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Deliverable Nature	
R = Report, P = Prototype, D = Demonstrator, O = Other	R
Dissemination Level	
PU = Public PP = Restricted to other programme participants (incl. the Commission Services) RE = Restricted to a group specified by the consortium (incl. the Commission Services) CO = Confidential, only for members of the consortium (incl. the Commission Services)	PU

A. Abstract / Executive Summary

The research activity within this period was concentrated on two directions. Firstly, we studied the importance of adding TEOS and MgO in the process of obtaining Nd:YAG ceramics and observed how the sintering process or the re-milling of a sample before the vacuum sintering influences the quality of the final Nd:YAG ceramics. The work was performed in collaboration with the Institute of Science and Technology for Ceramics (ISTEC) from Faenza, Italy, the research group of Prof. Laura Esposito. Secondly, we have obtained $Sm^{3+}:Y_3Sc_xAl_{5-x}O_{12}$ (Sm:YSAG) transparent ceramic and we have investigated the spectroscopic properties of such a material; this work was entirely performed in the Laboratory of Solid-State Quantum Electronics from INFLPR.

B. Deliverable Report

1   Introduction

The ceramic techniques allow nowadays obtaining of poly-crystalline laser media with very good optical quality, featuring easy manufacturability at competitive prices. Such ceramic materials can be obtained for the realization of good output performances in free generation mode, in passively Q-switched regime, but also for the generation of sub-ps laser pulses. The general purpose of our work is the fabrication of rare-earth ions doped ceramics and disordered crystals with wide fluorescence band suitable for generation of laser pulses close to 100-fs duration.

2   Objectives

In previous works, we used a solid-state synthesis method to obtain Nd:YAG ceramics that were opaque or partially transparent. We did more investigation in order to improve the Nd:YAG ceramic quality, by investigation the influence of some factors (like adding of TEOS and MgO in the preparation stage, performing pre-sintering at various temperatures, or re-milling several samples before sintering in vacuum) on the Nd:YAG ceramic quality. We obtained Nd:YAG ceramics sample with good transparency and similar absorption spectra to that of Nd:YAG single crystal. We have also investigated a new ceramic material, cubic Sm:YSAG, due to its properties and possible use as laser material and phosphor. Absorption spectrum and emission spectra around several bands in the visible spectrum were recorded.

3   Work performed / results / description

3.1. Improvements of Nd:YAG ceramic quality

The procedure shown in the diagram of Fig. 1 was used to fabricate Nd:YAG ceramics. As in our previous attempts, powders of α-Al_2O_3, Nd_2O_3 and Y_2O_3 were weighted in respect to stoichiometric ratio of Nd:YAG (1.0 at.% Nd). Tetraethyl orthosilicate (TEOS) was used as sintering aid and mixing was done in ethyl alcohol using a mill with alumina balls. Clustering was avoided by adding polyethylene glycol (PEG-400) few hours before ending the mixing process. The drying of the powder was made with a spray-drying Buchi 250 machine ($70^oC/40^oC$ temperature at the entrance/output, respectively). Shaping was obtained by pressing the mixed powders at 20MPa. For removal of some organics residues the samples were annealed (in the pre-sintering stage). A high pressure ISOLAB FPG-7680 installation (Stansted Fluid Power Ltd., UK) was used to press each sample at 245-MPa pressure (cold-isostatic pressing). Sintering was performed in vacuum and finally the samples were annealed in air.

In comparison with our previous attempts, in these new experiments the influence of several parameters on the quality of Nd:YAG ceramics was studied, as follow:
- TEOS was added in various ratios;
- MgO was inserted in order to limit the grain growth;
- Pre-sintering was performed at several temperatures (1400^oC, 1450^oC and 1500^oC);
- After pre-sintering some samples were re-milled and then cold-isostatic pressured again.

