

MÖSSBAUER SPECTROSCOPY ON ^{151}Eu

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Rezumat. Spectroscopia Mössbauer reprezintă absorbția și emisia rezonantă, fără recul a radiațiilor gama de joasă energie; efectul este semnificativ când nucleele sunt înglobate într-o matrice rigidă. Ea oferă informații despre starea chimică și/sau vecinătatea nucleului Mössbauer. Izotopul ^{151}Eu este unul din cei 3 izotopi care pot fi studiați la temperatura camerei alături de izotopii ^{57}Fe și ^{119}Sn . În ultimii ani a crescut numărul de studii cu izotopul ^{151}Eu pentru clase largi de material: materiale optice avansate, sticle, materiale ceramice speciale etc. Autorul expune, după o scurtă prezentare a spectroscopiei Mössbauer și a izotopului ^{151}Eu , rezultatele sale originale obținute în ultimii ani în spectroscopia Mössbauer a ^{151}Eu : un nou detector cu flux de gaz pentru măsurători de retroîmprăștiere cu electroni sau raze X de joasă energie, posibilitatea de a efectua măsurători în gama nano este elucidată și demonstrată; investigarea schimbărilor morfologice induse de tratamentele termice efectuate pe cristale YAG:Eu, sintetizate prin metoda sol-gel, studii de suprafață și volum pe nanofosfor $\text{YVO}_4:\text{Eu}$ privind schimbările locale induse de tratamentele termice efectuate pe nanocristale etc.

Cuvinte cheie: Spectroscopie Mössbauer, ^{151}Eu , studii de suprafață, cristale YAG:Eu; nanofosfor $\text{YVO}_4:\text{Eu}$.

Abstract. Mössbauer spectroscopy is based on the resonant recoil free absorption and emission of low energy γ -rays; the effect is significant when the nuclei are imbedded in a rigid matrix. It offers information about chemical state and/or environment of the Mössbauer nucleus. ^{151}Eu isotope is one of the 3 isotopes which can be investigated at room temperature, near ^{57}Fe and ^{119}Sn . In the last years increased the number of studies with ^{151}Eu isotope for a large class of materials: advanced optical materials, glass materials, special ceramic materials, etc. The author presents, after a short presentation of Mössbauer spectroscopy and ^{151}Eu isotope, the original results obtained by him in the last years in Mössbauer Spectroscopy on ^{151}Eu : a new flow detector for backscattering measurements with electrons or low energy X rays, the possibility to do surface measurements in the nano range using ^{151}Eu isotope is elucidated and demonstrated; investigation of the morphological changes induced by the thermal treatments of YAG:Eu crystals synthesized by sol-gel method; volume and surfaces studies on $\text{YVO}_4:\text{Eu}$ nanophosphor concerning local changes induced by the thermal treatments of nanocrystals, etc.

Keywords: Mössbauer spectroscopy, ^{151}Eu , surface studies, Eu: YAG nanocrystals, Eu: YVO_4 nanophosphor.

1. INTRODUCTION

Mössbauer spectroscopy [1 – 3] is based on the incorporation of the emitting and absorbing nuclei within a solid matrix, which enables resonant recoil free absorption and emission of γ -rays. Its importance lies in the very narrow line width of the emitting photon resulting from the relatively long lifetime of the excited nuclear state - typically of 10^{-8}s , corresponding to a natural line width of the order of 10^{-8}eV - and the consequent ability to probe the variations in nuclear energy levels resulting from any discrete changes in the chemical state and/or environment of the Mössbauer nucleus. Such

changes in nuclear energy levels are measured by modifying the energy of the probing γ -rays by applying a Doppler shift: a Mössbauer spectrum therefore consists of a plot of counts against applied Doppler velocity (positive and negative). Significant recoil-free-fractions occur only for gamma energies less than 150 keV, and whilst some isotopes have quite low energy gamma rays, as the energy of the gamma ray increases so also does the necessity of collecting data with the sample and or source at low temperatures. This limitation obviously means that room or high temperature Mössbauer work is possible only for a limited number of isotopes: e.g. ^{57}Fe , ^{119}Sn , ^{151}Eu .

