

DYSPROSIUM DOPED CALCIUM GERMANATE (Ca_2GeO_4) AS A CANDIDATE FOR LED APPLICATION

Iovka I. Koseva¹, Peter Tz. Tzvetkov¹, Petar I. Ivanov², Maria N. Gancheva^{1*}, Velin S. Nikolov¹

¹Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

²Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria

Abstract

Powder samples of Ca_2GeO_4 doped with 0.2, 0.5, 1, 2 and 3 at% Dy^{3+} were prepared using conventional solid state synthesis technique. XRD analyses show obtaining of the pure phase at all dopant concentrations. Emission and excitation spectra contain the characteristic peaks of Dy^{3+} ion. The Dy^{3+} excitation spectrum in the range from 300 to 500 nm show characteristic transitions of Dy^{3+} , attributed to the $f-f$ transitions. The strongest peak is located at 348 nm corresponding to the $^6\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$ transition. In the luminescent spectra the two emission peaks of Dy^{3+} appears at 483 nm ($^4\text{F}_{5/2} \rightarrow ^6\text{H}_{15/2}$ transition) corresponding to blue color and at 575 nm ($^4\text{F}_{5/2} \rightarrow ^6\text{H}_{13/2}$ transition) corresponding to yellow one. CIE coordinates of the samples show different emission colors in the yellow region depending on the active ion concentration. The obtained results confirm that as prepared dysprosium doped materials could be used as yellow phosphors.

Keywords: Germanate phosphor, Materials for LED, Rare-earth ions, X-ray diffraction, Photoluminescence

1. INTRODUCTION

Luminescent materials based on germanate compounds are used as fluorescent lamps, modern flat screens and displays due to their low energy consumption, long lifetime, high stability, good brightness, robustness, fast switching, small size and high efficiency. According to Wang et al., luminescent materials would reduce the universal electricity consumption up to 50% [1]. Ca_2GeO_4 is with orthorhombic structure, space group $Pbmn$ and crystal lattice parameters $a=5.24 \text{ \AA}$, $b=11.40 \text{ \AA}$, $c=6.79 \text{ \AA}$ [2, 3]. This compound is well known as a host for Cr^{4+} activated laser materials [4-6]. Only few articles are published on doping of Ca_2GeO_4 with rare earth ions. All investigations on Tb^{3+} doped Ca_2GeO_4 [7] and Eu^{3+} doped Ca_2GeO_4 [8-10] are under excitation length in the range 240-260 nm, where peaked the Re-O charge transfer. In modern technologies InGaN chip is common used as an excited light source emitting in the range 340-430 nm. Therefore it is necessary to find out proper rare earth ion which can be excited in this range and to emit in the visible range with high efficiency. The only article on Dy^{3+} doped Ca_2GeO_4 describes in details the afterglow luminescence of this material [11]. Dysprosium ion possesses two dominant emission bands in the blue (460-500 nm) and the yellow (560-600 nm) regions. The first is assigned to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ magnetic dipole transition which is slightly dependent on the local symmetry. The latter one is assigned to the hypersensitive electric dipole transition $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$, which intensity is strongly influenced by the Dy^{3+} environment [12, 13]. For this reason Dy^{3+} ion could be used as a single dopant in white light emitting materials. Color could be tuned by adjusting the yellow to blue ratio in the emission spectrum [14].

The main aim of this work is to find out the optimal concentration of Dy^{3+} ion in Ca_2GeO_4 matrix when the emission is strongest upon excitation in the range 340-430 nm and to use these results for further investigations on materials containing the mentioned compound.

2. MATERIALS AND METHODS

2.1. Materials

CaCO₃ (p.a.Valerus), GeO₂ (99.99%, Alfa Aesar) and Dy₂O₃ (99.99%, Alfa Aesar) were used as raw materials.

2.2. Methods

Solid state synthesis were carried out in a resistive furnace with Kantal heating wire permitted maximum working temperature of 1200°C and in a chamber furnace with MoSi₂ heating elements permitted maximum working temperature of 1550°C. Samples were synthesized in platinum crucibles. First the mixture was heated at 700°C for decomposition of the calcium carbonate and then the powder was heated at 1300°C during 3 hours with two intermediate grinding in agate mortar.