The vacuum sintering was done with the help of Prof. Laura Esposito, at the Institute of Science and Technology for Ceramics (ISTEC), Faenza, Italy.
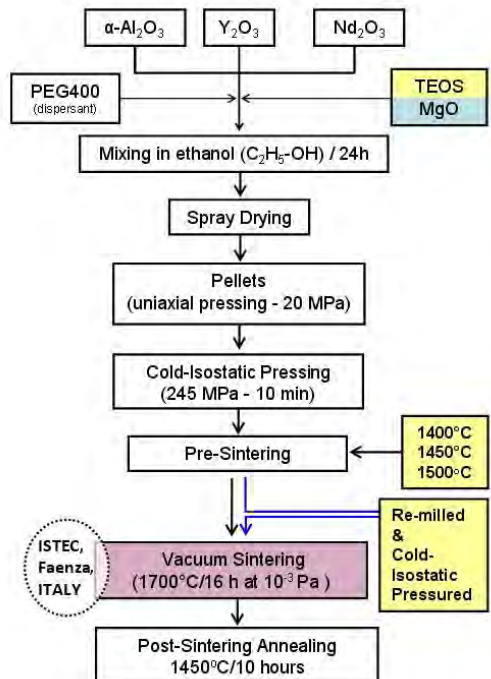

Fig. 1 The solid-state phase synthesis method used Nd:YAG ceramic. TEOS and/or MgO were added in the mixing process. Sintering was performed at various temperatures. After sintering some samples were re-milled and cold-isostatic pressured before vacuum sintering.

A SHIMADZU XRD 6000 diffractometer (CuKα, (λ = 1.5418 Å) was used to investigate the composition, whereas each sample microstructure (HRD; the secondary phases and the crystalline condition) was determined with a HITACHI S2600N electronic microscope.
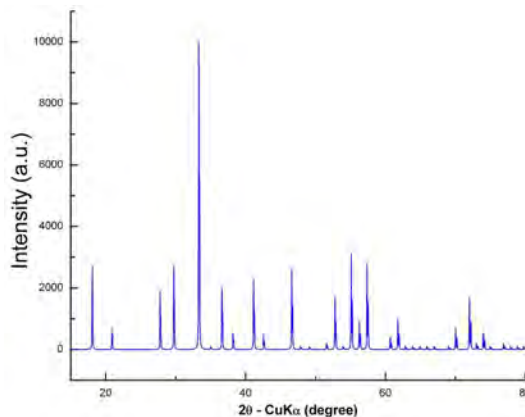

Fig. 2 Typical HRD of Nd:YAG.

Some examples will be presented. It was observed that in comparison with the structure of Nd:YAG (Fig. 2), the presence of TEOS and a too high sintering temperature leads to an increase of the secondary phase as well as of the porosity. Thus, increasing the sintering temperature from 1450°C (Fig. 3a) to 1550°C (Fig. 3b) increases the YAlO$_3$ (YAP) phase from 10% to 16%, respectively; furthermore, the Y$_4$Al$_2$O$_9$ (YAM) phase remains almost constant (at 4% for 1450°C and 6% for 1550°C).
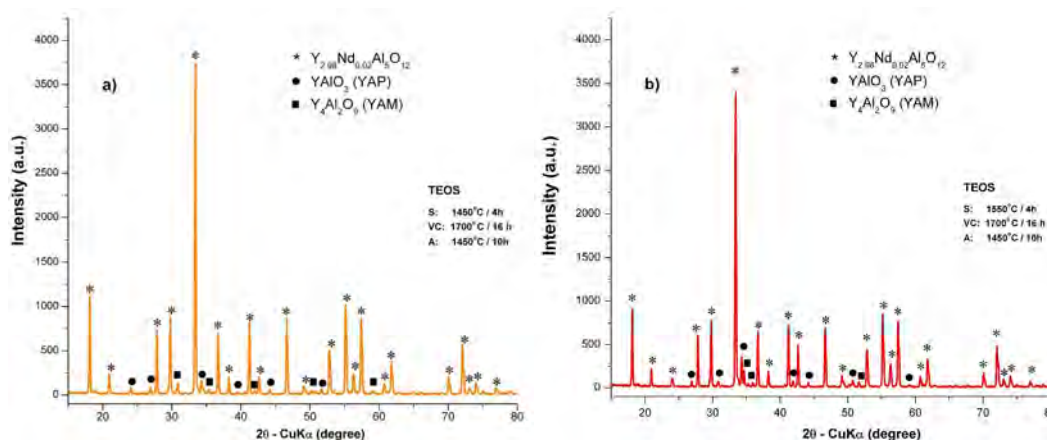
Fig. 3 HRD of YAG ceramics obtained by adding TEOS and using sintering (S)
temperatures of **a)** 1450°C and **b)** 1550°C.

