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Structural and spectroscopic properties of Yb³⁺-doped MgAl₂O₄ nanocrystalline spinel

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Abstract

The magnesium spinel (MgAl₂O₄) powders doped with Yb³⁺ ions have been synthesized by the sol-gel method and heat-treated in the range of 700 – 1000°C for 3 h. XRD patterns indicated that the powders have a cubic structure with high crystallite dispersion. Nanoparticles are obtained as a function of dopant concentration and sintering temperature in the range of 10-30 nm. The main Yb³⁺ zero-phonon line is located at 976 nm and spectroscopic properties of Yb³⁺ ions are characterized by broad absorption spectra and emission spectra even at low temperature revealing a strong distorted spinel lattice due to high inversion rate between Mg²⁺ tetrahedral sites and Al³⁺ octahedral sites. The substitution of Mg²⁺ ions by Yb³⁺ ions favors the creation of Yb³⁺ ion pairs which are pointed out by cooperative luminescence spectra observed at around 500 nm. Luminescence decays are influenced by both Yb³⁺ contents and energy transfer between ions and by the presence of pairs and aggregates. A detailed analysis in connection with observed structural and spectroscopic measurements has been done and described.

Keywords: Photoluminescence; MgAl₂O₄ Spinel powders, Yb³⁺ doping, Nanocrystallites

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1. Introduction

Nanomaterials activated by lanthanide ions are extensively investigated due to their specific luminescent properties^{1,2}. Potential applications of these materials were found in high-performance displays and devices like plasma display devices (PDP), field emission displays (FED), cathode ray tubes (CRT) and electroluminescent displays (EL)³⁻⁶, luminescent markers for biological applications and for optical ceramics⁷. Mainly because of stable chemical properties the most promising materials for applications are metal oxides⁸.

The MgAl₂O₄ is the best representative material of the wide family of complex oxides with spinel crystalline structure which are important in technological applications as host materials for various phosphors for light-emitting. The crystal structure of MgAl₂O₄ is cubic with space group *Fd-3m* (O_{h}^{7} , No. 227 in the International Tables)⁹. Mg, Al, and O are at Wyckoff position *8a*, *16d*, and *32e*, respectively (see Fig.1)¹⁰⁻¹². In an ideal spinel structure the anions are on an approximate close-packed fcc lattice, with the Al and Mg cations at octahedral and tetrahedral interstitial positions, respectively. Spinel is highly prone to cation disorder: some, in inverted spinel even all, Mg ions may exchange positions with Al ions. This problem is particularly severe in synthetic spinels. Natural spinels have less cation disorder. Site mixing among two kinds of cations is known in synthetic crystals up to 25%¹³ and is expected to introduce various centers of positive or negative local charge¹⁴⁻¹⁶.

In this work, the MgAl₂O₄ spinel nanocrystalline powders doped with ytterbium ions were prepared using fast and economic synthesis way so-called the modified Pechini's method. The research of new and cheap luminescence materials for applications involving large number of different types of host lattices should be made. Our interest has been primarily concerned with structural characterization, luminescence spectra, and decays of Yb³⁺-doped spinels nanocrystals. In particular our interest was concerned with the structural changes occurring in Yb³⁺:MgAl₂O₄ with different sizes of crystallites and the investigation of their luminescence properties.

2. Experimental

2.1. Synthesis

Nanocrystalline MgAl₂O₄ doped with Yb³⁺ ions were prepared by sol-gel process. Concentration of the optically active Yb³⁺ ions has been set to 0.5, 1, 2 and 5mol% in against to the appropriate Mg²⁺ molar content. Ytterbium oxide, Yb₂O₃ (99.99%, spectral pure), nitric acid, HNO₃ (63%, ultra-pure, POCh S.A.), aluminum chloride hexahydtrate, AlCl₃·6H₂O (ReagentPlus[®], 99%, Sigma-Aldrich), magnesium nitrate hexahydtrate, Mg(NO₃)₂·6H₂O (ACS reagent, ≥99%, Sigma-Aldrich), citric acid monohydrate (ACS reagent, ≥99.0%, Sigma-Aldrich) and ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich) were used as the starting materials.