Following resonant absorption of a gamma ray, the nucleus may de-excite by emission of a gamma ray or by the process of internal conversion where an inner (K or L) shell electron is emitted. Accompanying conversion electron emission is a characteristic X-ray emitted as a result of the repopulation of the inner energy levels. Detecting the three backscattered particles permits surface studies to be performed. The conversion signal is quite high for the ^{57}Fe , ^{119}Sn and ^{151}Eu isotopes.

Volume/interface/surface information can be easily extracted from spectra by local character and the site specificity of Mössbauer spectroscopy.

Mössbauer spectroscopy is studying the following hyperfine interactions:

a) Isomer shift (σ) arises because the nuclear energy levels are sensitive to changes in electron density at the nucleus, from differences in local topology as well as in valence state of the Mössbauer isotope. It is, therefore, possible to determine changes in oxidation state or gain an indication on the strength of bonding between the Mössbauer isotope and the surrounding atoms or ions. The value of σ (which must be considered relative to the natural line width of the γ -ray) depends directly upon the difference in radii of the ground and excited nuclear states.

b) Electric quadrupole splitting (ΔE_Q) arises for any nucleus with nuclear spin quantum number I greater than $1/2$ and which, therefore, possess a non-spherical charge distribution. The magnitude of this non-sphericity is given by the nuclear quadrupole moment Q , the sign of which depends on the shape of the deformation. If the symmetry of the surrounding electronic charge is not spherical (for the atomic electrons) or cubic (for the surrounding ions) the degeneracy of the nuclear spin is lifted and two or more absorption lines are seen, the number depending on the values of I in the ground and excited states.

c) Magnetic hyperfine splitting. Any interaction between the nuclear dipole moment with a magnetic field lifts the degeneracy of the magnetic sublevels and gives rise to $2I + 1$ levels. Separation between the peaks in the spectrum is proportional to the magnetic field at the nucleus. Evaluation of the magnetic hyperfine splitting permits to gain extremely useful information about the magnetic properties of the investigated compounds, information about directions of easy magnetization and size of magnetic interactions. Particle size determination may also be made since the temperature at which magnetic ordering occurs depends critically on the particle size.

All mentioned hyperfine interactions can occur simultaneously. In magnetically ordered compounds with a non-vanishing electric field gradient the shape of the spectrum depends on the relative strengths of the magnetic dipole and the electric quadrupole interaction.

d) Recoil free fraction (f -factor). A necessary condition for absorption to occur is that the emitting and absorbing atoms form part of a rigid lattice, such that recoil energy associated with emission and absorption of the γ -quantum is taken up by the lattice as a whole. The probability of such an event depends on the size of the recoil energy and the spectrum of quantified vibration energy levels that describes the motion of the lattice. The intensity of the Mössbauer effect is thus determined by recoil free fraction or f -factor $f = \exp(-k^2 \langle x^2 \rangle)$, where k is the wave number of the γ radiation ($k = 2\pi/\lambda$), $\langle x^2 \rangle$ is the mean squared displacement of atoms from their average position due to lattice vibrations.

From these parameters, we have to derive the phase analysis and the site population for the various sites in a specific phase. Sometimes these hyperfine interactions might be time-dependent (diffusion, superparamagnetism and life-time). Additionally, the measuring efficiency might depend on the material and its temperature.

