Characterization and optical properties of Er^{3+} and Ho^{3+} doped $ZnGa_2O_4$

M. VASILE[a,b*], P. VLĂZAN[b], I. GROZESCU[b], N. AVRAM[a,c]
aDepartament of Physics, West University of Timisoara, Timisoara, 300223, Romania
bNational Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, 300224, Romania
cAcademy of Romanian Scientists, Bucharest, 050094, Romania

The UV-visible optical absorption spectra of Er^{3+} and Ho^{3+} impurity ions in Er- and Ho- doped of zinc gallate ($ZnGa_2O_4$) system registered at room temperatures are presented. Zinc gallate is a normal spinal crystal structure, with Zn^{2+} ions in the tetrahedral sites and Ga^{3+} ions in the octahedral sites. $ZnGa_2O_4{:}Er^{3+}$ and $ZnGa_2O_4{:}Ho^{3+}$ particles were obtained by the hydrothermal method in basic medium using a Teflon-lined strainless steel autoclave tightly sealed.

1. Introduction

As one of the available searching for short-wavelength solid-state laser, the effect of frequency up-conversion on certain rare-earth ions in different matrix has been investigated widely in past two decades. At present, all practical miniaturized solid-state lasers from ultraviolet to green spectral range have attracted much attention because of a wide range of applications in the fields of high-density optical data storage, all color display, optical fiber communications, biomedicine and infrared sensors.

As activator, erbium has many absorption bands from ultraviolet to far infrared light, where the bumping sources are easily available. Erbium ion has attractive applications in eyesafe laser and atmosphere system as the low threshold [1, 2]. Erbium ion doping of different microelectronic materials has attracted the attention of optoelectronics engineers and material scientists, due to the relatively intense intra-4f emission at 1.55 μm which was attributed to the $^4I_{15/2}$ transition form Er^{3+} [3] which coincides with the minimum transmission loss of standard optical telecommunication silica fibers [4]. Many studies focused on this emission from Ho doped materials for applications in the areas of remote sensing [5] and medicine [6]. Especially interesting is the 2.1 μm emission from holmium (Ho) ions in medicine because of the relative maximum of absorption of water around this wavelength, so that it can be used in many different tissues of the human body [7]. The advantage of using single doped Ho lasers with direct pumping of the $^5I_8$ level is that there is not dependence on energy transfer from other ions, which lends it self to various radiative and non-radiative losses.

Zinc gallate ($ZnGa_2O_4$) is a normal spinal crystal structure which crystallizes in the cubic space group Fd3m (O_h^7), with lattice constant a=8.3358Å [8]. The energy band gap of this crystal is about 4.4eV [9] and $ZnGa_2O_4$ shows blue photoluminescence without doping via transition of a self-activated center.

The aim of this paper is to present the results of the synthesis of $ZnGa_2O_4$ particles by the hydrothermal method using.

2. Experimental procedure

Powder phosphors of $ZnGa_2O_4$: TR, where TR = Er^{3+} and Ho^{3+}, were prepared by hydrothermal method. Hydrothermal method synthesis involves mixing ions (nitrates, acetates or oxides) acting as oxidizing reagents with filler that acts as the reducing agent. This redox mixture consisted in zinc nitrate-$Zn(NO_3)_2 \cdot 6H_2O$, galium oxide-Ga_2O_3, erbium oxide-Er_2O_3 and holmium oxide-Ho_2O_3. The proportion of each reagent was defined according to its respective molar ratio Zn:Ga of 1:2. The resulting mixture was then adjusted to a special pH=12 with sodium hydroxide solution under vigorous stirring. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and sealed tightly and was introduced in an oven at 210^0C for 4 h. It results a white precipitate that was filtrated and washed for many times with distillated water and ethylic alcohol, then dried in oven at 105°C for 4hours. After drying was achieved characterization of obtained material by X-ray diffraction (XRD) on an X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.5418 Å) incident radiation. Regarding identification of the morphology, dimension and composition of the sample was used field emission-scanning electron microscopy (SEM; Model INSPECT S), energy dispersive spectroscopy (EDAX) and atomic force microscopy (AFM; Model Nanosurf easyScan). The unpolarized absorption spectrum of Er, Ho:$ZnGa_2O_4$ was measured with a and UV-VIS-NIR spectrophotometer

(Model Lamda 950). All measurements were performed at room temperature.

3. Results and discussion

3.1 Characterization

Hydrothermal method is a success method regarding materials obtaining with a high degree of crystalinity and also homogeneity of particle's size.

Fig. 1 shows the XRD patterns of $ZnGa_2O_4$: Er^{3+} and Ho^{3+} samples obtained from Ga_2O_3, $Zn(NO_3)_2 \cdot 6H_2O$, Er_2O_3 and Ho_2O_3 by hydrothermal method of at 210^0C for 4 h.