Using the process of adding MgO besides TEOS and performing sintering at 1400°C we
have obtained a ceramic sample with 3% of the $Y_{0.06}Al_{1.94}O_3$ phase (Fig. 4a). An increase of
the sintering temperature at 1450°C, for a similar probe, was not benefic as YAP composition
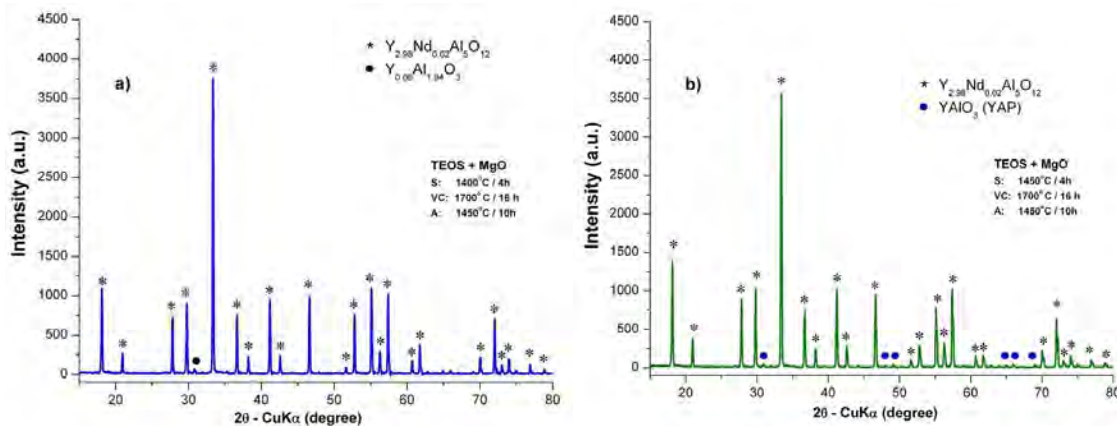increased to 13% (Fig. 4b).

Fig. 4 HRD of YAG ceramics obtained by adding TEOS & MgO, sintering temperatures
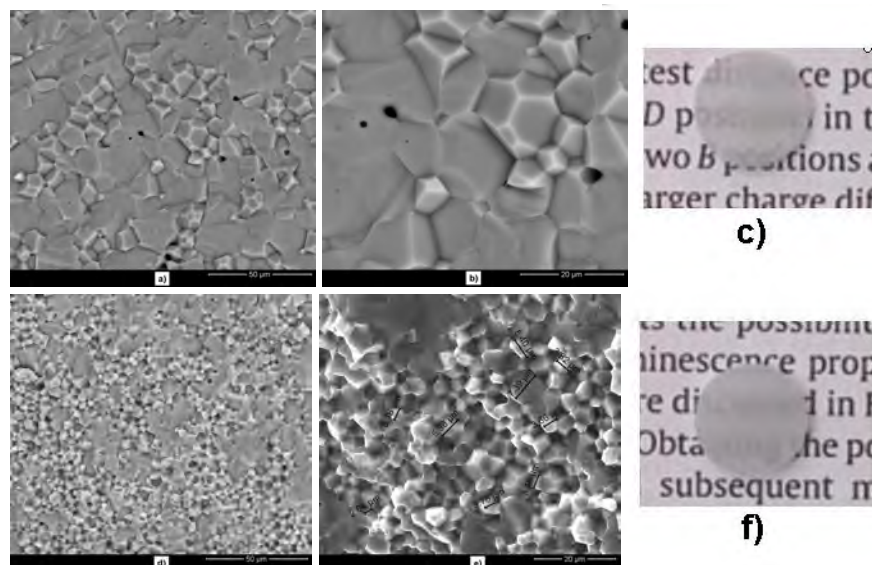of **a)** 1400°C and **b)** 1450°C.