2. EXPERIMENTAL

Mössbauer measurements were carried in transmission geometry and backscattering geometry at room temperature. Transmission measurements were effected with a standard Elscint Promeda 50 Mossbauer spectrometer. Backscattering measurements were made with versatile counter for conversion Mössbauer spectroscopy, suitable for surface studies [4]. The detector, version of a gas-flow proportional detector, permits the detection of conversion electrons or conversion X-rays by changing the detection gas and the volume of the detection space. Its design, in a cylindrical geometry, and construction make possible, easily, the mentioned changes. The improved design of the detector is found to be superior design than those previously reported for such devices [5], [6]. The anode, 50 μm gold-coated tungsten wire, is placed in the center of the detector by means of a stainless steel ring. On the ring is realized anode configuration. The ring can be changed easily with another having other anode configuration. In this way the measurements efficiency can be optimized. The detection space is a 40 mm diameter cylinder with a variable height around anode ring, from 0 to 38 mm. The detection volume can be choose symmetrical or not in respect with anode plan. The changes of the detection volume and detection gas (94% He + 6% CH₄ or 99% He + 1% C₄H₁₀ for electrons; 92% Ar + 8% CH₄ for X-ray) lead to possibilities to detect conversion electrons or conversion X-rays. The front side of the detector is closed with a thin window of aluminised mylar. On the rear side of the detector is mounted a removable sample holder equipped with a thin aluminised mylar window. The sample holder allows an easy manipulation of the sample, outside the detector and can always be repositioned in a reproducible manner with respect to the detector body. The holder also allows performing simultaneously surface and transmission measurements. The performances of the detector were demonstrated by test measurements on stainless steel and natural iron samples. The Eu₂O₃ powder [7], one of the most studied compounds by Eu Mössbauer spectroscopy, has been used as sample for test measurements. For backscattering measurements it has been deposited on support by a solvent.

We used an 80 mCi ¹⁵¹Sm diffused in samarium oxide, source supplied by Amersham QSA England. Backscattering measurements were carried on Elscint AME-50 Mössbauer spectrometer by inserting the mentioned flow gas proportional counter into spectrometer. In order to absorb unfavourable Eu LX-rays (5.84 ÷ 7.64 keV) from the source; a thin aluminium filter is placed in front of the detector. This filter can absorb more than 80% of the X-rays. The surface measurements have been conducted at a high degree of accuracy, ensuring the same geometry of the detection space and the same gas flow rate for measurements. The count rate for ¹⁵¹Eu isotope is low compared with measurements for ⁵⁷Fe, ¹¹⁹Sn isotopes. The parameters of the Mössbauer spectra were calculated using a computer fitting program, which assumes a Lorentzian line shape. The isomer shifts were referred to α -Fe, or relative to the source Sm₂O₃-matrix or relative to Eu₂O₃ etalon.

The amplitude spectrum of the detector, adjusted for X-ray, with the Eu₂O₃ sample inside the detector is shown in Figure 1. The amplitude spectrum of the backscattered photons obtained without filter displays a visible structure and has a good resolution for low energy X-ray and low effectiveness for Mössbauer radiation. This fact proves the performance of the detector.

3. ¹⁵¹EU MÖSSBAUER ISOTOPE

There are 45 chemical elements studied by Mössbauer effect [8] but there are only three Mössbauer isotopes which can be studied at room temperature: ⁵⁷Fe, ¹¹⁹Sn and ¹⁵¹Eu due low energies of the Mössbauer transitions.

The isotopic abundance of ¹⁵¹Eu is 47.8(5) % [9] and energy of the Mössbauer transition is 21.54 keV.

The decay diagram used in the studies with this isotopes is represented in Figure 2 and the secondary radiations emitted by the de-excitation of the 21.54 keV nuclear excited state of ^{151}Eu are given in Table 1 [10], [11]. There are not conversion electrons emitted by de-excitation of isotope ^{151}Eu nucleus, comparatively with the isotopes ^{57}Fe , ^{119}Sn .

I demonstrated theoretical and experimental [12] the possibility to do surface measurements on sample containing ^{151}Eu for practically the same depth range as for isotopes ^{57}Fe , ^{119}Sn . Consulting the site <http://ie.lbl.gov/toi/xray.asp> (now the access is at: <http://ie.lbl.gov/toi/xraySearch.asp>), managed by Firestone, one of the authors of the reference book in this field [5], I found that Eu-151 emits Auger electrons. The characteristics of low energy Auger electrons (energy < 10 keV) are presented in Table 2. Their energies are closed to those of conversion electrons emitted by ^{57}Fe Mössbauer isotope.