The Yb₂O₃ oxide was dissolved in HNO₃ before reaction and diluted with water to form 1M solution. In this method, for the synthesis of 4 mmol of the product, stoichiometric amount of Yb(NO₃)₃·6H₂O solution, AlCl₃·6H₂O and Mg(NO₃)₂·6H₂O were taken and made into a homogeneous solution with deionized water. To the above solution, 50 mmol of citric acid monohydrate (Alfa Aesar, p.a.) and 35 mmol of ethylene glycol (Sigma-Aldrich, p.a.) were added and then the solution was heated to 80°C to make it viscous. In that way, the obtained resin, containing proper molar ratios of all substrates, has been annealed at temperature range 700 to 1000°C for 3h. Then the white powders of Yb3+-doped MgAl2O4 have been formed.

2.2. XRD and TEM analysis

In order to check the development of the crystal phase, XRD patterns of the prepared materials were obtained after heating in the range at 700 to 1000°C for 3 h. The X-ray diffraction (XRD) patterns were collected in 2 Θ range of 10–120° with X'Pert PRO X-ray diffractometer (Cu, K α 1: 1.54060 Å) (PANalytical). The XRD patterns were assigned using the Joint Committee on Powder Diffraction Standards (JCPDS) database and then were analyzed.

Transmission electron microscopy measurements for the Yb³⁺:MgAl₂O₄ powders were carried out on a Tecnai G2 20 X-Twin TEM (Fei, Hillsboro, USA) or a H-8100 TEM of the Hitachi company (Tokyo, Japan) equipped with a Penta FET EDX detector (Oxford Instruments, UK). An acceleration voltage of 200 kV was applied. To prepare the samples, a

suspension of the sample in ethanol was dropped on a copper or gold grid coated with carbon and then dried in air.

2.3. Absorption spectra

Absorption spectra in the 850-1050 nm spectral range were recorded in the temperatures from 4 to 298 K with a Cary-Varian 5000 Scan spectrometer equipped with an Oxford CF 1204 helium flow cryostat. The pellets used for the absorption measurements were prepared under 20 MPa pressure.

2.4. Emission and excitation spectra

The emission and excitation spectra of the Yb³⁺ were measured with a frequency doubled Nd:YAG laser (10 ns, 10 Hz) pumping a Quantel two-amplifier-stage, dye laser containing a mixture of DCM and LD698 and followed by a hydrogen Raman cell shifter to generate a beam in the 920–960 nm range. The specific infrared fluorescence is selected by using a Jobin Yvon HRS1 monochromator fit with a 600 grooves/mm grating blazed at 1 μ m. The signal is detected by a slow North Coast germanium cell, cooled by liquid nitrogen, and sent into a Stanford boxcar averager SRS 250. The decay kinetics were recorded with a Lecroy LT 342 digital oscilloscope connected to a fast North Coast germanium cell.

3. Results and discussion

3.1. XRD and TEM analysis

The formation of the crystalline Yb³⁺ doped MgAl₂O₄ nanopowders was followed by the XRD measurements (**see Fig. 2**). All the samples prepared utilizing sol-gel technique shown detectable crystallinity at all range of proposed sintering temperatures (700 – 1000°C). Comparison of the resulting diffraction patterns with the reference standard of the MgAl₂O₄ (**ICSD 31373**) confirms presence of single phase, cubic structure (*Fd-3m* (No. 227)) of the final product with octahedral Al³⁺ and tetrahedral Mg²⁺ sites¹².



Fig.1. Primitive unit cells of spinel of cubic MgAl₂O₄ with space group *Fd-3m* (O_h^7 , No. 227)¹².



Fig.2. Selected X-ray powder diffraction patterns of 5%mol Yb³⁺-doped MgAl₂O₄ nanospinels annealed at temperature range 700 to 1000°C and theoretical pattern of cubic MgAl₂O₄.

The structural refinement was performed using a Maud program version 2.33^{17} and based on the MgAl₂O₄ crystals with cubic structure using a better approximation as well as indexing of the Crystallographic Information File (CIF) and employing CIF No. 31373^{12} . The quality of structural refinement is checked by R-values (R_w , R_{wnb} , R_{all} , R_{nb} and σ), and these numbers are easy to detect as they are consistent with a cubic structure. However, a difference in plotting observed and calculated patterns is the best way to judge the success of Rietveld refinement. Moreover, other parameters with additional functions were applied to find a structural refinement with better quality and reliability. **Fig. 3.** shows a good agreement between the observed XRD pattern and the theoretical fit result for $Yb_{0.005}Mg_{0.995}Al_2O_4$ which indicates the success of the Rietveld refinement method as display small differences near to zero in the intensity scale as illustrated by a line ($Y_{Obs} - Y_{Calc}$). More details regarding Rietveld refinement are displayed in **Tables I and II**. The observed general trend is as follows all unit cell parameters decrease with the increase of the annealing temperature or in other words with increase of the grain size.



