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MÖSSBAUER SPECTROSCOPY STUDY ON YVO_4:Eu LUMINESCENT MATERIAL

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Abstract. The information about the local neighborhood of Eu Mössbauer isotope locating in yttrium vanadate nanoparticles was obtained by the room temperature measurements, in transmission and electron backscattering geometry. The Eu has the valence state 3+ and two different quadrupole elementary patterns can be distinguished up to around $T_0 = 700^0$C. At higher temperatures, the Mössbauer spectra consist in a single quadrupole pattern. Electron-backscattering spectra revealed a tendency to change T_0 and a higher distortion of the Eu neighborhood.

Key words: Mössbauer spectroscopy, Eu-151, YVO_4, Auger electrons.

1. INTRODUCTION

YVO_4:Eu^{3+} is a strong luminescent material, largely used as red phosphor [1] in colour television cathode ray tube displays and high pressure mercury lamps [2]. The recent studies show that nanosized YVO_4:Eu^{3+} is a significant promise for plasma display panels (PDP) [3]. Eu^{3+} ion substitues the Y^{3+}-site (point symmetry D_{2d}) in zircon type structure of YVO_4 [4] (space group $I4_1/amd$, lattice parameters a = 7.1183 Å, c = 6.2893 Å [5]). Droping dimension from bulk to nanocrystals changes the metal-lygand covalency and the splitting of the energy levels.

One of the useful structural techniques to study bulk-crystalline or nanocrystalline powders is the Mössbauer effect spectroscopy technique, in transmission or electron backscattering geometry. The main advantage of the Mössbauer spectroscopy compared with other techniques consists in the possibility to non-destructively detect the valence state of Mössbauer hosting ion, the paramagnetic and ordered magnetic phases in a simple way. In the present work the advantage of Mössbauer effect consists especially to mark off the different ionic vicinities around the Mössbauer probe, by means of the hyperfine interactions

between the local electric and magnetic crystalline fields and the Mössbauer isotope. Using Eu as sensitive probe for Mössbauer spectroscopy, the local changes induced by the thermal treatments of YVO_4 nanocrystals are evidenced. The present work continue the previous investigation of optical interesting crystalline media doped with the rear earth ions [6, 7].

2. EXPERIMENTAL

$YVO_4:Eu^{3+}$-nanocrystals (with nominal 5 at.% Eu) have been obtained by the precipitation procedure. Two solutions, $Y(NO_3)_3$ and $Eu(NO_3)_3$ were prepared and added to a solution of NH_4VO_3 adjusted to pH 12.5 with NaOH. The obtained colloid was heated at 60^0C for one hour under magnetic stirring. The nanocrystals of $YVO_4:Eu^{3+}$ were extracted from the resulted suspension by filtering and then heating for one our at 60^0C. The resulting nanopowders were annealed in air at various temperatures $T \in$ [300 ÷ 1300^0C] for four hours. More experimental detailes are given in ref. [8, 9].

X-ray diffraction (XRD) measurements were carried out on a DRON-2 diffractometer, using $Cu_{K\alpha}$ radiation (1.54051Å). For all samples the scan parameters included an angular resolution of 0.04 degrees and a scan speed of 2 degrees/minute.

Mössbauer measurements were performed in the velocity range $v \in$[–21 mm/s ÷ +21 mm/s], at room temperature by standard transmission (ME) and electron backscattering (CEMS) techniques, using AME-20, AME-50 Elscint conventional constant-acceleration spectrometers with a ^{151}Sm source in samarium oxide matrix. The velocity calibration has been performed using α-Fe_2O_3 standard. The backscattering measurements used the detection of Auger [10] electrons with energies around 7 keV. The measurements were conducted at a high degree of accuracy with a new detector, gas-flow proportional detector with a 99% He + 1% C_4H_{10} mixture [11]. The CEMS spectra were recorded in perpendicular backscattering geometry, *i.e.* with the incident γ-ray direction perpendicular to the sample plane. The powder samples for CEMS were fixed on a support with a solution of 5% colloidon in amyl acetate. The parameters of the Mössbauer spectra were calculated using a computer fitting program, in the hypothesis of Lorentzian line shape [12]. A background correction and a smoothing procedure of the spectra were performed before the fitting runs.

3. RESULTS AND DISCUSSION

XRD patterns of YVO_4 nanopowders annealed in air at three temperatures (60, 600 and 1200^0C) are shown in Fig. 1. The diffractograms revealed the YVO_4 powder pattern and have been indexed as a single phase. The results of the Rietveld

structure refinements indicated an increase of crystallite size with the annealing temperature: 12 nm, 48 nm and 60 nm respectively.

The Mössbauer experimental spectra of YVO_4 nanopowders annealed in air at different temperatures and fitting patterns are plotted in Fig. 2 (transmission spectra) and 3 (backscattering spectra). The Mössbauer fit parameters are given in Table 1.

