Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 76 (2015) 106 – 110

Physics
Procedia

The 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014)

Up-conversion and photoluminescence in Er^{3+} single crystal MgAl-spinel

N. Mironova-Ulmane *, A. Sarakovskis, V.Skvortsova

Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, LV-1063, Riga, Latvia

---

Abstract

Traditional and up-conversion luminescence of $MgAl_2O_4$ single crystal doped with erbium ions obtained by the Verneuil method has been investigated. The time resolved spectral measurements of the green and red up-conversion luminescence bands show that a build-up part is present in the up-conversion luminescence kinetics. This means that energy transfer process is involved in the creation of the luminescence. Considering rather small concentration of Er^{3+} in the material (0.12 mass %), the expected up-conversion mechanism should be excited state absorption since the average distance between erbium ions is high. The above-mentioned considerations suggest that clustering of the activator ions is present in the material, which is supported by SEM analysis.

Keywords: $MgAl_2O_4$, up-conversion luminescence, erbium, energy transfer

---

1. Introduction

Research and development of materials containing rare earth (RE) ions has received special attention in recent years due to their photoluminescent properties [1–4]. Magnesium aluminum ($MgAl_2O_4$) phosphor can show efficient luminescence in the presence of certain suitable dopants, particularly rare earths, in the lattice [5]. Phosphors, especially doped with erbium, are widely reported in the literature and have been used in visible up-conversion laser

---

* Corresponding author. Tel.: (+371)26358870; fax (+371) 67132778.
E-mail address: nina@cfi.lu.lv

doi:10.1016/j.phpro.2015.10.020

and efficient NIR lasers which could be used in the application of the display technologies, optical data storage and biomedical systems [6, 7].

Magnesium aluminum spinel, $MgAl_2O_4$, is a structurally and compositionally interesting crystal since it can exhibit significant deviations from the stoichiometric composition $MgO\cdot nAl_2O_3$ (where, 1< n< 2.8) [8, 9] because of the ability of the lattice to tolerate substantial cation disorder. It is of interest to study the entry of RE ions in another oxide crystal $MgO\cdot nAl_20_3$ which crystallizes in a spinel structure. For n >1 in partially reversed nonstoichiometric [10] spinel excess cation vacancies in the octahedral sites appear, which can lead to the formation of increased size of the coordination polyhedra, which may include RE ions. The spinel belongs to double oxides of the $A^{2+}(B^{3+})_2O_4$ type, where A is Mg^{2+}, Fe^{2+}, Mn^{2+} or other bivalent ions, and B is Al^{3+}, Fe^{3+}, Cr^{3+}, Mn^{3+} or other trivalent ions. Magnesium aluminium spinel $MgO\cdot nAl_20_3$ (if stoichiometric, n=1) is a cubic-type face centred crystal. The elementary cell consists of 8 formula units AB_2O_4. Oxygen ions create a close-packed arrangement with 64 tetrahedral and 32 octahedral interstices per cell. If 8 bivalent ions occupy 8 tetrahedral (A) sites, and 16 trivalent ones – 16 octahedral (B) sites, the spinel is described by the space symmetry group $O^7{}_h$ and is called "normal". For the "inverse" spinel, a half of the trivalent (B) ions are located in the tetrahedral position; the other part of B and A ions is usually statistically distributed between the octahedral positions. If we use an inversion parameter i, the chemical formula of magnesium aluminium spinel may be expressed by $^{IV}(Mg_{1-i}Al_i)^{VI}[Mg_{-i}Al_{2-i}]O_4$,where $^{IV}(\ )$ and $^{VI}[\ ]$ represents the tetrahedral (A sites; 8a) and the octahedral sites (B site;16d). Assuming i = 1, we obtain a formula Al [MgAl] O_4 for the inverse spinel.

In the present report the results of up-conversion luminescence studies in Er^{3+} doped $MgAl_2O_4$ will be shown and the details of the mechanisms responsible for the up-conversion luminescence will be discussed.