Fig. 3. The Rietveld profile fits of X-ray diffraction data of $Yb_{0.005}Mg_{0.995}Al_2O_4$ annealed at 900°C.

The difference between the unit cell parameters of the MgAl₂O₄ single crystal and nanoparticles doped with ytterbium ions, as higher values of all of them in latter case, is as a matter of fact caused by the so-called grain size effect (**see Table I**). Reduction of the particle size contributes to the creation of negative pressure on the crystal lattice and leads directly to a lattice cell volume expansion^{18,19}. Actually this behavior was one of the expected features as a result of reducing of the grain size.

Table I. Unit cell parameter (*a*), crystal cell volume (*V*), theoretical grain surface (*S*) and radius (*R*) as well as refine factor (R_w) are presented for Yb³⁺ doped MgAl₂O₄ nanoparticles as a function of dopant concentration and sintering temperature.

Sample of Yb:MgAl ₂ O ₄		a [Å]	V [ų]	grain size [nm]	R _w [%]
single crystal ¹²		8.0806(4)	527.63(5)	_	-
	0.5%,	8.08087(9)	527.68629(1)	12.78±0.01	8.13
	1%,	8.08085(4)	527.68139(3)	12.82±0.01	7.90
700°C	2%	8.08164(2)	527.83577(8)	11.24±0.01	6.54
	5%	8.07750(7)	527.02598(6)	10.69±0.01	5.69
	0.5%	8.08474(1)	528.44322(5)	12.23±0.01	8.43
	1%	8.08487(8)	528.47009(0)	11.02±0.01	8.80
800°C	2%	8.08307(9)	528.11739(2)	10.41±0.01	7.31
	5%	8.08135(4)	527.81579(3)	9.89±0.01	6.00
	0.5%	8.08976(5)	529.42898(9)	17.30±0.01	7.15
	1%,	8.08722(8)	528.93104(9)	16.80±0.01	8.80
900°C	2%	8.08774(0)	529.03151(5)	12.99±0.01	6.31
	5%	8.09052(1)	529.57743(1)	12.93±0.01	4.82
	0.5%	8.08975(9)	529,42781(1)	29.88±0.01	6.52
	1%	8.09240(9)	529.94826(3)	23.64±0.01	8.00
1000°C	2%	8.09103(1)	529.67758(6)	21.97±0.01	5.22
	5%	8.08851(5)	529.18361(1)	18.21±0.01	5.17

Sample		$Eu_{0.005}Mg_{0.995}Al_2O_4$, Z = 8						
Space group	Space group			Cubic <i>Fd-3m</i> (227)				
Calculated cell								
parameters		V = 529.42898(9) Å ³						
R _w			7.15%					
R _{wnb}								
R _{all}		5.39%						
R _{nb}		7.07%						
σ		2.45%						
		Selected con	tacts					
Mg Yb – Yb Mg		3.5030(0) Å						
Mg Yb –O		3.3536(0) Å						
AI – AI		2.8602(0) Å						
AI – O		1.9487(0) Å						
Mg Yb – O – Al	122.064(0) °							
Atom	Wyckoff	x	У	7	B _{iso}	Occ.		
Atom	positions			2		(<1)		
Mg1	8a	0	0	0	1.207(4)	0.995		
Al1	16d	0.6251	0.62510	0.62510	0.373(1)			
01	32e	0.3846	0.3846	0.3846	0.179(8)			
Yb1	8a	0	0	0	1.259(0)	0.005		

Table II. Atomic parameters for $Yb_{0.005}Mg_{0.995}Al_2O_4$ annealed at 900°C.

Accordingly to the HRTEM study (Fig. 4) the particles of $MgAl_2O_4$ doped with 2 mol% Yb³⁺ sintered at 700 and 900°C, respectively, are circular reminding shape of the flat plates and forming large groups of agglomerates with the average size of 10 nm. These results show that values calculated by Rietveld's calculation and Scherrer's equation are consistent with that observed by TEM technique. It is worth to notice that even after high temperature of annealing (1000 °C), the particle sizes remain small and do not exceed 30 nm.



Fig.4. Transmission electron micrographs of 2 mol% Yb^{3+} -doped MgAl₂O₄ nanospinels annealed at 700 and 900°C.