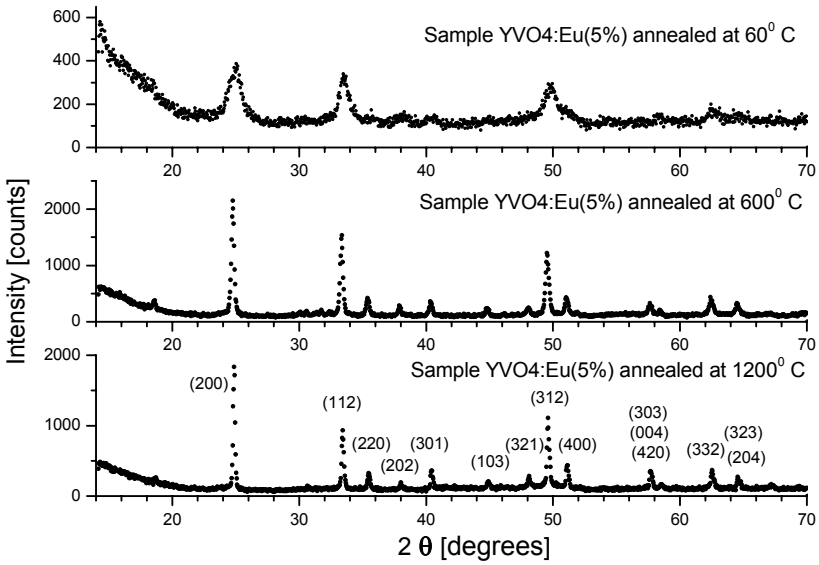

Fig. 1 – The X-ray diffraction patterns on YVO_4 nanopowders annealed in air at various temperatures.

Up to 700°C, the Mössbauer spectra consist in two main contributions: a central broad (~ 8 mm/s ÷ 9 mm/s) as preponderant (~ 65%) line-resonance (A) and a less large (~4 mm/s ÷ 5 mm/s) and less intense (~ 35%), resonance (B), at around $v \in$[5 mm/s ÷ 7 mm/s]. This behaviour can be ascribed to the presence of Eu ions in different possible micro-environments in YVO_4:Eu structure. So, the spectra of the "as prepared" samples and of the samples annealed up 700°C were fitted with two superimposed quadrupole ^{151}Eu-elementary patterns (I7/2, ± M_e> $^{+}$– > I5/2, ± M_g >$^{+}$, [13], called A and respectively B patterns, characterised by the following hyperfine parameters: the isomer shift δ relative to the source Sm_2O_3-matrix, quadrupole parameter $eQ_{7/2}V_{zz}$, resonance line width Γ_{obs} and relative areas. The main constraints of the fit procedure have been the same line-widths and theoretical intensities of the pattern's resonances. Generally, one can observe that $\Gamma_{obs,A}$ values are different in comparison with $\Gamma_{obs,B}$ ($\Gamma_{obs,A}<\Gamma_{obs,B}$ for $T > 60$°C), but the half line widths of the elementary patterns resonances are in the theoretical limits, $\Gamma_{obs}/2 \in$ [1.12 ÷ 1.69] mm/s, corresponding to well-defined micro-environments B and A. The two different micro-environments of ^{151}Eu, correspond to different distorted oxygen polyhedrons ($/eQ_{7/2}V_{zzA}/ < /eQ_{7/2}V_{zzB}/$) of

trivalent Eu-ions. One can remarks the low values of δ (~ 0.0 mm/s) for A-pattern, suggesting an Eu-O chemical bond similar to that observed in Eu_2O_3. The central shifts of both elementary patterns correspond to trivalent europium [14, 15]; the values for A patterns indicate a more ionic chemical bonding Eu-O than for B patterns. A pattern can be assigned to symmetric oxygen-surrounding of ^{151}Eu and B pattern corresponds to a very asymmetric one, coming from particle surface contribution. As the annealing temperature increases, the feature of the spectra changes too. The intensity of the B doublet decreases up to its disappearance and A doublet becomes more symmetric at T_o ~700°C. The observed differences between the parameters given by transmission and backscattering spectra could be explained by the differences of information obtained in the utilised geometries. The transmission geometry gives mainly a volume information and backscattering geometry give mainly a surface information. For our samples, the backscattering spectra suggest a higher distortion of the Eu neighborhood at surface.

