynomial fit of Mössbauer spectral parameters \( \delta \), \( \varepsilon_Q \) and \( A_{obs} \) vs. apparent average size, one can be obtained. In Fig. 5 one can see the graphs and empirical relations of \( T_{an} \) and \( A_{obs} \) vs. the apparent average size of YAG-crystallites.

The slow changes of the Mössbauer spectral parameters can be explained taking into account the contributions of the Mössbauer probes on crystallite boundary CB (surface) and in volume one CV to MS. In the case of very small
crystallite (≤ 40 nm), $^{151}$Eu on CB give the main contribution. The growth of crystallite and the increasing of its apparent average size induce an increasing of the $^{151}$Eu-volume contribution and all MS parameters go to their limit-values. So, Eu-O bond is more and more slight ionic, the distortion of the Eu-O-local polyhedron becomes slower changeable and $f$ factor (depending by CV through $\theta_D$) has a slight increasing.

The fluorescence spectrum for powder annealed at 900°C in the spectral domain 11 500–17 500 cm$^{-1}$ is shown in Fig. 6. This spectral domain spans the transitions $^5D_0 \rightarrow ^7F_J$ ($J = 0, \ldots, 6$), labeled $F_J$ in Fig. 6. We note the presence of the fluorescence line corresponding to the transition $^5D_0 \rightarrow ^7F_0$. The fluorescence lines are wide, characteristic for the amorphous phase.

The fluorescence spectrum (in the same spectral domain) of the powder sample annealed at 930°C is presented in Fig. 7. A drastic change of the luminescence spectrum is observed. This time the fluorescence lines are narrow, characteristic for the crystalline (garnet) phase. This means that in the temperature
interval 900–930°C takes place the transition amorphous – crystalline. This transition was confirmed by X-ray diffraction and FT-IR measurements [9]. Since now the symmetry at the Eu$^{3+}$ position is D$_2$, the transition $^5D_0 \rightarrow ^7F_0$ is no longer observed.

The apparent average crystallite size for the YAG:Eu nanopowder [9] increases with annealing temperature. In the annealing temperature interval 930–1300°C, this size increases from 32 nm to 82 nm. Obviously, the optical properties of the YAG:Eu nanopowders depend on the crystallite properties (dimension and shape distribution) but is more convenient to represent the results function of the annealing temperature. In fact, the measured properties are the result of averaging in individual crystallites (function of the ratio surface/volume) and of the averaging on the crystallite size distribution in powder.
For higher annealing temperatures (larger crystallites) the fluorescence lines become narrower. The annealing temperature dependence of the line widths of the three spectral lines of transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) and for two well-isolated lines of the transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_4 \) is given in Figs. 8 and 9.

![Fig. 8 - Dependence of the line-width - annealing temperature for the three fluorescence lines of the transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \).](image)

![Fig. 9 - Dependence of the line-width - annealing temperature for two isolated lines belonging to the transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_4 \).](image)

The transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) is a magnetic dipole one. The magnetic dipole transitions are parity allowed and their intensity is practically not sensitive at the changes in the neighborhood of the Eu\(^{3+}\) ion. On the other hand, the electric dipole transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) (a hypersensitive transition [10, 11]) is very sensitive to the structural changes. Therefore, the usual practice [12] is to monitor the ratio of the transition intensities \( R' = \frac{I(5\text{D}_0 \rightarrow 7\text{F}_2)}{I(5\text{D}_0 \rightarrow 7\text{F}_1)} \), the intensity of the magnetic dipole transition playing the role of an internal standard. Because the
transition intensities are proportional with the area under the fluorescence lines, we shall calculate the ratio of the respective areas: \( R = A(^5D_0 \rightarrow ^7F_2) / A(^5D_0 \rightarrow ^7F_1) \). The dependence of this ratio on the annealing temperature is presented in Fig. 10.

![Fig. 10 – Dependence of the ratio \( R \) on the annealing temperature. Inset: the evolution of \( R \) after the phase transition.](image1)

The ratio \( R \) decreases significantly with the annealing temperature (approximately 1.5 times) denoting an increase of the local symmetry [12]. The higher the symmetry, the lower is the ratio \( R \). We note that for the amorphous powder (lower local symmetry – Fig. 10) this ratio is close to 7. Another measurable indicator of the evolution of the nanocrystalline YAG:Eu powders with the annealing temperature is the maximum splitting of the \(^7F_1\) level, \( \Delta E \) [13]. In Fig. 11 we observe a reduction of the maximum splitting of the \(^7F_1\) level with increasing annealing temperature from approx. 172 cm\(^{-1}\) to 167 cm\(^{-1}\). We note that the

![Fig. 11 – Dependence of the maximum splitting of the \(^7F_1\) level \( \Delta E \) of the annealing temperature.](image2)
value of 167 cm⁻¹, obtained for the YAG:Eu powder annealed at 1400°C, corresponds to the bulk material value [14]. For the amorphous powder (annealed at 900°C, Fig. 3) the maximum splitting is much larger: 328 cm⁻¹. Since the value of the maximum splitting is proportional with the crystal field intensity [13], the intensity of the crystal field decreases with the increase of the annealing temperature, i.e. the crystal field intensity decreases with the increase of the crystallite dimension.

4. SUMMARY

Two experimental techniques (Mössbauer and optical spectroscopy) put into evidence the morphological changes of the YAG:Eu nanocrystalline powders synthesized by a sol-gel method, inducing by the thermal treatments. Both methods exhibit drastic changes of the monitored parameters at the phase transition amorphous-crystalline, followed by a slow evolution of these parameters with the increase of the annealing temperature. This slow evolution is due to the increase in size of the nanocrystals. The spectroscopic parameters of the two techniques could monitor the increase in size of the nanocrystals and empirical relations could be established vs. the diameter of crystallites, via annealing temperature in the growing process of YAG crystal.

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REFERENCES