3.2. Spectroscopic analysis

3.2.1. Yb³⁺ energy level diagram and structure

The Yb³⁺ ions have only two Stark-split energy manifolds: the ${}^{2}F_{7/2}$ ground state and the $^{2}F_{5/2}$ excited state. In Fig. 5, Stark levels are distributed in these manifolds and labelled from 1 to 4 in the ground state and from 5 to 7 in the excited state from the lowest energy to the highest energy, respectively. Depending of the local symmetry the two manifolds are split by the crystal field. In the MgAl₂O₄ spinel face centered cubic lattice, with a lattice parameter of a = 8.08976(5) Å (see Table 1), 8 magnesium ions are occupying tetrahedral sites and 16 aluminum ions are occupying octahedral sites. Yb³⁺ ions, characterized by large ionic radius of 85.8pm, can substitute both Mg²⁺ (65 pm) tetrahedral sites and Al³⁺ (50 pm) octahedral sites. The situation is even more complex since up to 30 % of cation are inverted creating socalled anti-site disorder²⁰⁻²⁴: the Mg²⁺ divalent ions on tetrahedral positions are located in the Al³⁺ trivalent ions of octahedral lattice positions and vice-versa. Consequently, Yb³⁺ ions can be observed either in octahedral or tetrahedral positions and when substituting Mg²⁺ cations the natural way is to replace three Mg^{2+} cations by two Yb^{3+} luminescent cations. Then, the probability to create pairs and aggregates is high. In addition other perturbed Yb³⁺ ions exist also within the surface of the grains. It means there are several reasons to increase disorder in spinel lattice and to observe an important broadening of absorption and emission spectra.

3.2.2. Absorption spectra

Fig. 5 presents the absorption for 5 mol% Yb³⁺:MgAl₂O₄ (a) and 0.5 mol% Yb³⁺:MgAl₂O₄ (b) compositions, respectively. The spectra consist of broad weakly resolved bands located between 850 nm and 1050 nm and corresponding to the three Stark components of the Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ electronic transitions. One interesting feature is the extended absorption spectra starting at very short wavelength (875 nm) showing a high crystal field of the spinel lattice. The strongest absorption line is the 0-phonon line at around 976 nm. This is the transition from the lowest Stark level of the ${}^{2}F_{7/2}(1)$ ground state to the lowest Stark level of the ${}^{2}F_{5/2}(5)$ excited state. This line appears broad (line-width 7.34 nm) and is the result from a superposition of several components with relative intensities depending mainly on the inversion degree between Mg²⁺ octahedral and Al³⁺ tetrahedral sites. Two others, much less intensive and less separated components are more difficult to spectrally solve. We have noted two broad bands located at around 912 nm and 935 nm corresponding to ${}^{2}F_{7/2}(1) \rightarrow {}^{2}F_{5/2}(6)$ and ${}^{2}F_{7/2}(1) \rightarrow {}^{2}F_{5/2}(7)$ transitions, respectively, by also taking account of the excitation spectra shown in the next section. It can be noted that measurements at low temperature (4K and 120K) lead to only slight narrowing and slight better resolution of the components.



Fig.5. Absorption spectra of 5 mol% (**a**) and 0.5 mol% (**b**) Yb^{3+} -doped MgAl₂O₄ nanospinels recorded at 4, 120 and 298K.

3.2.3. Photoluminescence spectra

The selected emission spectra of the samples of MgAl₂O₄ obtained at different temperatures and doped with different Yb³⁺ contents are plotted in Fig. 6 and Fig. 7. The studied materials exhibit the luminescence in the near-infrared region from the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions of the Yb³⁺ ions with the most intense component at around 976-977 nm (socalled zero-phonon line (5 \rightarrow 1) and did not practically change with the Yb³⁺ content and temperature of synthesis. It corresponds to the transitions from the lowest Stark level of the ${}^{2}F_{5/2}$ excited state (5) to each of the four Stark levels of the ${}^{2}F_{7/2}$ state (1, 2, 3, 4) respectively. The emission transitions have been marked at the corresponding lines. Contrary to absorption spectra and room temperature emission spectra, high resolution emission spectra are reached at low temperature (77K) in Fig. 7. The 4 broad components are clearly resolved. The red shift of the 0-phonon line is also well observed when Yb³⁺ concentration increases from 0.5 to 5 mol%. These emission spectra illustrate again the strong disorder of the Yb³⁺-doped MgAl₂O₄ nanospinels. Room temperature excitation spectra of Yb³⁺ emission monitored at 1010 nm in 2 mol% Yb^{3+} -doped MgAl₂O₄ nanospinels has been shown in Fig. 8 as an example to clearly point out the three Stark absorption components at 977, 935 and 912nm respectively, which are difficult to assign from absorption spectra. The line-width of the 0-phonon line can be measured at 975.30 nm.