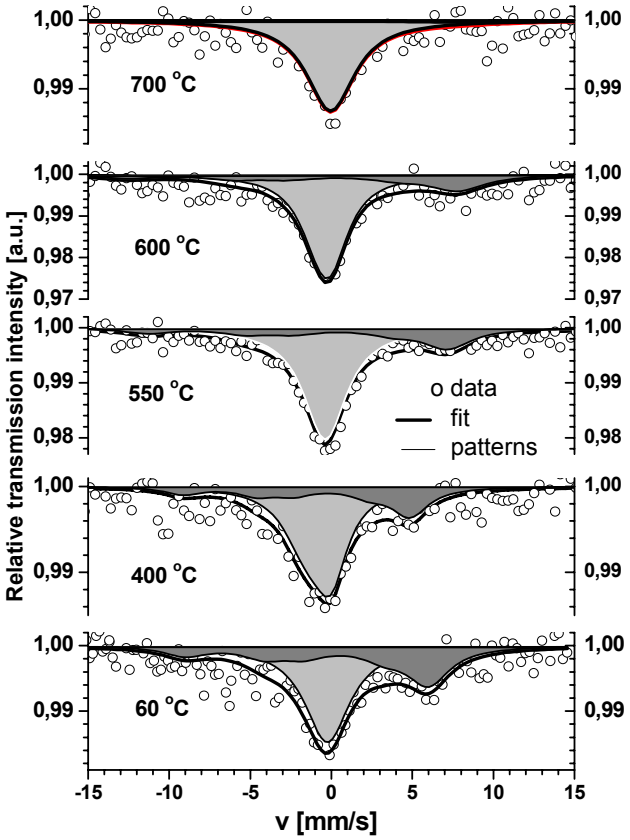

Fig. 2 – The experimental transmission spectra of the YVO_4:Eu powders annealed at various temperatures and fitting patterns.

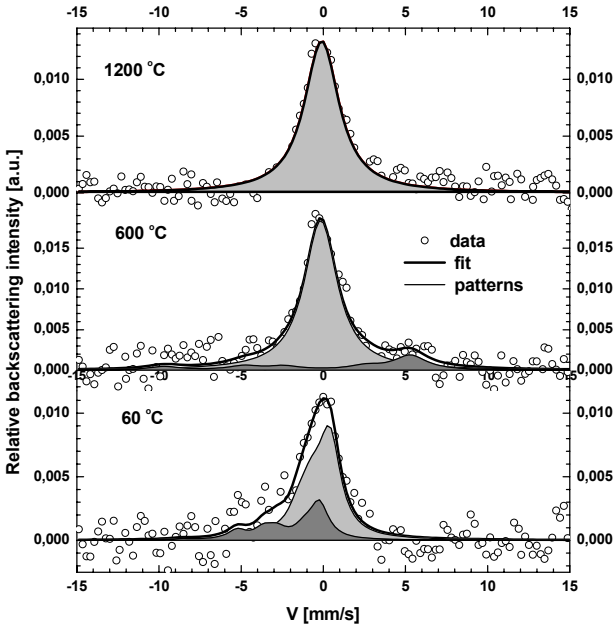

Fig. 3 – The experimental backscattering spectra of the YVO_4:Eu powders annealed at various temperatures and fitting patterns.

Table 1

The values of the hyperfine parameters obtained from spectra

Annealing temperature	Spectrum type	Computed Mössbauer parameters				
		Sublattice	δ_{Sm2O3} [mm/s]	$eQ_{7/2}V_{ZZ}$ [mm/s]	$\Gamma_{obs}/2$ [mm/s]	Area [%]
1200^0 C	backscattering	A	–0.03	–6.3	1.09	100
900^0 C	transmission	A	–0.02	–0.05	1.18	100
700^0C	transmission	A	–0.02	–1.69	1.79	100
600^0 C	backscattering	A	–0.17	1.26	1.35	83
		B	0.21	70.01	1.40	17
600^0 C	transmission	A	–0.35	5.02	1,37	70
		B	0.88	95.04	2.08	30
550^0C	transmission	A	–0.30	–	1.60	70
		B	0.89	86.32	1.78	30
400^oC	transmission	A	–0.74	10.82	1.47	68
		B	0.11	65.31	1.37	32
60^0 C	backscattering	A	–0.22	9.20	1.68	71
		B	–1.94	23.36	1.44	29
60^0 C	transmission	A	–0.24	–0.33	1.69	57
		B	0.90	69.81	1.60	43
Errors			±0.05	±2.06	±0.06	±3

The best fit of the transmission spectra for the sample annealed at $T > 700^0$C was obtained considering only one pattern with hyperfine parameters values much closed to the doublet A parameters.

The increase of the particle size diminishes the surface contribution to the Mössbauer spectrum, consequently the volume contribution becomes dominant at the annealing temperature of $T > 700^0$C. The fit results for the annealed samples revealed a critical temperature $T_0 \approx 700^0$C, suggesting a transition state in the growth process of YVO_4:Eu crystallite.

4. CONCLUSIONS

The analysis of the experimental ^{151}Eu Mössbauer spectra revealed the presence of two inequivalent Eu^{3+} ions in the YVO_4:Eu lattice. They are located in two different distorted oxygen polyhedrons. The Mössbauer backscattering spectra exhibit different hyperfine parameters in comparison with the transmission spectra on the same sample. These differences indicate changes arround the Mössbauer nuclei located near particle surface. At higher temperatures Mössbauer spectrum consists in a single quadrupolar doublet. A critical temperature $T_0 \approx 700^0$C, suggesting a transition state in the growth process of YVO_4:Eu crystallites was identified.

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