Synthesis and Photoluminescence Properties of $\text{Ca}_2\text{Ga}_2\text{SiO}_7\text{:Eu}^{3+}$ Red Phosphors with an Intense $5\text{D}_0 \rightarrow 7\text{F}_4$ Transition

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Synthesis and photoluminescence properties of $\text{Ca}_2\text{Ga}_2\text{SiO}_7:\text{Eu}^{3+}$ red phosphors with intense $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition

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Supporting Information Placeholder

ABSTRACT: Novel melilite type $\text{Ca}_2\text{Ga}_2\text{SiO}_7 : \text{Eu}^{3+}$ red emitting phosphors with different Eu^{3+} contents were synthesized via high temperature solid-state reaction. Crystal structure, optical absorption and photoluminescence properties were investigated while DFT calculations were performed on host lattice. The excitation spectra indicate that phosphors can be effectively excited by near-ultraviolet light for a potential application in white light-emitting diodes. Due to the abnormally high intensity emission at about 700 nm arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition of Eu^{3+} , the phosphors $\text{Ca}_2\text{Ga}_2\text{SiO}_7 : \text{Eu}^{3+}$ show a deep red emission with chromaticity coordinates (0.639, 0.358). This high intensity has been attributed to the presence of noncentrosymmetric sites for Eu^{3+} ions and is shown to be potentially interesting for applications as light emitting diodes (LEDs) for Solid-State Lighting (SSL) and display devices.

White light emitting diodes (WLEDs) have been attracted much attention due to their considerable impact on issues such as energy consumption and environment. Therefore, WLEDs are thought to have brought a revolution in energy-efficient lighting and are promising to replace conventional light sources such as incandescent and fluorescent lamps in the near future^{1,2}. The most common approach to obtain white light is to employ the yellow-emitting $\text{YAG}:\text{Ce}^{3+}$ phosphor and blue InGaN chips. Unfortunately, the drawbacks of this method are a low color rendering index (CRI <80) and a high correlated color temperature (CCT) because of the scarcity of red emission^{3,4,5}. Thus, it is meaningful to develop some novel red-emitting phosphors with improved properties for application in WLEDs. Currently, the most extensively studied red emitting rare-earth ion is the trivalent Eu^{3+} which is a relevant component of artificial white light with its main emission around 615 nm. If the spectral features of the generated white light need to be similar to that of natural white light, the multiband Eu^{3+} emissions are expected to be quite useful because of the better overlap⁶. Currently Eu^{3+} -doped luminescent materials are widely used as commercial red phosphors in lighting and displays^{7,8}, such as $\text{YVO}_4:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. However, most of the present Eu^{3+} -doped phosphors show dominant emissions corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (~593 nm) or $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (~612 nm) transition of Eu^{3+} ions. On the contrary, the intense $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (~700 nm) emission is relatively rare^{7,8}.

Gallate based oxides can act as host materials for light emitting diodes, detectors, photocatalysis, high voltage and multicolor

phosphors^{9,10}. The calcium gallate $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ belongs to the melilite family and has been much investigated as solid-state laser^{11,12}. Very recently, the first study about rare-earth (Eu^{2+} , Tb^{3+} and Ce^{3+}) doped $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ powder and its photoluminescence for WLEDs has been published¹³. However, till now no investigation has been reported about the luminescence properties of Eu^{3+} -doped $\text{Ca}_2\text{Ga}_2\text{SiO}_7$. Thus, this paper presents the analysis of luminescence properties of Eu^{3+} -doped $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ with intense $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (~610 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (~700 nm) emissions.

Figure 1. Room-temperature powder XRD patterns of the samples $\text{Ca}_2\text{Ga}_2\text{SiO}_7 : x\% \text{Eu}^{3+}$ (with $x = 0, 1, 2, 3, 4$ and 5%).

The compound $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ belongs to the melilite family with the space group $P-42_1m$ ($n^\circ. 113$, $a = 7.793 \text{ \AA}$, $c = 5.132 \text{ \AA}$ ¹⁴). This structure is built upon a regular tetrahedral site fully occupied by Ga^{3+} and a much distorted tetrahedral site where Si^{4+} and Ga^{3+} are randomly distributed. In this framework, the Ca^{2+} cations are located in an eightfold coordinated site called a Thomson cube. According to the results presented in **Fig. 1**, all the obtained samples crystallized in the melilite (ICSD file 027428). When the dopant concentration exceeds 5%, a detailed analysis of the patterns showed very weak diffraction peaks at 31.8° or 32.1° , which indicates the appearance of an unidentified impurity phase. Because of similar ionic radii in an eightfold coordination, the Eu^{3+} ions ($r = 1.066 \text{ \AA}$ ¹⁵) are expected to substitute Ca^{2+} ($r = 1.12 \text{ \AA}$ ¹⁵). Replacing divalent calcium ion by trivalent europium ion necessitates balancing the extra positive charge. It may easily

occur by mean of Ca-vacancies formation or incorporation of interstitial O^{2-} ions (one per two Eu^{3+} ions). In our case, we considered the formation of cationic vacancies by using the formal composition $Ca_{2-3x/2}Eu_xGa_2SiO_7$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$).