2. Experimental

Single crystals of $MgO.nAl_20_3$ (n = 2.0-2.8) were grown by the Verneuil method. The erbium has been added to the mixture in the ErO_3 form. The content of the Er in the spinel single crystals was determined by instrumental neutron activation analysis with respect to medium-life radionuclides. The composition of the spinel single crystals and the concentrations of the RE ions introduced into the charge and found in the single crystals are presented in [11]. As may be seen, the degree of entry of the RE ions into the $MgO\cdot nAl_20_3$ crystals, defined as the ratio C_0/C_i, varies from 10^{-3} to 0.2 [11]. The size of the voids $r_{tet} = 0.0557$ nm and $r_{oct} = 0.0541$ nm [10] are appreciably less than the radii of the activator ions $r_{Er} = 0.089$ nm. With the introduction of Er^{3+} ions cationic (and possibly anionic) vacancies are concentrated in their vicinity, which leads to the formation of coordination polyhedral with appreciable fluctuations in the field parameters. The large difference in the radii of the crystal-forming and activator ions also explains the low value of 0.12 mass % instead of 0.5 mass % [11], which indicates a low solubility of the RE oxides in magnesium-aluminium spinel.

The photoluminescence was excited by a tunable (210 nm–2300 nm) pulsed solid state laser NT342/3UV (pulse duration ~ 4 ns) from Ekspla. The up-conversion luminescence was excited by a temperature controlled laser diode (LD) from Thorlabs (λ=980 nm). Luminescence decay kinetics was measured by Andor SR-303i-B monochromator/spectrometer coupled to a photomultiplier tube (time resolution better than 10 ns) and digital oscilloscope Tektronix TDS 684A. Overall temporal resolution of the system is better than 10 ns. Luminescence lifetime values were determined from decay kinetics by mathematical methods. Luminescence spectra were measured by Andor SR-303i-B spectrometer coupled to iCCD camera (Andor iStar). All the spectral measurements were conducted at 15 K using closed cycle helium cryostat. The structure of the samples was studied by a scanning electron microscope (SEM, TESCAN Mira\LMUField-Emission-Gun). The elemental composition of magnesium aluminum spinel was assessed by energy dispersive X-ray spectrometry (EDS, Oxford instruments 7378) performed on the SEM.

3. Results and discussion.

3.1 Traditional luminescence

The photoluminescence spectra of synthetic spinel MgO•2Al_2O_3 containing Er^{3+} are given in Fig. 1 and energy level for traditional luminescence diagram of Er^{3+} in Fig. 2.

Under excitation at 450 nm a broad luminescence band with some sharp features at 550 nm and 660 nm appears. The sharp lines in the green and red spectral regions can be attributed to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ electronic transitions in Er^{3+}. The main band centred at 525 nm is due to Mn^{2+} ions in tetrahedral coordination for nonstoichimetric spinel (n>2.5), 625 nm is due to Mn^{2+} ions in octahedral coordination and 720 nm can be ascribed as the luminescence of Cr^{3+} ion [12]. In the spinel spectra some zero-phonon lines were observed in the region of the Cr^{3+} ions electron transition $^2E_g \rightarrow {}^4A_{2g}$: R-lines predetermined by Cr^{3+} ions which replace Al^{3+} ions in the octahedral sites of the spinel lattice [13] and N-lines related to the Cr^{3+} ions the local symmetry of which differs from symmetry of sites occupied by Al^{3+} in normal spinel [14].

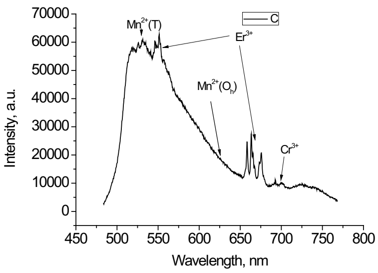

Figure1.Traditional luminescence spectrum excited at 450 nm.

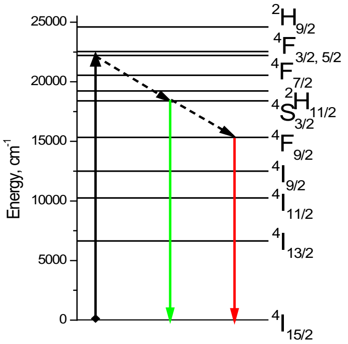

Figure 2. Energy level diagram for traditional luminescence diagram of Er^{3+}.