Fig. 1. Pulse height spectrum of photons scattered from a Eu_2O_3 sample obtained with detector adjusted for X-ray.

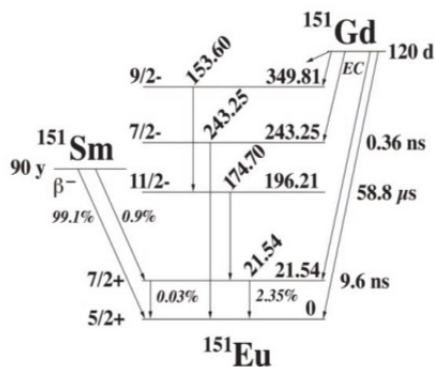
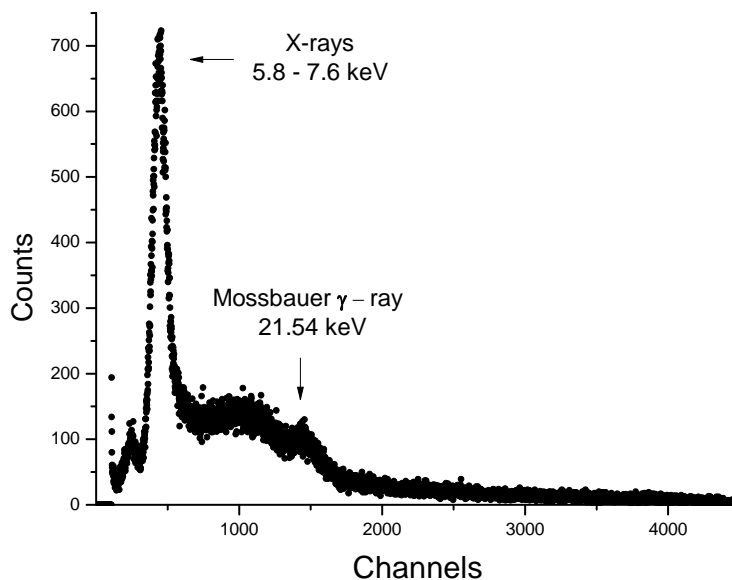


Fig. 2 The decay diagram for the Mössbauer isotope ^{151}Eu

Table 1

The secondary radiations emitted by the de-excitation of the 21.54 keV nuclear excited state of ^{151}Eu

| Secondary radiation | Energy (keV) |
|-------------------------|--------------|
| γ -ray radiation | |
| γ_M ray | 21.54 |
| X-ray transition | |
| L_α line | 5.843 |
| L_β line | 6.571 |
| L_γ line | 7.644 |

The amplitude spectrum obtained with ^{151}Sm source and Eu_2O_3 sample inside, in a geometry like that used for conversion electrons of ^{57}Fe isotope is presented in Figure 3. The electron pulse height spectrum proves the existence of the Auger electrons. It displays a visible structure, a large peak corresponding to electron energies.

Table 2

Low energy Auger electrons from Eu (Z=63)

| Assignment | Energy (keV) | Intensity per 100 vacancies in the: | | | |
|----------------------|--------------|-------------------------------------|-----------------------|-----------------------|-----------------------|
| | | K-shell | L ₁ -shell | L ₂ -shell | L ₃ -shell |
| Eu L ₃ -X | 6.464 | 43 | | | 85 |
| Eu L ₂ -X | 7.104 | 20 | | 70 | |
| Eu L ₁ -X | 7.539 | 1.5 | 43 | | |