It is seen from the form of the peaks in the XRD pattern that the $ZnGa_2O_4$: Er^{3+}, Ho^{3+} spinel particles have a high degree of crystallinity. The XRD patterns demonstrate the formation of high crystalline quality $ZnGa_2O_4$. The diffraction peaks in the patterns are indexed to spinel (space group Fd_{3m}) phases. The intensity of the peaks relative to the background signal demonstrates high purity and good quality of the samples. All specimens showed (311) peak with the highest intensity in the XRD patterns. The particles showed the XRD patterns of $ZnGa_2O_4$ doped whit Er^{3+} and Ho^{3+} crystalline phases composed of (311) peak indicating the standard powder diffraction pattern of $ZnGa_2O_4$ and (220) peak of preferred orientation.

The mean crystallite grain size (d) of the powder samples was calculated using Scherrer's formula [10]:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2}} \cos\theta$$

where β is the half-width of the diffraction peak in radians, β_0 corresponds to the instrumental broadening, $K = 180/\pi$, λ is the X-ray wavelength, and θ is the Bragg diffraction angle. The average grain size determined from XRD line broadening is 600 – 800 nm.
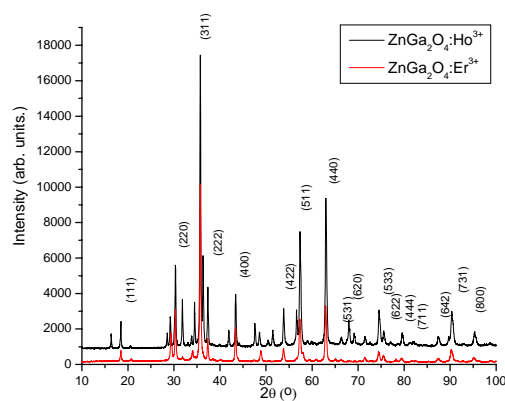
The SEM image shown in Fig. 2 provides direct information about size and morphology type of the $ZnGa_2O_4$: Er^{3+}, Ho^{3+} compound obtained by hydrothermal method.

By SEM images we can observe that particles have oblong form (bars) and dimension between 600-900 nm.
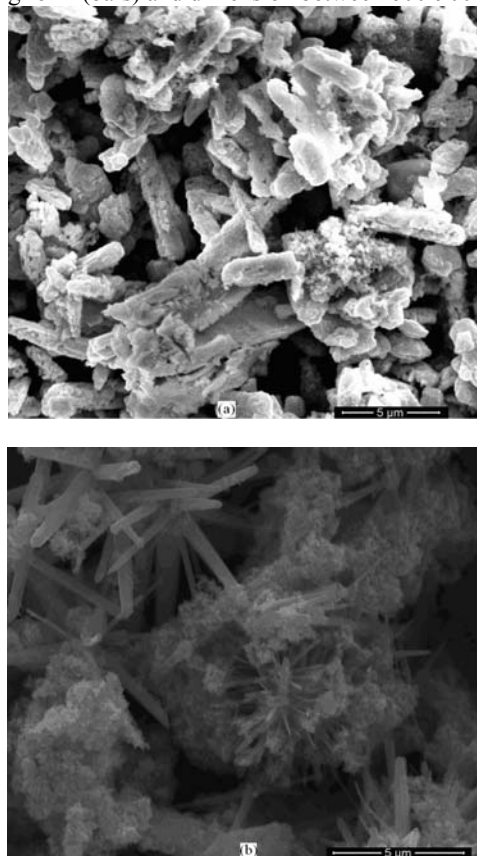

Fig. 2. SEM image of (a) $ZnGa_2O_4$:Er^{3+} and (b) $ZnGa_2O_4$:Ho^{3+}.

Fig. 1. XRD patterns of $ZnGa_2O_4$:Er^{3+} and of $ZnGa_2O_4$:Ho^{3+} samples obtained by hydrothermal method.
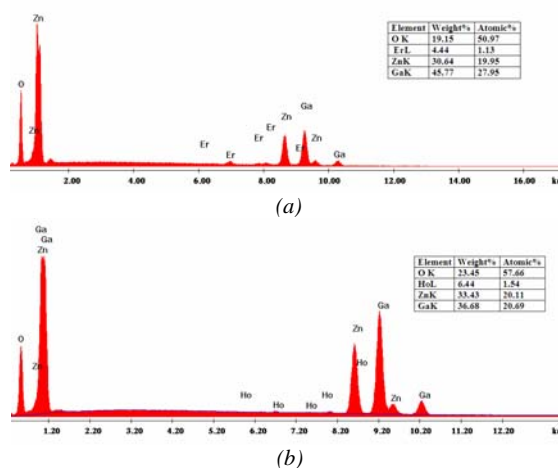
Fig. 3. EDX analysis of (a) $ZnGa_2O_4$:Er^{3+} and $ZnGa_2O_4$:Ho^{3+} compound obtained by hydrothermal method.