Fig. 5 SEM images of the samples with TEOS aid that were sintered at 1550°C [**a)** and **b)**] and at
1450°C [**d)** and **e)**]. Photos of the Nd:YAG ceramics are shown in **c)** and **f)**, respectively.

The Nd:YAG ceramics obtained with TEOS aid were characterized by unimodal distribution of the grain-size distribution, with average-grain size of about 4.25 µm for the sample sintered at 1550°C (Fig. 5a, b) and of ca. 3.96 µm for the probe sintered at 1450°C (Fig. 5d, e). Still, these ceramic samples were opaque (Fig. 5c and Fig. 5f).
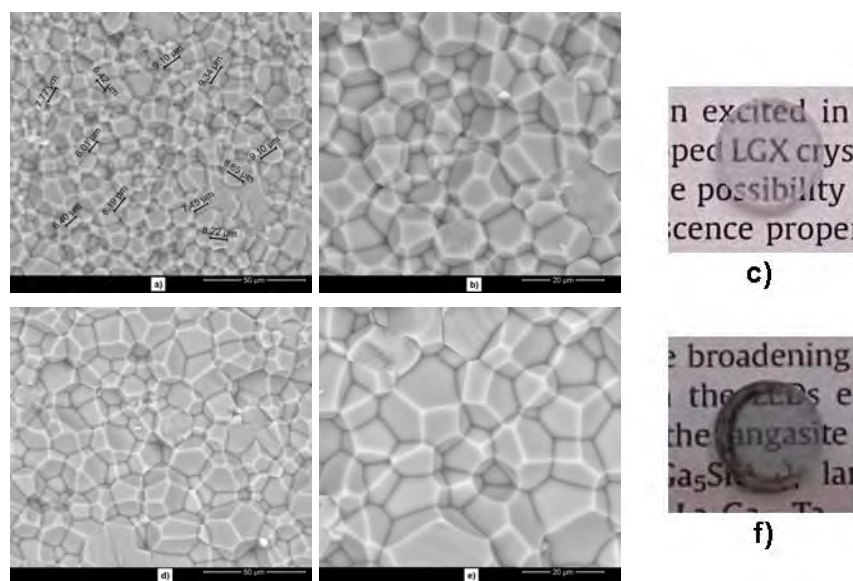

Fig. 6 SEM images of the samples with TEOS and MgO, sintering at 1400°C (Fig. 6a and Fig. 6b) and at 1450°C (Fig. 6d and Fig. 6e). The Nd:YAG ceramics were transparent (Fig. 6c and Fig. 6f, respectively).

For the samples discussed here, with TEOS and MgO added, the grain distribution was unimodal when sintering was done at 1400°C (Fig. 6a and Fig. 6b); the average grain size was ~7.7 µm. The similar Nd:YAG that was sintered at 1450°C presented bimodal grain distribution (Fig. 6d and Fig. 6e) with the grain sizes ranging from 6.80 µm to 16.97 µm. The encouraging aspects are that both samples were transparent (Fig. 6c and Fig. 6f).

Table I Some conclusions of present investigations are summarized.