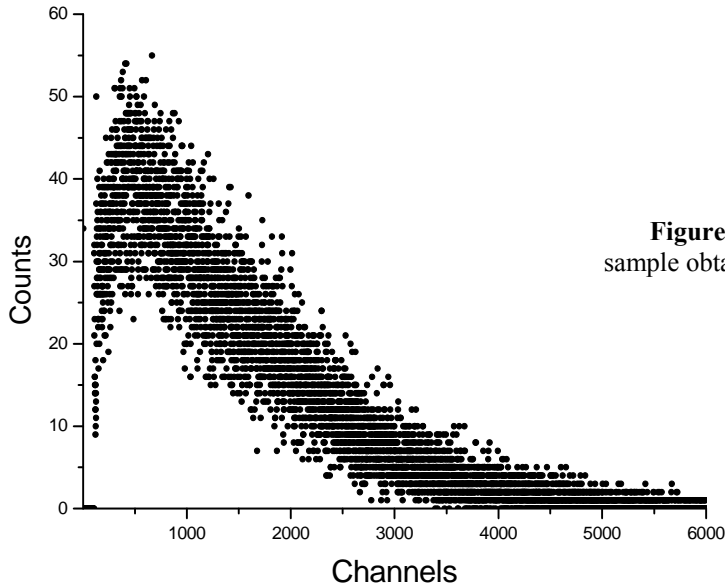


Figure 3 Pulse height spectrum from a Eu₂O₃ sample obtained with detector adjusted for low energy electrons

Figure 4 Mössbauer spectra of Eu₂O₃ obtained by Auger electrons and transmitted gamma radiation:
 ○ data, — fit.

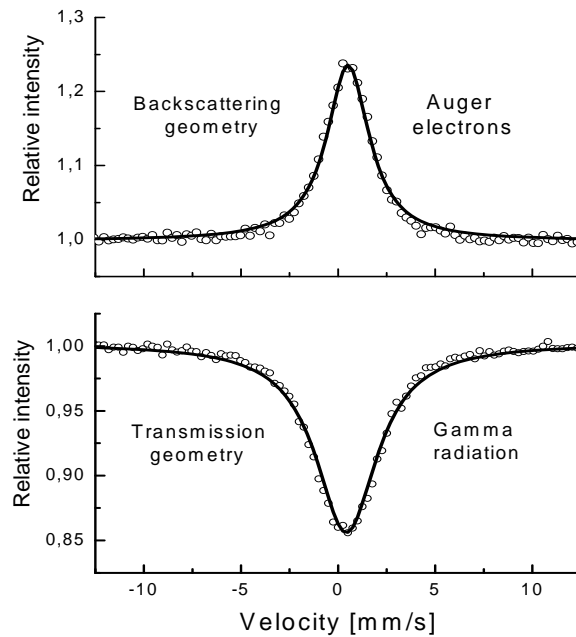


Figure 4 shows the two Mössbauer spectra: one obtained in the same geometry as given amplitude spectrum and other in transmission geometry for a Eu₂O₃ sample with 10 mg/cm² thickness.

The parameters obtained in backscattering geometry: resonance effect (ϵ) = 23.69 ± 0.05 %, line width (w) = 2.56 ± 0.03 mm/s are better than those obtained in the transmission: $\epsilon = 14.65 \pm 0.05$ %; $w = 3.35 \pm 0.03$ mm/s [12]. The spectra had been fitted with a single lorentzian line not considering a difference in the two forms of Eu₂O₃ and a quadrupole interaction. Whether there is or not a difference in the two chemical shifts is not clear from the relevant literature [14, 15]. The source supplier gave in its test report a full width at half height of 2.40 mm/s after deduction of absorber (europium fluoride) thickness contribution. The presented data prove the possibility to do surface measurements on sample containing Eu by detection of Auger electrons delivered in the decay process of the ¹⁵¹Eu Mössbauer nucleus. A higher resonance effect and a lower line width are obtained for Eu₂O₃ sample in backscattering geometry compared with transmission geometry. The preparation procedure of sample for surface measurements reduces count rate and can decrease the resonance effect.

Mössbauer spectra for ¹⁵¹Eu can be obtained also by detection of conversion X-rays [4], [11]. We obtained the following parameters for a Eu₂O₃ sample: resonance effect (ϵ) = 9.67 ± 0.05 %, line width (w) = 2.43 ± 0.03 mm/s. The line width is better than those obtained in the transmission for a Eu₂O₃ sample with 10 mg/cm² thickness. The detection of the conversion X-rays compensate smaller resonance effect by its significant smaller line width: 2.43 mm/s instead 3.35 mm/s in transmission.