2.2.1. Characterization

Structural characterization was carried out by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer with Cu K_α radiation and SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2θ range from 10 to 80° with a step 0.04° and 1s step⁻¹ counting time. X-ray diffractograms were identified using the Diffractplus EVA program [15]. The emission and excitation spectra were measured on Horiba Fluorolog 3-22 TCS spectrophotometer equipped with a 450 W Xenon Lamp as the excitation source. All spectra were measured at room temperature.

3. RESULTS AND DISCUSSION

The structure of Ca₂GeO₄ is an olivine structure where Ca²⁺ ions occupy two different octahedral crystallographic positions. The Ca1 cation is surrounded by six anions with an average Ca-O distance of 2.3630 Å and located at the center of inversion. The coordination of the Ca2 cation is also octahedral with an average Ca-O distance of 2.3954 Å. Coordination polyhedra are slightly distorted.. The Ge atom is enclosed in a tetrahedron and the average Ge-O distance is 1.7636 Å. Ge and Ca2 cations lie in mirror planes[2, 16]. The ionic radius of dysprosium (0.912 Å) is closed to that of calcium (0.99 Å), so it is expected that the dysprosium ion would prefer to substitute the calcium ion [17].

XRD patterns of the Ca₂GeO₄, pure and doped with 0.2, 0.5, 1, 2 and 3 at% Dy³⁺ are presented on Figure 1. The results confirm that all obtained samples are pure phase compared with PDF File 26 0304. The crystal lattice parameters are almost unchanged with increasing of the dopant concentration.

The excitation spectra of Dy³⁺ doped Ca₂GeO₄ monitored at 575 nm in the wavelength range 300-500 nm are presented on Figure 2. They consist of sharp peaks absorbed from the 4f levels of Dy³⁺ ion and correspond to the transitions ⁶H_{15/2}→⁶P_{3/2} (323 nm), ⁶H_{15/2}→⁶I_{9/2} (336 nm), ⁶H_{15/2}→⁶P_{7/2} (348 nm), ⁶H_{15/2}→⁶P_{5/2} (363 nm), ⁶H_{15/2}→⁶F_{7/2} (385 nm), ⁶H_{15/2}→⁴G_{11/2} (423 nm), ⁶H_{15/2}→⁴I_{15/2} (452 nm) and ⁶H_{15/2}→⁴F_{9/2} (472 nm). The observed peaks are already described in the literature [13, 18]. The strongest peak is centered at 348 nm. As can be seen, the intensity of the peaks in the spectra increases up to 1 at% Dy³⁺.

The emission spectra of Dy³⁺ doped samples monitored at 348 nm in the wavelength range 400-650 nm are presented on Figure 3. They display two separate peaks in the blue region (483 nm) and in the yellow region (575 nm) corresponding to ⁴F_{9/2}→⁶H_{15/2} and ⁴F_{9/2}→⁶H_{13/2} transitions respectively. The blue emission belongs to a magnetic-dipole transition and the yellow one belongs to a hypersensitive electric-dipole transition. The intensity of the latter one is strongly influenced by the chemical environment of the active ion. The blue peak is stronger when the dopant is located in a high symmetry site with inversion center and when the yellow peak dominates the doping ion is located at low symmetry site [14, 18]. In Ca₂GeO₄ compound the Dy³⁺ ion is at low symmetry local site without inversion symmetry center and the yellow emissions in the luminescent spectra are stronger. The highest emission is observed at 0.5 and 1at% Dy³⁺ dopant concentrations.