The EDX analysis of the oxides demonstrates the formation of stoichiometric the zinc gallate doped with Er^{3+} and Ho^{3+} (Fig. 3 (a) and (b)).
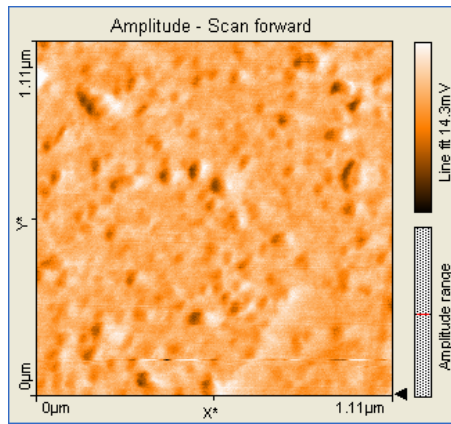
(a)
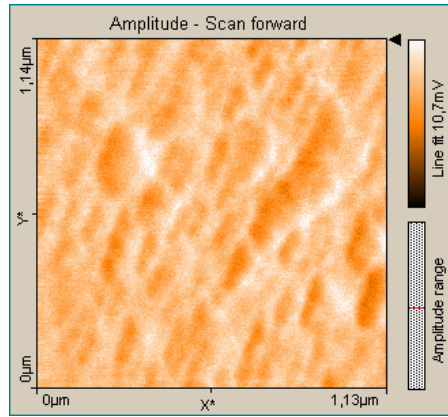
(b)

Fig. 4. (a) and (b) AFM image of $ZnGa_2O_4$:Er^{3+} and Ho^{3+} obtained by hydrothermal method.

Fig. 4 (a) and (b) shows AFM surface morphology of $ZnGa_2O_4$:Er^{3+} and $ZnGa_2O_4$:Ho^{3+} obtained by hydrothermal method. The roughness and surface morphology of the $ZnGa_2O_4$:Er^{3+}, Ho^{3+} thus obtained by hydrothermal method are different according to autoclavation conditions.

3.2 Optical properties

$ZnGa_2O_4$ have Fd_{3m} space group. In the normal spinel (AB_2O_4) oxide structure, Zn^{2+} ions occupy the tetrahedral coordinated A sites whereas Ga^{3+} ions occupy B sites, that are octahedrally coordinated. The broad emission band at 608 nm [11] can be assigned to self-activated centers originating from octahedral Ga – O group in the spinel lattice [12]. The oxygen vacancies are most probably associated with formation of Ga^{3+} ions. It was reported that the absorption and corresponding emission peaks originated from the self-activated optical centers of tetrahedral Ga – O groups shifted to a higher energy when compare to peaks originated from those of octahedral Ga – O groups. It is supposed that blue emission to be related with the formation of new self activated optical centers due the tetrahedral Ga– O groups in the spinel lattice.

According to particle size decreasing, we can observe blue shift in the absorption spectra and in the same time it is supposed that the number of Ga^{3+} ions in tetrahedral sites increases with the decrease of those in octahedral sites. The blue shift to quantum-size effect (the increased band - gap) [13].

Some authors [14, 15] reported that the shape anisotropy could affect symmetry of crystal fields around the activation center, giving the different luminescence behavior. Although much work remains to be done to fully understand these phenomena of blue-shift for the as-synthesized $ZnGa_2O_4$ phosphors, it is speculated that these phenomena are also caused by the quantum-size effect.

The absorption spectra of $ZnGa_2O_4$: Er^{3+} and Ho^{3+} are shown in Figs. 5 and 6, respectively.

The optical absorption spectrum of Er-doped $ZnGa_2O_4$ is detected in the 400-1600nm (or 25000-6250cm^{-1}) region at room temperature includes a number of well-resolved characteristic absorption bands (Fig. 5). In accordance with the energy-level diagram and the literature data [16, 17], all the observed absorption bands are assigurend to the electronic f-f-transitions of Er^{3+} ions from the ground $^4I_{15/2}$ state to different excited states.