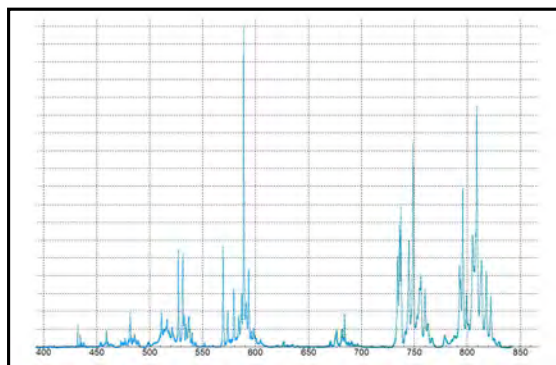| Nr. crt.	● Presintering temperature/ Sintering in vacuum/ Annealing ● Sintering aids	Phases - (%)	Grain size distribution / Average grain size (µm)	Comments
1.	● 1450 $^\circ$C/1700 $^\circ$C/1450 $^\circ$C ● TEOS	$Y_{2.96}Nd_{0.02}Al_5O_{12}$ - 86% $YAlO_3$ (YAP) - 10% $Y_4Al_2O_9$ (YAM) - 4%	Unimodal 4.25	A high sintering temperature decreases the grain size and increases the porosity (mixed inter and intra-granular) and the quantity of secondary phases.
2.	● 1550 $^\circ$C/1700 $^\circ$C/1450 $^\circ$C ● TEOS	$Y_{2.96}Nd_{0.02}Al_5O_{12}$ - 78% YAP - 16% YAM -6%	Unimodal 3.96	
3.	● 1400 $^\circ$C/1700 $^\circ$C/1450 $^\circ$C ● TEOS+MgO	$Y_{2.96}Nd_{0.02}Al_5O_{12}$ - 97% YAP - 3%	Unimodal 7.68	MgO decreases the content of secondary phases and seems to influence the sintering temperature. The sample with TEOS and MgO showed the best transparency and had the best densification; thus, adding MgO has a positive influence on the densification process and also promotes transparency.
4.	● 1450 $^\circ$C/1700 $^\circ$C/1450 $^\circ$C ● TEOS+MgO	$Y_{2.96}Nd_{0.02}Al_5O_{12}$ - 87% YAP - 13%	Bimodal 6.80 to 16.97	

Fig. 7 The absorption spectrum of 1.0-at.% Nd:YAG ceramic obtained with TEOS and MgO, and 1400°C sintering temperature.

Some conclusions of our work are given in Table I. The absorption spectrum of a transparent Nd:YAG ceramic sample (Fig. 6f) is presented in Fig. 7. Principal absorptions band of Nd could be recognized showing similarity with a spectra of Nd:YAG single crystal.

3.2. Sm^{3+}:YSAG transparent ceramic

Cubic $Y_3Sc_xAl_{5-x}O_{12}$ crystals are attractive laser-host materials due to their high thermal conductivity, broad spectral region, chemical stability, or strong Stark splitting and relatively low phonon energies. However, it is very difficult to grow large-size single crystals with high quality because of the high melting point (~1950°C). On the other hand, polycrystalline ceramics [1] have lower sintering temperature, about 1750°C. Moreover, because of the absence of segregation coefficient, ceramics can be doped with a higher fraction of active ions. With the increasing demand of various visible lasers and light sources, further investigations on Sm^{3+} ion have become more important with the development of InGaN and GaN laser diodes in the 405 nm range. Sm^{3+} ion, with electronic configuration $4f^5$, exhibits large absorption cross sections for wavelength pumping radiations in the visible domain (350-550 nm) and strong emission also in the visible range, corresponding to $^4G_{5/2} \rightarrow {}^4H_{7/2}$ transition (at 617 nm for Sm:YAG [2], 610 nm for $Sm:LiNbO_3$ [3], 594 nm for $Sm:SrAl_{12}O_{19}$ [4], 613 nm for Sm:(Ca, Mg, Zr) GGG [5], 612 nm for $Sm:Sc_2O_3$ [6], 608 nm for $Sm:Y_2O_3$ [7], and 593 nm for $Sm:Sr_{1-x}RE_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ [8]).