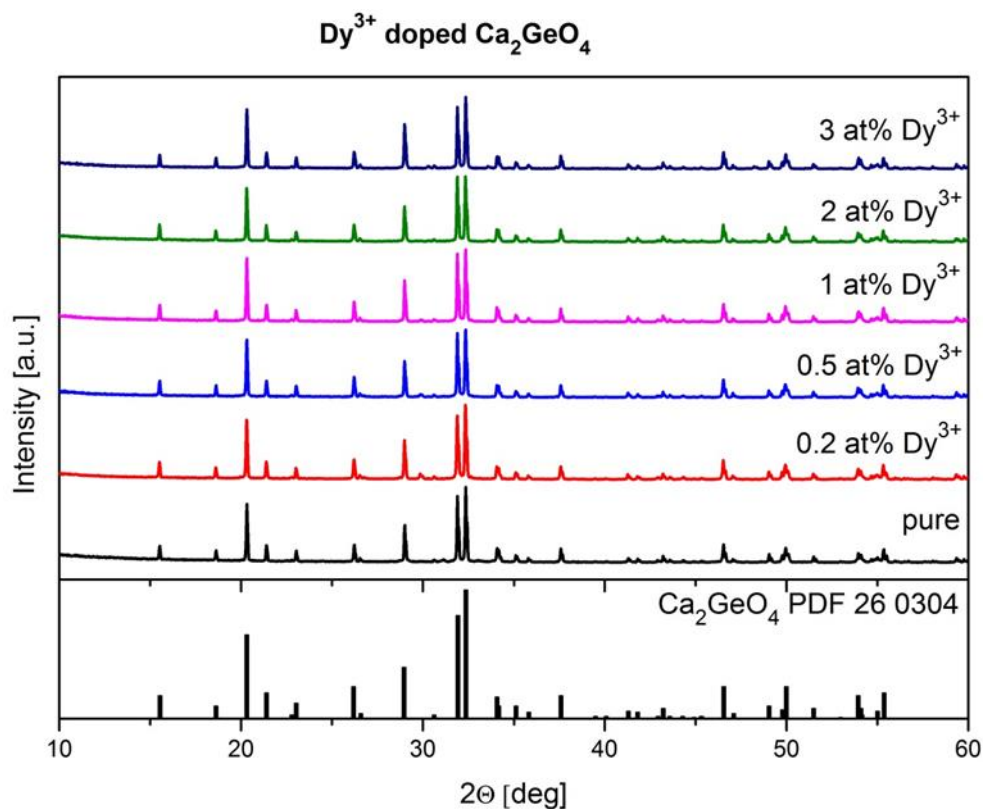


Fig. 1. XRD patterns of the pure and Dy³⁺ doped Ca₂GeO₄ samples, compared with Ca₂GeO₄ PDF file 26 0304.

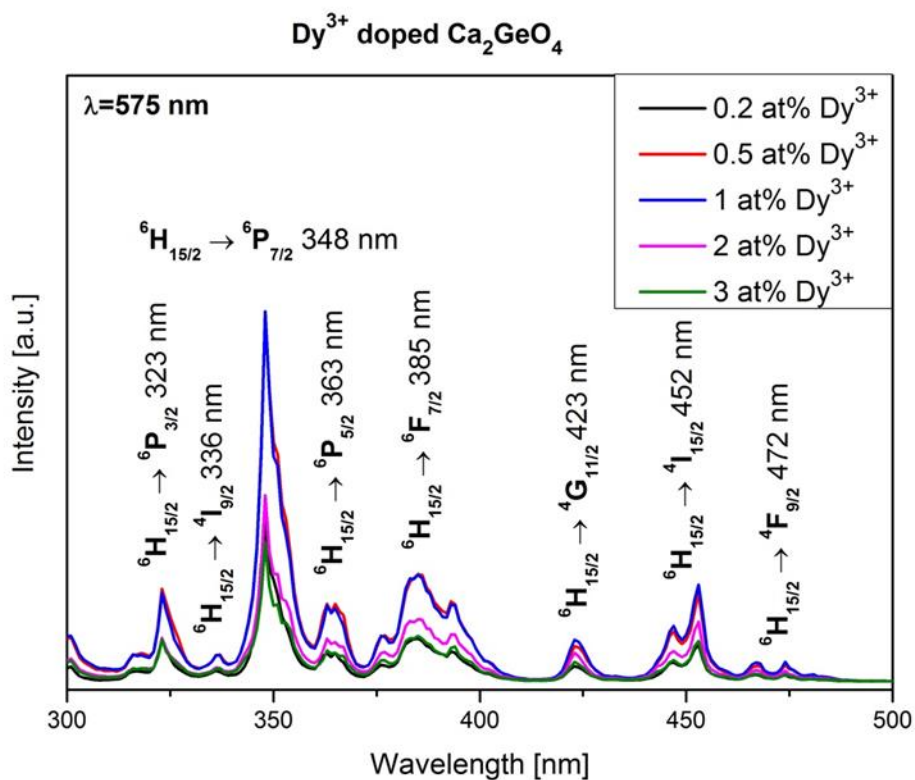


Fig. 2. Excitation spectra of Dy³⁺ doped Ca₂GeO₄ monitored at 575 nm.