The analysis of the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ emission lines of Yb³⁺-doped MgAl₂O₄ powders shows broadening with increasing of the dopant content which indicates large distortion of the local environment symmetries of Yb³⁺. The broadening of the emission bands is characteristic for materials when a trivalent rare-earth ion substitutes divalent ion²⁴. In such cases, charge compensation by association of two Yb³⁺ cations in place of three Mg²⁺ cations perturbs the local structure of optical centers²⁵ since a vacancy has been created.

The slight shift of the 0–0 emission line seen only in luminescence spectra of the obtained samples when Yb^{3+} concentration increases is probably connected to the multisite distribution of nano-MgAl₂O₄²⁶ and the well known re-absorption effect by energy transfer between resonant 0-phonon lines.



Fig.6. Emission spectra of Yb^{3+} -doped MgAl₂O₄ nanospinels annealed at 700 °C with different concentrations of Yb^{3+} ions, measured at 298K.

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Fig. 7. Emission spectra of Yb^{3+} -doped MgAl₂O₄ nanospinels annealed at 700 °C with different concentrations of Yb^{3+} ions, measured at 77K.



Fig.8. Excitation spectra of 2% Yb³⁺-doped MgAl₂O₄ nanospinels with emission monitored at 1010 nm, measured at 298K.

3.2.4. Cooperative luminescence

Since the first observation by Nakazawa and Shionoya in YbPO₄²⁷, cooperative luminescence of ytterbium ions has been reported in several hosts, crystals or glasses²⁸⁻²⁹. Cooperative luminescence is indeed an effective way to indicate the formation of Yb³⁺ pairs and clusters in crystals and glasses. The cooperative emission center is assigned either from two neighboring Yb³⁺ ions isolated in the host or even from Yb³⁺ ions aggregates. The cooperative luminescence results from the simultaneous de-excitation of two Yb³⁺ ions in the blue range at around 500 nm which corresponds to the twice energy of the IR emission spectrum of the Yb³⁺ isolated ions²⁷. Yb³⁺ ion is unique case among rare earth ions by the simplicity of the energy level diagram in the near IR with the absorption spectrum between 900 and 1100 nm and the emission spectrum between 950 and 1150 nm.

The theoretical cooperative emission spectrum can be calculated taking into account all energetic combinations between Stark levels of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ manifolds. The cooperative luminescence spectrum F(E) is then related to the infrared one *f*(*E*) by:

$F(E)=\int f(E)f(E-E') dE'$

This cooperative fluorescence emission has a very low efficiency and naturally is favored for the shortest distances between Yb³⁺ ions. The calculation of the shortest distance d between Yb³⁺ ions in the dipole-dipole interaction has been estimated at d = 4.5 Å³⁰. In this nanospinel crystallites the shortest distances of 3.5 Å between Mg²⁺ cations mentioned in Table I should allow an easy observation of Yb³⁺ ion pairs when Yb³⁺ trivalent ions substitute Mg²⁺ divalent ions.

Under pumping into the 0-phonon line in the near IR with a CW laser diode this is possible to observe a bluish-green up-conversion light for Yb³⁺-doped MgAl₂O₄, already for samples containing a small amount of 0.5 mol% Yb³⁺ activator ions. The visible luminescence spectrum measured around 500 nm at room temperatures is shown in Fig. 9 under CW laser diode at 975 nm and in Fig. 10 in 2 mol%-doped MgAl₂O₄ under the pumping excitation of a pulsed Ti-sapphire laser at 976 nm. As it is seen, the emission spectra appear at twice energy of the NIR luminescence energy as a signature of the cooperative luminescence of Yb³⁺ ions, it means Yb³⁺ pairs. The convolution spectrum drawn in red color fits well the experimental spectrum of the cooperative emission and moreover allows clearly the separation between

Yb³⁺ pairs and rare earth impurities like Tm³⁺ and Er³⁺ ions. Time resolved spectroscopy of the cooperative luminescence spectra is really a good probe of the presence of both pairs and impurities from the raw materials on the basis of short life times of pairs and higher lifetimes of Tm³⁺ and Er³⁺ ions as we already shown it earlier³¹. In all Yb³⁺-doped materials, impurities observed by up-conversion energy transfer process contribute to the quenching of Yb³⁺ ions either in glasses³⁰ or in crystals³². Detailed analysis of the consequent gain in laser materials have been presented by Boulon et.al.³³.