The broadening of R- and N-lines takes place in synthetic stoichiometric spinel as shown in [15]. Supposing that some of the nearest cations of a Cr^{3+} ion are substituted by Mg^{2+} ions, the distorted crystal field influences the chromium ion. Then Cr^{3+} emission is shifted to longer wavelength side. If considerable number of Mg and Al cations has substituted one for another in a crystal, there will be less normally arranged Cr^{3+} ions in this crystal. Then the R- and N-lines draw nearer. The lines of the phonon-assisted sideband become broadened, too. Structure of synthetic nonstoichiometric spinels (n>1) has to be more disordered, since in addition to the site exchange the so-called stoichiometric vacancies are present in the structure. Therefore, the numbers of different versions of cation location in the 2nd coordination sphere increases. Moreover, the absence of a cation affects Cr^{3+} ion stronger than Mg^{2+} substituted for $Al^{3+.}$ The number of Cr^{3+} ions with normal arrangement becomes negligible.

3.2 Up-conversion luminescence

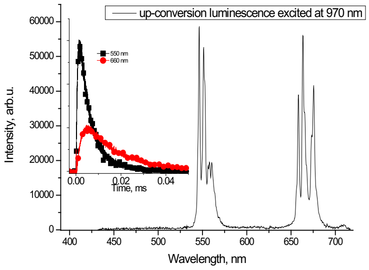

Figure 3. Up-conversion luminescence spectrum excited at 980 nm. Inset: kinetics for 550 and 660 nm luminescence bands

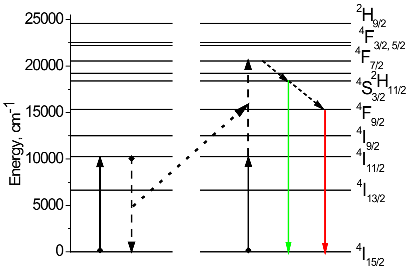

Figure 4. Possible mechanism of green and red up-conversion luminescence. Radiative, non-radiative and energy transfer processes are indicated by solid, dashed and dotted lines, respectively.

Up-conversion luminescence spectra have been measured for the sample under excitation at 980 nm (Figure 3). Two strong luminescence bands at around 540 nm and 660 nm have been detected corresponding to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ electronic transitions, respectively. Luminescence decay kinetics has been measured at low temperature revealing a pure energy transfer nature of the up-conversion process in the generation of the both bands. One of the possible mechanisms is shown in the energy level diagram.

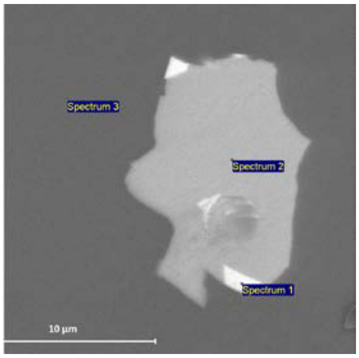

Fig.5 SEM image from single crystals $MgAl_2O_4$ doped Er

Table 1. Concentration of chemical elements, mol%

Spectrum	O	Mg	Al	Er
Spectrum 1	67.93	0.78	19.70	11.58
Spectrum 2	66.33	3.92	24.63	5.12
Spectrum 3	66.51	6.10	27.38	--

The EDX spectroscopy method was used for investigation of concentration of chemical elements (Table 1). EDS analysis shows nonhomogeneous distribution of erbium concentration in the sample having Er-rich regions (~11 mol%) and regions with very low or undetectable Er content.

The time resolved spectral measurements of the green and red up-conversion luminescence bands show that a build-up part is present in the up-conversion luminescence kinetics. This means that energy transfer process is involved in the creation of the luminescence. Considering rather small concentration of Er^{3+} in the material (0.12 mass % obtained by neutron activation measurements), the expected up-conversion mechanism in the case of homogeneous distribution of erbium in the material should be excited state absorption since the average distance between erbium ions is high. The above-mentioned considerations are in-line with EDX measurements and confirm the clustering of the activator ions in the material.

Conclusions

Erbium doped MgAl-spinel was synthesized. Erbium concentration determined by neutron activation measurements was estimated as 0.12 mass %. EDS analysis shows nonhomogeneous distribution of erbium concentration within the sample. The time resolved measurements of the up-conversion luminescence show strong involvement of energy transfer mechanism in the creation of the luminescence implying that the distance between Er^{3+} ions is small. The above-mentioned considerations suggest that clustering of the activator ions is present in the material

Acknowledgement

This work was supported by Latvian Science Council Grant No. 187/2012. Financial support from Latvia-Belarus bilateral research project is acknowledged.