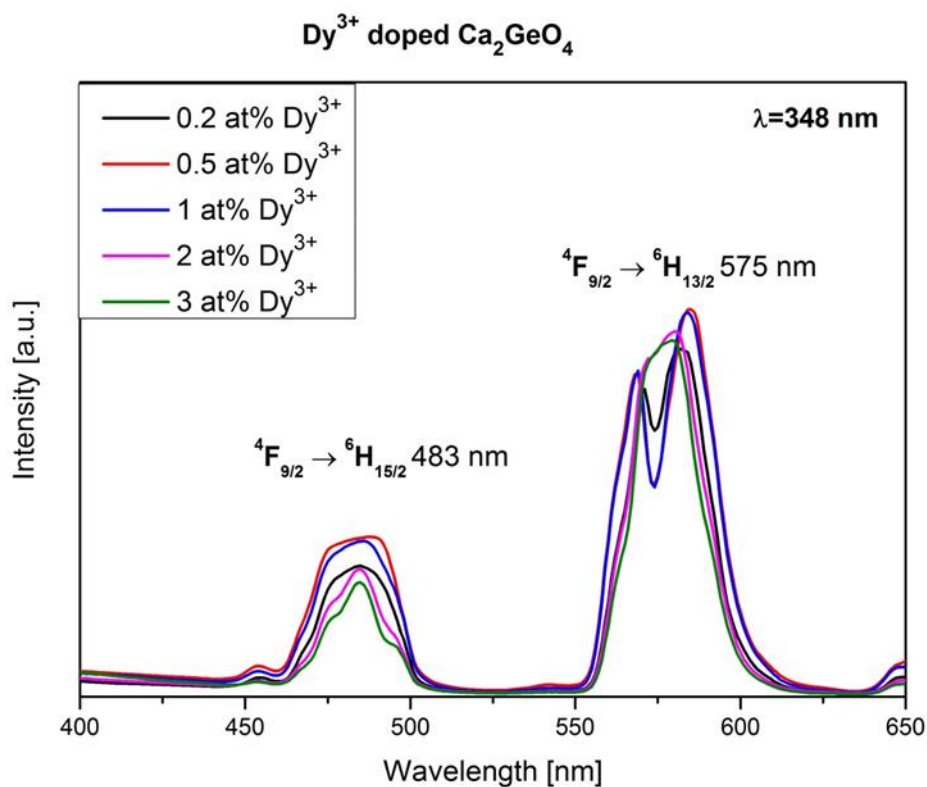


Fig. 3. Emission spectra of Dy³⁺ doped Ca₂GeO₄ monitored at 348 nm

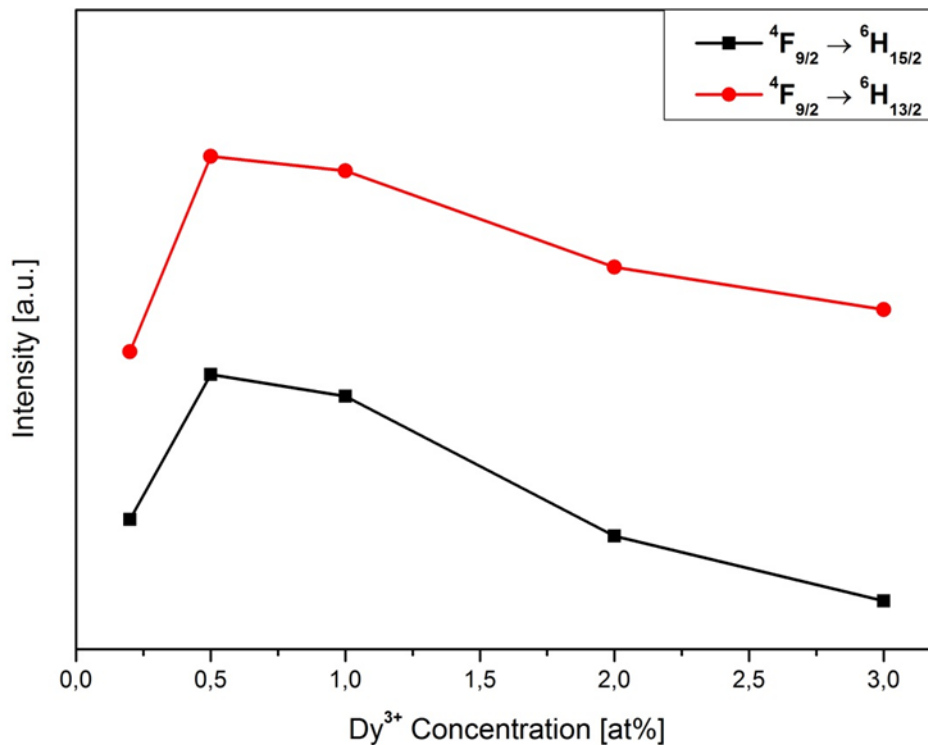


Fig. 4. Luminescent intensity dependence of the $4F_{9/2} \rightarrow 6H_{15/2}$ and $4F_{9/2} \rightarrow 6H_{13/2}$ transitions on the concentration of the Dy³⁺ ion.