The backscattering measurements by detection of electrons or X-rays were performed for the first time in Romania.

In the last years increased the number of studies with ¹⁵¹Eu isotope for a large class of materials: advanced optical materials (with special properties) based on crystals YAG, LGS, LGT doped with Eu, glass materials, special ceramic materials (Pb-Ti doped with Eu), inter-metallic compounds (Eu-Zn) with specific magnetic properties, high-T_c superconductors, rare-earth intermetallic compounds RM₂X₂ (M = transition metal, X = Si, Ge, or P), etc.

4. MÖSSBAUER INVESTIGATION OF Eu:YAG NANOCRYSTALS

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 [15].

Yttrium aluminates based on the system Y₂O₃–Al₂O₃ are promising materials with regard to their optical, mechanical, chemical, and thermal properties. The yttrium aluminum garnet (YAG–Y₃Al₅O₁₂) crystallizes in the cubic form and exhibits outstanding properties when doped with lanthanide or transition elements. Usual applications include laser active media and phosphors.

The YAG:Eu nanocrystals were obtained by a nitrate-citrate sol-gel method [16]. The final mixture was evaporated at 80°C until a transparent viscous gel was obtained. The gel was decomposed at 600°C for 6 h obtaining a black fluffy powder in an amorphous state. The powder was calcinated at 850°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°C), for 4 hours each. After a thermal treatment at 930°C, pure crystalline YAG phase was obtained.

Mössbauer were performed on powder samples annealed at 900, 930, 1000, 1100, 1200, 1300, 1400 for 4 hours and 1400°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 and the spectra are shown in Figure 5.

Spectrum of the sample annealed at 900°C shows a central peak and an additional one at $\sim +7$ mm/s, which has not found in the other spectra. The most probably, the additional peak is either a strong component of a ¹⁵¹Eu large quadrupole splitting pattern or more probably a signal of Mössbauer probe in primary chemical ingredients, Eu(NO₃)₃ for example. Mössbauer spectra for the samples annealed at $T_{an} \geq 930^\circ\text{C}$ evidence a very large and slightly asymmetric transmission peak

closed to center. 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 γ ray transition of ^{151}Eu . The obtained parameters are showing abrupt changes from $T_{an} = 900^\circ\text{C}$ to $T_{an} = 930^\circ\text{C}$ (known as amorphous-crystalline temperature of YAG). 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 $T_{an} > 930^\circ\text{C}$ revealed slower changes of spectral parameters vs. increasing T_{an} . The slow changes of the Mössbauer spectral parameters can be explained taking into account the contributions of the Mössbauer probes on crystallite boundary (surface) and in volume one to spectra. The growth of crystallite and the increasing of its apparent average size induce an increasing of all MS parameters go to their limit-values. All data for the spectra annealed at $T_{an} \geq 930^\circ\text{C}$ evidence 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.