Fig. 9. Cooperative luminescence spectra at 298 of 0.5% mol Yb³⁺-doped MgAl₂O₄ nanospinels annealed at 1000°C. The pumping excitation is CW laser diode at 975nm.



Fig. 10. Time resolved spectroscopy of the cooperative luminescence spectra in 2 mol%-doped $MgAl_2O_4$ annealed at 1000°C. The pumping excitation was a pulsed Ti-sapphire laser at 976 nm. The convolution spectrum drawn in red color allows clearly the separation between Yb³⁺ pairs and rare earth impurities like Tm³⁺ and Er³⁺ ions.

3.2.5. Energy level diagram of Yb³⁺ ions in MgAl₂O₄ nanospinels

Fig. 11 represents a summary of the spectroscopic results by combining experimental absorption and emission spectra of the highest population of Yb^{3+} ions in MgAl₂O₄ nanospinels at 120K. At room temperature the spectra were not enough structured to assign the transitions. The most probable situation is associated to the sites in substitution of Mg²⁺ cations in both tetrahedral and also octahedral symmetries due to inversion degree. The ionic radii are closer than Yb³⁺ and Al³⁺ ones and the easy detection of Yb³⁺ pairs are in favor with this assumption when three Mg²⁺ cations are substituted by two Yb³⁺ activator ions and the creation of one vacancy. As a result the energy level diagram is shown for this selected Yb³⁺ population.



Fig. 11. a) Absorption and emission spectra at low temperature (120K) of 5 mol% Yb^{3+} -doped MgAl₂O₄ and b) Energy level diagram of Yb^{3+} ions calculated from the experimental data.

3.2.6. Decay curves and decay times

In order to see how the synthesis conditions influence the luminescence quenching, emission decays for samples doped with different concentration of Yb³⁺ ions were recorded at room temperature. The collected decays normalized to the signal intensity are shown in Fig.12. As it can be seen, the decay curves are non-exponential and strongly dependent on concentration of Yb³⁺ ions. Additionally, with increasing the annealing temperature, the decays become significantly faster. Two types of profiles can be seen, a fast one within the first 50µs assigned to Yb³⁺ pairs and even Yb³⁺ aggregates due to resonant energy transfer ${}^{2}F_{7/2} \leftrightarrow {}^{2}F_{5/2}$ between similar Yb³⁺ neighbour ions and the second one with roughly the same decay time due to Yb³⁺ ions. We have mentioned the integrated lifetime at long time for each sintering temperature. As can be seen directly in Fig. 12 the slope of decay curves at long time have the tendency to be the same value and to characterize the radiative lifetime of Yb³⁺ ions.



Fig.12. Decay curves of the fluorescence from ${}^{2}F_{5/2}$ at λ_{em} = 1015 nm of 5 mol% Yb³⁺-doped MgAl₂O₄ nanospinels and measured at 298K under λ_{ex} = 925 nm.

4. Conclusion

In the present work, the sol-gel Pechini's method was successfully applied to obtain a cubic structure of Yb³⁺-doped MgAl₂O₄ spinel nanopowder. Furthermore, taking into account known difficulties in controlling the phase purity the modified Pechini's method gives the best results in the preparation of spinel nanopowders. Detailed study of spinel structures presented almost complete crystallization and were confirmed by X-Ray diffraction and Rietveld analysis. It was found and detailed described the regularity with observed structural and spectroscopic measurements. The Yb³⁺ absorption spectra at 4K and room temperature reveal a strong distorted spinel lattice due to high inversion rate between Mg²⁺ tetrahedral sites and Al³⁺ octahedral sites which are both substituted by Yb³⁺ activator ions. Nanoparticles of 10-30 nm are obtained as a function of dopant concentration and sintering temperature. The substitution of Mg²⁺ ions by Yb³⁺ ions favors the creation of Yb³⁺ ion pairs at 3.50 Å which are easily pointed out by cooperative luminescence spectra observed at around 500 nm. Luminescence decays are influenced by both Yb³⁺ contents, sintering temperature and resonant energy transfers between neighbor ions with the presence of

pairs and aggregates. Quenching of Yb^{3+} ions is also due to energy transfer to Er^{3+} and Tm^{3+} impurities which are observed by up-conversion mechanism.

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The sol-gel Pechini's method was successfully applied to obtain Yb^{3+} -doped MgAl₂O₄ spinel nanopowder and it was found and detailed described the regularity with observed structural and spectroscopic measurements.