Figure 4 presents the luminescent intensity dependence of the two transitions mentioned above on the concentration of the active ion. As can be seen, the luminescence is highest at 0.5 and 1at% Dy³⁺ in the host. In higher concentrations the luminescence decreases because of the concentration quenching effect.

According to Blasse [13], critical average short distance between two active ions could be calculated using the equation:

$$R_c = 2[3V/4\pi X_c N]^{1/3},$$

where V is the volume of the unit cell of Ca₂GeO₄ (405.61 Å³), X_c is a critical concentration of Dy³⁺, N is the number of the center cations in Ca₂GeO₄ unit cell (8). In the case of Ca₂GeO₄ doped by 0.5 at% Dy³⁺, which is the critical concentration, R_c is 5.79 Å. The intensity ratios of yellow-to-blue (Y/B) emissions of samples with different Dy³⁺ concentrations varies between 2.24 and 3.34, therefore the luminescence color is in the yellow region. It could be changed to some extent by varying the dopant concentration. The intensity ratios (Y/B) and the chromaticity coordinates of all investigated samples are presented in Table 1 and on Figures 5 and 6.

CIE	Y/B	x	y
0.2 at%Dy ³⁺ :Ca ₂ GeO ₄	2.62	0.43	0.42
0.5 at%Dy ³⁺ :Ca ₂ GeO ₄	2.24	0.42	0.40
1 at%Dy ³⁺ :Ca ₂ GeO ₄	2.39	0.43	0.41
2 at%Dy ³⁺ :Ca ₂ GeO ₄	3.16	0.44	0.43
3 at% Dy ³⁺ :Ca ₂ GeO ₄	3.34	0.44	0.43

Table 1. Intensity ratios (Y/B) and chromaticity coordinates of Dy³⁺ doped Ca₂GeO₄ samples.

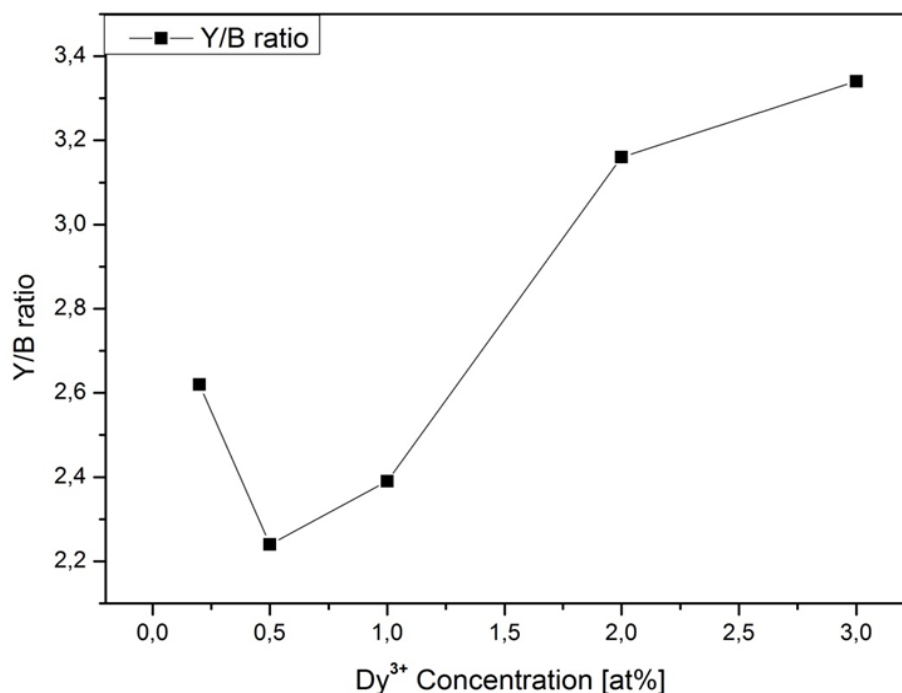


Fig. 5. Concentration dependence of the intensity ratios (Y/B) of Dy³⁺ doped Ca₂GeO₄ samples