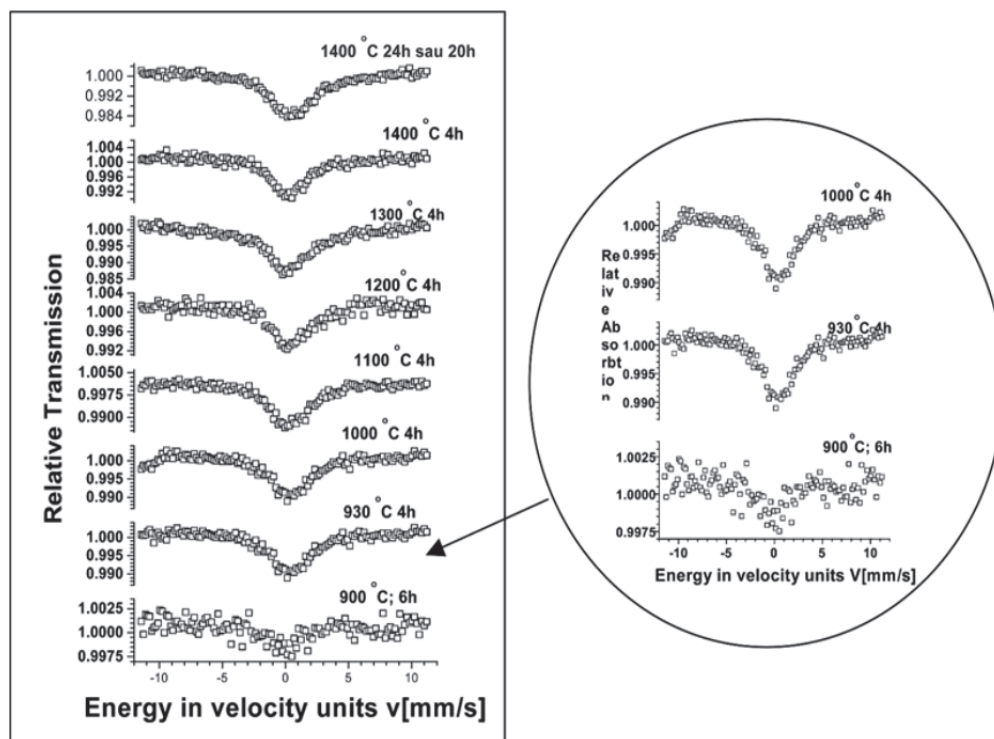


Fig. 5 Mössbauer spectra of the YAG:Eu sample annealed at specified annealed temperatures.

5. MÖSSBAUER INVESTIGATION OF $\text{YVO}_4:\text{Eu}$ NANOPHOSPHOR

$\text{YVO}_4:\text{Eu}^{3+}$ is a strong luminescent material, largely used as red phosphor in colour television cathode ray tube displays and high pressure mercury lamps. The recent studies show that nanosized $\text{YVO}_4:\text{Eu}^{3+}$ has significant promise in plasma display panels (PDP) [17].

$\text{YVO}_4:\text{Eu}^{3+}$ -nanocrystals (with nominal 5 at.% Eu) have been obtained by the precipitation procedure [18]. The resulting nanocrystals were separated from solution by filtering and then heated for

one hour at 60°C. The nanopowders were annealed in air at various temperatures $T \in [300^\circ\text{C} \div 1300^\circ\text{C}]$ for four hours. X-ray diffraction patterns of YVO_4 nanopowders annealed in air at three temperatures (60, 600 and 1200°C) revealed the YVO_4 powder patterns with a single phase. The Rietveld structure refinements indicated an increase of crystallite size as the annealing temperature: 12 nm, 48 nm and 60 nm respectively [19]. Mössbauer measurements were performed at room temperature in transmission and backscattering geometry by electron detection [19, 20, 21]. The backscattering spectra are presented in Figure 6.

The values of the hyperfine parameters obtained from spectra are given in table 3 where $\delta_{\text{Sm}_2\text{O}_3}$: isomer shift relative to the source in Sm_2O_3 -matrix, $eQ_{7/2}V_{zz}$: quadrupole parameter, Γ_{obs} : line width, **A**: relative area of subspectrum.

Up to 700°C, the Mössbauer spectra consist in two main contributions: a central broad as preponderant line-resonance (A) and a less large and less intense resonance (B), around $v \in [5 \text{ mm/s} \div 6 \text{ mm/s}]$. This behaviour can be ascribed to the presence of Eu ions in different possible micro-environments in $\text{YVO}_4:\text{Eu}$ structure. The spectra of the “as prepared” samples and of the annealed samples up 700°C inclusively, were fitted with two superimposed quadrupole ^{151}Eu -elementary patterns, called A and respectively B pattern, corresponding to well-defined A and B micro-environments. The two different micro-environments of ^{151}Eu , correspond to different distorted oxygen polyhedrons of trivalent Eu-ions [7]. The low values of δ for A-pattern, suggest Eu-O chemical bond similar to that observed in Eu_2O_3 and slowly different for B. The values of A patterns indicate a more ionic chemical bonding Eu-O than for B patterns. A pattern corresponds to symmetric oxygen-surrounding of ^{151}Eu and B pattern corresponds to an asymmetric one, close to particle surface. As the annealing temperature increases, the B contribution intensity decreases up to its disappearance and A becomes more symmetric at $T_o \sim 700^\circ\text{C}$. Mössbauer parameters of backscattering spectra suggest a higher distortion of the Eu neighborhood at surface. The best fit for the sample annealed at $T > 700^\circ\text{C}$ has one pattern. The temperature dependence of the Mössbauer line-shapes of spectra suggests the effect of nanocrystals growth vs. annealing temperature, as one was observed by XRD spectra. The particle growth diminish the surface contribution to spectrum, consequently the volume contribution becomes dominant at the annealing temperature of $T > 700^\circ\text{C}$.