We therefore decided to get a closer insight into the nature of Sm^{3+} luminescent centers in $Y_3Sc_xAl_{5-x}O_{12}$ (x=1, 2) transparent ceramic and to evaluate its potential as phosphors or laser material, not yet explored. For preparing the ceramic samples, high purity α-Al_2O_3, Y_2O_3, Sc_2O_3 and Sm_2O_3 powders were used as starting materials. The selected compositions were $Sm_{0.03}Y_{2.97}Sc_2Al_3O_{12}$ and $Sm_{0.03}Y_{2.97}Sc_1Al_4O_{12.}$ The powders were magnetically mixed in stoichiometric ratio in anhydrous ethylic alcohol. As sintering additive, 0.5 wt.% of TEOS was used. The alcohol solvent was removed by drying the slurry at 80°C. The dried powder was milled and pressed at low pressure (10 MPa) into pellets with half of inch diameter in a metal mold and then cold isostatically pressed at 240 MPa. Before sintering, the sample was heated at 800°C for removing organic substances used in preparation. Transparent Sm^{3+} doped in YS_2AG and YS_1AG ceramic were obtained by sintering 4h at 1700°C in high vacuum atmosphere [9].

High resolution spectroscopic investigation of 1.0-at.% Sm^{3+} doped YS_2AG and YS_1AG transparent ceramic at 300 K and 10 K were performed. The absorption spectra of most intense lines of Sm^{3+} ions in visible - UV domain around 405 nm, suitable for an efficient optical pumping with InGaN/GaN laser diode and assigned to a group of transitions that contain the spin-allowed $^6H_{5/2} \rightarrow {}^6P_{3/2}$, $^6P_{5/2}$ transitions, are illustrated in Fig. 8. At room temperature the absorption peak at 404.9 nm for x=1 is shifted at 405.2 nm for x=2. The line shift function compositional parameter x is observed in other absorption transition at 300K (Fig. 9). The dependence of Sm^{3+} spectral lines of the compositional parameter x is observed in all the absorption spectra: widths and shifts of the lines, asymmetric lines with inhomogeneous broadening suggesting multicenter structure. The multicenter structure is determined by the arbitrary occupancy of the octahedral sites by Sc^{3+} and Al^{3+} ions.
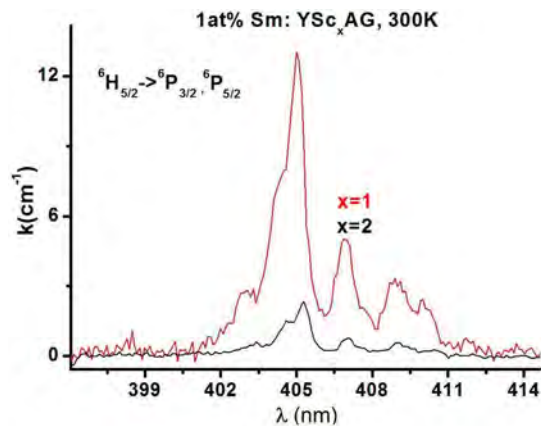
Fig. 8 Absorption spectrum into visible spectrum at 300 K of Sm doped YS_2AG and YS_1AG.

At low temperature the absorption spectra into infrared (IR) of $^6H_{5/2} \rightarrow ^6F_{7/2}$ and $^6H_{5/2} \rightarrow ^6F_{9/2}$ Sm^{3+} transitions, were measured for $Sm:YS_2AG$ and $Sm:YS_1AG$ (Fig. 10) and compared with those for $Sm:YAG$ [10]. In the case of $Sm:YS_1AG$ and $Sm: YS_2AG$ the absorption spectra revealed an inhomogeneous broadening and asymmetric lines which suggest unresolved multicenter structure while in the case of $Sm:YAG$ the lines are sharp, narrow and can be identified as Stark levels of terminal manifolds.
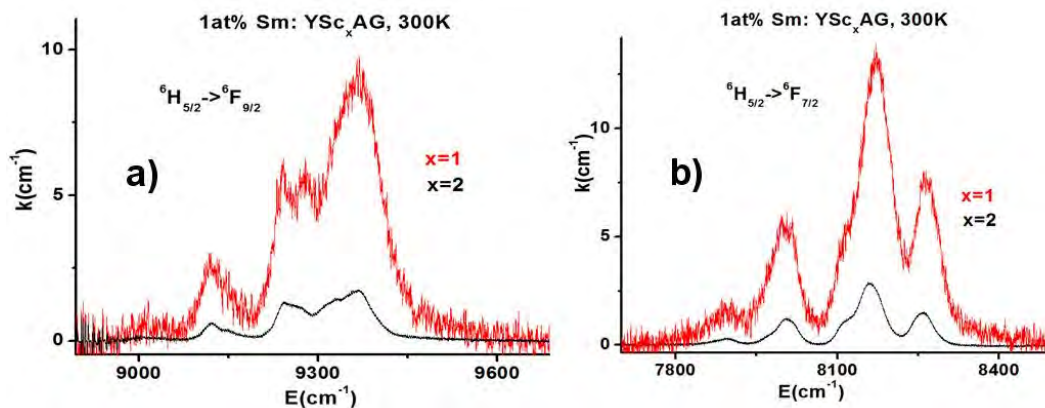