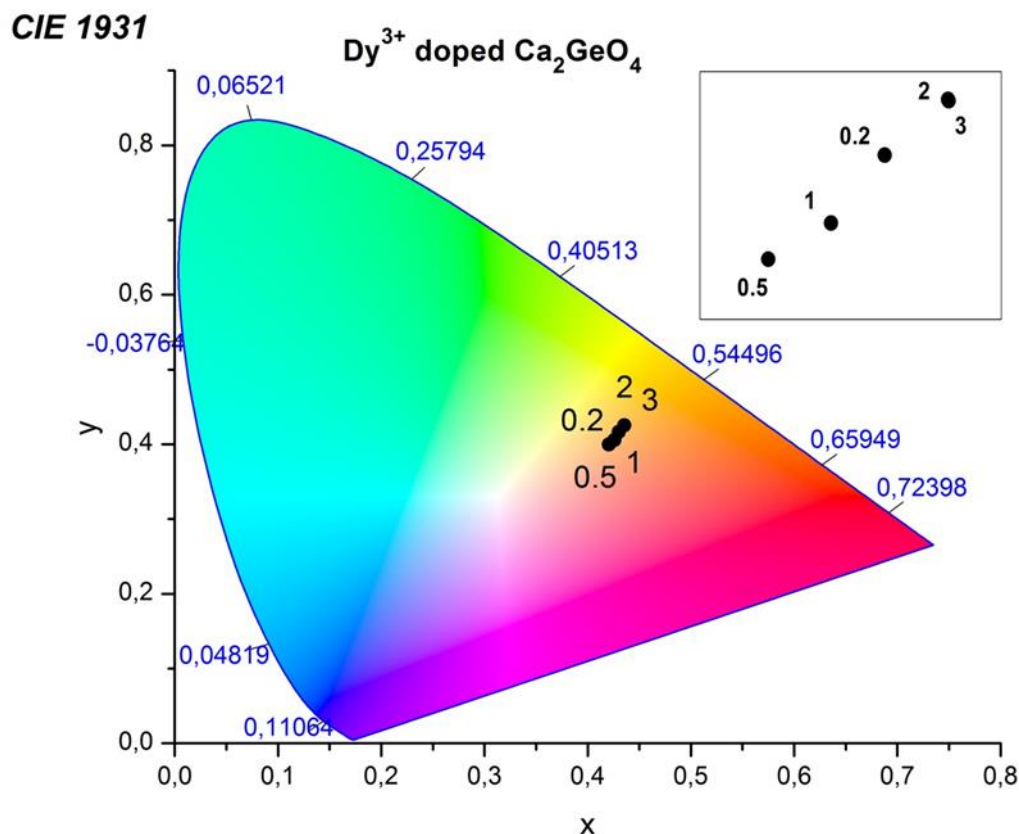


Fig. 6. CIE coordinates of Dy^{3+} doped Ca_2GeO_4 samples.

4. CONCLUSIONS

Powder samples of Ca_2GeO_4 doped with 0.2, 0.5, 1, 2 and 3 at% Dy^{3+} were prepared using conventional solid state synthesis technique. XRD analyses show obtaining of the pure phase at all dopant concentrations after heating at 1300 °C during 3 hours. The Dy^{3+} excitation spectrum in the range from 300 to 500 nm show characteristic transitions of Dy^{3+} , with strongest peak located at 348 nm ($^6\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$ transition). In the luminescent spectra in the range from 400 to 650 nm the two emission peaks of Dy^{3+} appears at 483 nm ($^4\text{F}_{5/2} \rightarrow ^6\text{H}_{15/2}$ transition) and 575 nm ($^4\text{F}_{5/2} \rightarrow ^6\text{H}_{13/2}$ transition) corresponding to blue and yellow colors. The highest emission is observed at 0.5 and 1at% Dy^{3+} dopant concentrations. The intensity ratios of yellow-to-blue (Y/B) emissions of samples with different Dy^{3+} concentrations vary between 2.24 and 2.34. Thus the color could be changed to some extend by changing the active ion concentration. CIE coordinates of the samples show different emission colors in the yellow region. The obtained results confirm that the described dysprosium doped materials could be used as yellow phosphors.