References

[1] Perrella, R. V., dos Santos, D. P., Poirier, G. Y., Góes, M. S., Ribeiro, S. J. L., Schiavon, M. A., Ferrari, I. L., 2014. Er^{3+}-doped Y_2O_3 obtained by polymeric precursor: Synthesis, structure and upconversion emission properties. Journal of Luminescence 149, 333-340.

[2] Sarakovskis A., Grube J., Doke G., Springis M., 2010 Selective excitation of up-conversion luminescence by Yb3+ Optical Materials 32 832–835.

[3] Sarakovskis, A., Grube, J., Doke, G., Springis, M., 2010 Excited state absorption and energy-transfer mechanisms of up-conversion luminescence in Er3+-doped oxyfluoride glass ceramics at different temperatures. Journal of Luminescence, 130 (5), pp. 805-811.

[4] Liu, H. Y., Kong, H., Jiang, D. M., Shi, W. Z., Ma, X. X., 2007. Microstructure and electrical properties of Er_2O_3-doped ZnO-based varistor ceramics prepared by high-energy ball milling. Journal of Rare Earths 25, 120- 123.

[5] Singh, V., Kumar Rai , R. V., Watanabe, S., Gundu Rao, T. K., Badie, L., Ledoux-Rak, I., Jho,Y. –D., 2012. Synthesis, characterization, optical absorption, luminescence and defect centres in Er^{3+} and Yb^{3+} co-doped $MgAl_2O_4$ phosphors. Applied Physics B: Lasers and Optics 108 (2), 437-446.

[6] Auzel, F., 2004. Upconversion and Anti-Stokes Processes with f and d Ions in Solids. Chem. Rev. 104, 139- 173.

[7] Shur, J. W., Yang, W. S., Suh, S. J., Lee, J. H., Fukuda, T., Yoon, D. H., 2002. Optical Properties of Er Doped Congruent and Stoichiometric $LiNbO_3$ Single Crystals. Cryst. Res. Technol. 37, 353- 358.

[8] Mironova, N. A., Skvortsova, V. N., Smirnov, A. S., Riekstinya, D. V., Grinvald, G. A., Litvinov, L. A., 1989. Anomalous Behaviour of $MgO\cdot 2.5\,Al_2O_3$ under Radiation. Phys, Stat. Sol. (a) 116, K 125 –K127.

[9] Soeda, T., Matsumura, S., Kinoshita, C., Zaluzec, N. J., 2000. Cation disordering in magnesium aluminate spinel crystals induced by electron or ion irradiation. J. Nucl. Mater. 283–287, 952-956.

[10] Patrat, G., Brunel, M., de Bergevin, F., 1974. Répartition et déplacements locaux des ions dans le spinelle $MgAl_2O_4$ non stoechiométrique. Acta Cryst. A30, 47-54.

[11] Gritsyna, V. T., Kol'ner, V. B., Damburg, N. A., Mironova, N. A., Skvortsova, V. N., 1985. Optical spectra of rare-earth ions in magnesium-aluminum spinel crystals. Journal of Applied Spectroscopy. Springer. 547-550. Translated from Zhurnal Prikladnoi Spektroskopii 42 (1985) 800 [in Russian].

[12] Mironova, N., Skvortsova, V., Smirnovs, A., Čugunov, L., 1996. Distribution of manganese ions in magnesium-aluminium spinels of different stoichiometries.Optical materials 6, 225- 232.

[13] Wood, D. L., Imbusch, G. F., Macfarlane, R. M., Kisliuk, P., Larkin, D. M., 1968. Optical spectrum of Cr^{3+} ions in spinels. J. Chem. Phys. 48, 5255-5263.

[14] Mikenda, W., Preisinger, A., 1981. N-lines in theluminescence spectra of Cr^{3+}- doped spinels. (II) Origins of N- lines. J. Luminescence 26, 67-83.

[15] Skvortsova, V., Mironova- Ulmane, N., Ulmanis, U., 2002. Neutron irradiation influence on magnesium aluminium spinel inversion. Nucl. Instr. and Methods in Physics Research B 191, 256-260.