Fig. 9 Infrared (IR) absorption spectra at 300 K temperature of Sm doped YS_2AG and YS_1AG: **a)** transition $^6H_{5/2} \rightarrow ^6F_{9/2}$ and **b)** transition $^6H_{5/2} \rightarrow ^6F_{7/2}$.
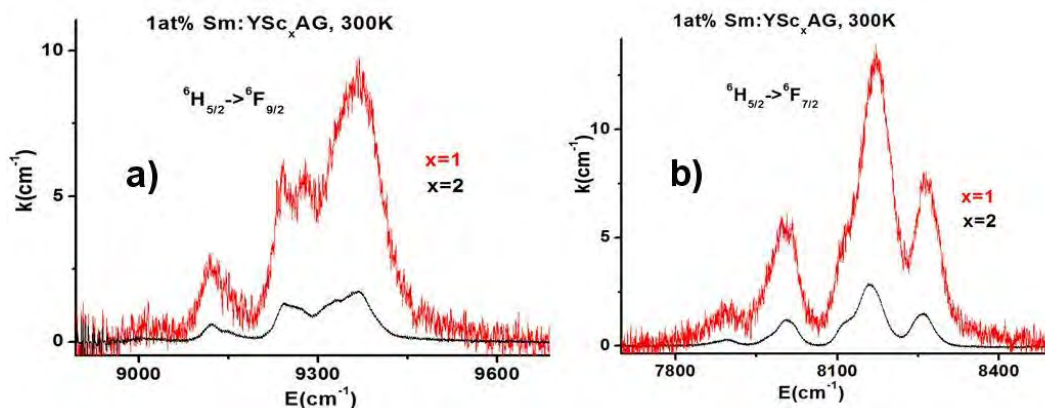

Fig. 10 Comparison between IR absorption spectra at 10 K temperature of **a)** Sm doped YS_2AG and YS_1AG and **b)** Sm:YAG.

Under excitation at 405 nm and 488 nm, the emission spectra at 300 K and 10 K of the 1-at. % Sm^{3+} doped YS_1AG and YS_2AG exhibit three distinct emission bands in visible domain: 550 - 580 nm, 580 - 630 nm and 635 - 680 nm corresponding to the $^4G_{5/2}{\rightarrow}^6H_{5/2,\ 7/2,\ 9/2}$ transitions, respectively. The most intense emission line is at 618 nm, for transition $^4G_{5/2}{\rightarrow}^6H_{7/2}$. At low temperature, the influence of the excitation wavelength on the band components can be observed in the emission spectra (Fig. 11).
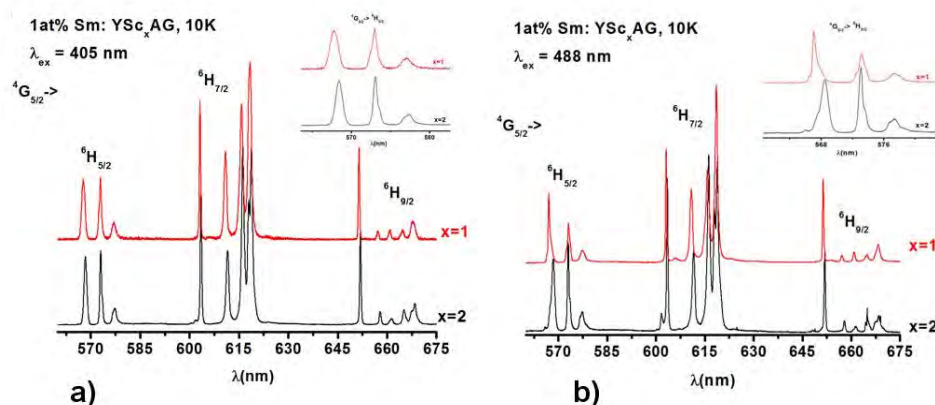