The transition peacks, centered at 408, 451, 487, 523, 540, 654, 800, 976 and 1550 nm corresponding to the transitions of $^4I_{15/2} \rightarrow ^4G_{9/2}$, $^4I_{15/2} \rightarrow ^4G_{11/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^2H_{11/2}$, $^4I_{15/2} \rightarrow ^4S_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$, $^4I_{15/2} \rightarrow ^4I_{9/2}$, $^4I_{15/2} \rightarrow ^4I_{11/2}$, and $^4I_{15/2} \rightarrow ^4I_{13/2}$ respectively.
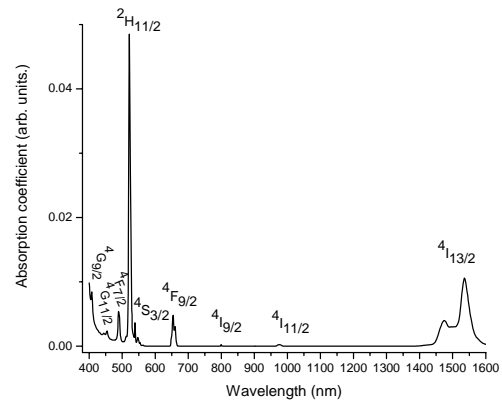

Fig. 5. Optical absorption spectra of Er-doped at $ZnGa_2O_4$.

The optical absorption spectrum of Ho –doped $ZnGa_2O_4$ is detected in the spectral range of 400-2000 nm (25000 - 5000cm^{-1}) consists of several absorption bands with a structure weakly resolved at the room temperature (see Fig. 6). In accordance to [17, 18], all the observed

absorption lines are assigned to electronic f-f-transitions in Ho^{3+} ions, in general from the ground $^5I_8$ state to various excited states. The assignment of the multiplets is complicated, because the Stark components of the $^5I_8$ ground state are populated at the room temperature and many excited levels, each of them very close one to another, are involved in the absorption transitions. Moreover, inhomogeneous broadening of the optical bands of Ho^{3+}, associated with disordering of the $ZnGa_2O_4$ structure, is revealed, too. As a consequence, most of the complex and weakly resolved bands observed by us can only be assigned to the groups of absorption transitions, as shown in Fig. 6.
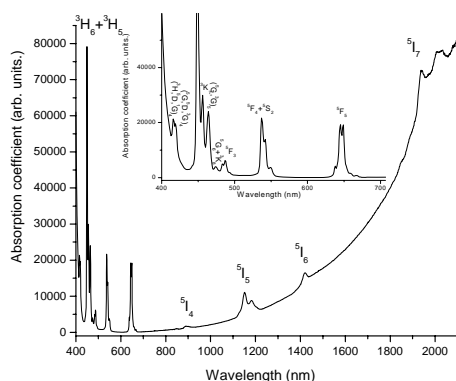

Fig. 6. Optical absorption spectra of Ho-doped in $ZnGa_2O_4$.

The transition peacks, centered at 416, 419, 445, 456, 465, 474, 488, 537, 648, 898, 1148, 1418 and 194 2nm corresponding to the transitions of $^5I_8 \rightarrow \left(^3H, ^5D, ^1G\right)_4$, $^5I_8 \rightarrow \left(^5G, ^5D, ^3G\right)_4$, $^5I_8 \rightarrow ^5H_6 + ^3H_5$, $^5I_8 \rightarrow ^3K_7$, $^5I_8 \rightarrow \left(^5G, ^3G\right)_5$, $^5I_8 \rightarrow ^5G_6 + ^3K_8$, $^5I_8 \rightarrow ^5F_3$, $^5I_8 \rightarrow ^5F_4 + ^5S_2$, $^5I_8 \rightarrow ^5F_5$, $^5I_8 \rightarrow ^5I_4$, $^5I_8 \rightarrow ^5I_5$, $^5I_8 \rightarrow ^5I_5$, $^5I_8 \rightarrow ^5I_6$ and $^5I_8 \rightarrow ^5I_7$, respectively.

4. Conclusions

$ZnGa_2O_4$ powders were synthesized by the hydrothermal method using as reactants Ga_2O_3, $Zn(NO_3)_2*6H_2O$, Er_2O_3 and Ho_2O_3. The reactant concentration and reaction medium have a particularly importance regarding hydrothermal synthesis. The X-ray diffraction shows a high crystallization degree for $ZnGa_2O_4$: Er^{3+}, Ho^{3+}. SEM analyses suggest that particles have oblong from and dimension between 600-900 nm.

The erbium and holmium impurities are incorporated into $ZnGa_2O_4$ network as Er^{3+} ($4f^{11}$, $^4I_{15/2}$) and Ho^{3+} ($4f^{10}$, $^5I_8$) ions, respectively. All the transitions of Er^{3+} and Ho^{3+} ions observed in the optical spectra of Er- and Ho-doped in $ZnGa_2O_4$ are identified.

The results of optical studies presented by us confirm that the $ZnGa_2O_4$ system could be promising materials for the "green" lasers, as well as the IR LED-pumped up-converted laser operating in the visible spectral range, when activated with Er^{3+} and Ho^{3+} ions.

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*Corresponding author: mihaela.vasile@icmct.uvt.ro