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REFERENCES

1. Wang T, Xu X, Zhou D, Qiu J, Yu X 2014, "Red phosphor $\text{Ca}_2\text{Ge}_7\text{O}_{16}:\text{Eu}^{3+}$ for potential application in field emission displays and white light-emitting diodes", *Materials Research Bulletin*, vol. 60, no. 12, pp. 876-881.
2. Eysel W, Hahn T 1970 "Polymorphism and solid solution of Ca_2GeO_4 and Ca_2SiO_4 ", *Zeitschrift für Kristallographie-Crystalline Materials*, vol. 131, no. 1-6, pp. 322-341.
3. Redhammer GJ, Roth G, Amthauer G, Lottermoser W 2008 "On the crystal chemistry of olivine-type germanate compounds, $\text{Ca}_{1-x}\text{M}_{1-x}\text{GeO}_4$ ($\text{M}^{2+} = \text{Ca, Mg, Co, Mn}$)", *Acta Crystallographica Section B*: vol. 64, no. 3, pp. 261-271.
4. Evans JM, Petričević V, Bykov AB, Delgado A, Alfano, RR 1997, "Direct diode-pumped continuous-wave near-infrared tunable laser operation of $\text{Cr}^{4+}:\text{forsterite}$ and $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ ", *Optics letters*, vol. 22, no. 15, pp. 1171-1173.
5. Petricevic V, Bykov AB, Evans JM, Alfano RR 2002, "Room-temperature near-infrared tunable laser operation of $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ ", *SPIE milestone series*, vol. 173, pp. 262-264.
6. Li C, Xu J, Liu W, Zheng D, Zhang S, Zhang Y, Zeng F 2015, "Synthesis and characterization of Cr^{4+} -doped Ca_2GeO_4 tunable crystal" *Journal of Alloys and Compounds*, vol. 636, pp. 211-215.
7. Yang HM, Shi JX, Liang HB, Gong ML 2006 "A novel green emitting phosphor $\text{Ca}_2\text{GeO}_4:\text{Tb}^{3+}$ ", *Materials Research Bulletin*, vol. 41 no. 4, pp. 867-872.
8. Hongmei Y, Jianxin S, Menglian G, Liang H 2010 "A novel red phosphor: $\text{Ca}_2\text{GeO}_4:\text{Eu}^{3+}$ ", *Journal of Rare Earths*, vol. 28 no. 4, pp. 519-522.
9. Shang M, Li G, Yang D, Kang X, Zhang C, Lin J 2011 "Red emitting $\text{Ca}_2\text{GeO}_4:\text{Eu}^{3+}$ phosphors for field emission displays", *Journal of Electrochemical Society*, vol. 158, no. 4, pp. J125-J131.
10. Zhang J, Zhou M, Qin Q, Yu M, Wang Y 2011 "The electronic structure and photoluminescence properties of $\text{Ca}_2\text{GeO}_4:\text{Eu}^{3+}$ in ultraviolet and vacuum ultraviolet region", *Journal of Luminescence*, vol. 131 no. 8, pp. 1636-1640.
11. Ermakova LV, Leonidov II, 2018, "Towards a new group of olivine-type afterglow phosphors: the case of $\text{Ca}_2\text{GeO}_4:\text{Dy}^{3+}$ ", *Materials Letters*, vol. 233, pp. 39-41.
12. Yen W, Shionoya S, Yamamoto H 2006 *Phosphor Handbook*. CRC Press, Print ISBN, 978-0
13. Blasse G. Grabmaier BC, 2012 *Luminescent materials*. Springer Science & Business Media
14. Liu RS, 2017, "Phosphors, up conversion nano particles, quantum dots and their applications" pp. 343-370, Berlin: Springer
15. Bruker AXS (2009) EVA 2, DIFFRACplus Evaluation Package
16. Ovsetsina TI, Yunin VV, Verin IA, Chuprunov EV 2004, "Crystal structure of calcium orthogermanate Ca_2GeO_4 ", *Vestnik Nizhegorodskogo universiteta im. Lobachevskogo. Ser. Fizika i matematika*, vol. 1, pp. 72-74 (in Russian)
17. Shannon RD, 1976, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides", *Acta Crystallographica section A: crystal physics, diffraction, theoretical and general crystallography*, vol. 32, no. 5, pp. 751-767.
18. Gaft M, Reisfeld R, Panczer G, 2015, *Modern luminescence spectroscopy of minerals and materials*. Springer