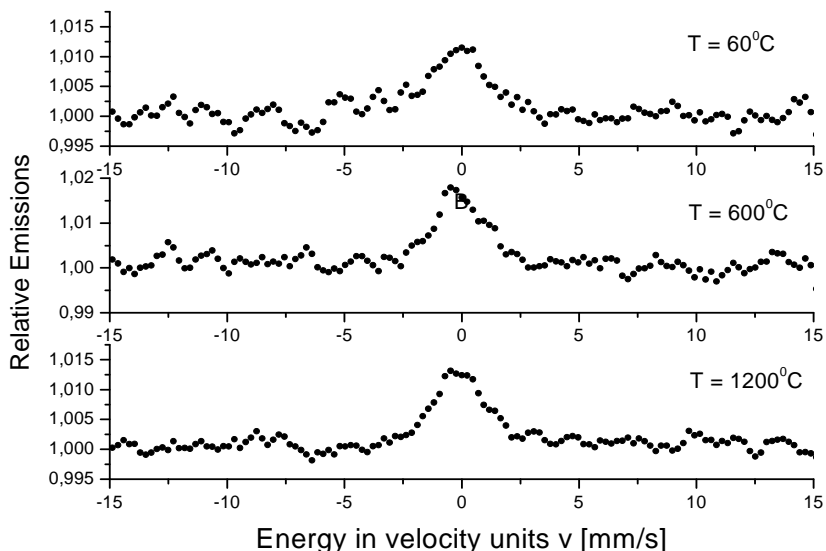


Fig. 6. The electron backscattering spectra of $\text{YVO}_4:\text{Eu}$ powders annealed at different temperatures.

Table 3

The values of the hyperfine parameters obtained from spectra

| Annealing temperature | Spectrum type | Computed Mössbauer parameters | | | | |
|-----------------------|----------------|-------------------------------|---|-------------------------|--------------------------------|----------|
| | | Sublattice | $\delta_{\text{Sm}_2\text{O}_3}$ [mm/s] | $eQ_{7/2}V_{ZZ}$ [mm/s] | $\Gamma_{\text{obs}}/2$ [mm/s] | Area [%] |
| 1200° C | backscattering | A | -0.03 | -6.3 | 1.09 | 100 |
| 900° C | transmission | A | -0.02 | -0.05 | 1.18 | 100 |
| 700° C | transmission | A | -0.02 | -1.69 | 1.79 | 100 |
| 600° C | backscattering | A | -0.17 | 1.26 | 1.35 | 83 |
| | | B | 0.21 | 70.01 | 1.40 | 17 |
| 600° C | transmission | A | -0.35 | 5.02 | 1.37 | 70 |
| | | B | 0.88 | 95.04 | 2.08 | 30 |
| 550° C | transmission | A | -0.30 | - | 1.60 | 70 |
| | | B | 0.89 | 86.32 | 1.78 | 30 |
| 400° C | transmission | A | -0.74 | 10.82 | 1.47 | 68 |
| | | B | 0.11 | 65.31 | 1.37 | 32 |
| 60° C | backscattering | A | -0.22 | 9.20 | 1.68 | 71 |
| | | B | -1.94 | 23.36 | 1.44 | 29 |
| 60° 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 |

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