Fig. 11 Absorption spectra at 10 K into visible spectrum of Sm doped YS_2AG and YS_1AG under excitation at **a)** 405 nm and **b)** 488 nm.

The emission lines present inhomogeneous broadening and asymmetric shapes, which suggest unresolved multicenter structure. Additional lines are present in these spectra, suggesting the existence of non-equivalent Sm^{3+} sites. These are clearly revealed in the $^4G_{5/2}{\rightarrow}^6H_{5/2}$ transition (the inserted pictures), as effects of excitation wavelengths. In order to elucidate these aspects further experiments are necessary [11], especially following the dependence on x compositional parameter of $Sm:Y_3Sc_xAl_{5-x}O_{12}$ transparent ceramics.

4   Conclusions

During the last period we continued our work for already obtained Nd:YAG ceramics; we succeeded to obtain samples with good transparency and similar absorption spectra to that of Nd:YAG single crystal. We have investigated the influence of several factors, like adding TEOS and MgO in the preparation stage, sample' pre-sintering at various temperatures or re-milling several samples before sintering in vacuum on the Nd:YAG ceramic quality. Furthermore, a new ceramic material was obtained by ceramic method, the cubic Sm:YSAG, a material that due to its properties can be used as laser material and phosphor. Absorption and emission spectra of Sm:YSAG were recorded at several bands in the visible and IR spectra.

The results were presented at four conferences, as follow:

1. C.A. Vasilescu, T. Dascalu, C. Stanciu, R. Barjega, C. Luculescu, N. Pavel, "Preliminary Synthesis for Transparent 1-at.% Nd-YAG Ceramics," The 14th International Balkan Workshop on Applied Physics, July 2-4, 2014, Constanta, Romania, presentation S2-P08, Book of Abstracts p. 119;

2. C. Vasilescu, T. Dascalu, G. Stanciu, N. Pavel, E. Vasile, R. Trusca, "Transparent 1.0-at.% Nd:YAG ceramic media," TIM 14 Physics Conference - Physics without frontiers, 20-22 November 2014, Timisoara, Romania; presentation CM-P19, Abstract Book, CM-P19;

3. F. Voicu, C. Gheorghe, S. Hau, L. Esposito, J. Hostasa, "Preliminary results on Sm^{3+}:YSAG transparent ceramic," 5th International Student Conference on Photonics, Orastie, Romania, 23-26 September 2014; presentation P.09, http://iscp.inflpr.ro/data/uploads/program/book-of-abstract-iscp2014.pdf;

4. F. Voicu, C. Gheorghe, S. Hau, L. Esposito, J. Hostasa, "Sm^{3+}:YSAG transparent ceramic," 10th Laser Ceramics Symposium (LCS), 1-5 December, 2014, Wroclaw, Poland; presentation P-18T, Book of Abstracts, ISBN 978-83-940861-0-7; P-18.

5a　References

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[11]　C. Gheorghe, A. Lupei, S. Hau, F. Voicu, "Compositional dependence of optical properties of Sm^{3+}-doped $Y_3Sc_xAl_{5-x}O_{12}$ polycrystalline ceramics," submitted to J. Alloys & Compd.