Absorption properties of the non doped host lattice were investigated to determine the optical band gap. Diffuse reflectance was recorded in finely ground sample and the band gap can be estimated according to the expression proposed by Tauc, Davis and Mott¹⁶:

$$[F(R_\infty)hv]^{1/n} = A(hv - E_g)$$

where A is a proportional constant, E_g is the optical band gap, hv is the photon energy in eV, the exponent n denotes the nature of the transition (in our case, we will consider a direct allowed transition, thus $n = 1/2$), and $F(R_\infty)$ is Kubelka-Munk function which can be defined as $F(R_\infty) = (1-R)/2R$ where R is the reflectance at the given wavelength. The $[F(R_\infty)hv]^2$ was plotted as function of hv and was reported in **Fig 2**. The optical band gap E_g was determined from the value associated with the intersection point of the line tangent to the plotted curve inflection point on the horizontal axis ($hv = 0$). As a result, the band gap of the non doped $Ca_2Ga_2SiO_7$ host lattice is equal to 5.37 eV.

Figure 2. Plot of $[F(R_\infty)hv]^2$ versus hv for the non doped $Ca_2Ga_2SiO_7$.

Figure 3. Density of states of the non doped $Ca_2Ga_2SiO_7$ compound.

DFT calculations were performed on the non doped $Ca_2Ga_2SiO_7$ to estimate the band gap using the VASP package. After optimization^{17,18,19}, cell parameters appear to be in a good agreement with respect to experimental ones. Indeed, the a and b optimized lattice parameters are computed around 7.90 Å whereas

it is 7.79 Å experimentally. Also, the c parameter is computed at 5.21 Å vs. 5.13 Å in the crystal. Based on these grounds, we now consider the electronic structure (DOS) of the compound. As expected, the Valence Band (VB) is mainly built upon O(2p) orbitals (**Fig. 3 + ESI**). One should notice that the Ga contribution is non-negligible in this region and especially, at the top of the VB, the “d” contribution is growing whereas the “s” and “p” are decreasing. The bottom of the Conduction Band (CB) is mainly localized on “d” orbitals of calcium. It allows us to assess that the charge transfer is from O(2p) to Ca(d) and Ga(s) orbitals. Finally, the gap (~ 3.4 eV) is underestimated at this level of accuracy (GGA). An additional test computation using the HSE²⁰ functional together with a $3 \times 3 \times 4$ k-mesh (25 % Hartree-Fock of exact exchange, a range-separation parameter equal to 0.2) tends to fit more accurately the observed gap (≈ 5 eV vs. 5.3 eV experimentally).

Figure 4. Excitation spectrum monitored at $\lambda_{em} = 616$ nm (blue) and emission spectrum monitored at $\lambda_{exc} = 393$ nm (red) of $Ca_2Ga_2SiO_7: 5\% Eu^{3+}$ at room temperature.

The photoluminescence excitation (PLE) and emission spectra of $Ca_2Ga_2SiO_7: 5\% Eu^{3+}$ are shown in **Fig. 4**. The excitation spectrum of gallosilicate shows a broad band at around 267 nm which is due to the charge transfer states (CTS) caused by the transfer of electron from oxygen 2p to the empty 4f orbital of Eu^{3+} . In addition, the PLE spectrum gets several sharp lines, which are due to the intra-configurational f-f transitions of Eu^{3+} , i.e., ${}^7F_0 \rightarrow {}^5D_2$ (464 nm), ${}^7F_0 \rightarrow {}^5D_3$ (413 nm), ${}^7F_0 \rightarrow {}^5L_6$ (393 nm) and ${}^7F_0 \rightarrow {}^5D_4$ (361 nm). Obviously, the most efficient excitation peak is the one originated from ${}^7F_0 \rightarrow {}^5L_6$ transition (393 nm) which means that this phosphor can be effectively excited by UV LED chip (around 400 nm). The emission spectra of Eu^{3+} activated $Ca_2Ga_2SiO_7$ consists in a multi-band emission at about 585, 597, 617, 650 and 700 nm which is assigned to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) transitions of Eu^{3+} ions, respectively. Among these emission peaks, the two most intense lines are the emissions located at 613 and 700 nm (red region) from ${}^5D_0 \rightarrow {}^7F_4$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions. It is well-known that ${}^5D_0 \rightarrow {}^7F_{0,1}$ transition is directed by selection rules for intermediate magnetic-dipole coupling $\Delta J = 0, \pm 1$, and the ${}^5D_0 \rightarrow {}^7F_{2,4,6}$ are allowed electric-dipole transitions. Generally, when the Eu^{3+} ion occupies a crystallographic site with inversion symmetry, its magnetic-dipole transition ${}^5D_0 \rightarrow {}^7F_1$ orange emission dominates in the emission spectrum, while the electric-dipole transitions ${}^5D_0 \rightarrow {}^7F_{2,4}$ red emission if the Eu^{3+} ion is located at a non-inversion center^{7,10}. The intense emissions of ${}^5D_0 \rightarrow {}^7F_{2,4}$ (617 and 700 nm) transitions in **Fig. 4** indicate that the Eu^{3+} ions in $Ca_2Ga_2SiO_7$ host occupy a site with non-inversion symmetry which is coherent with the melilite

structure. Furthermore, the presence of unique emission line at 576 nm ($^3D_0 \rightarrow ^7F_2$ transition) indicates that Eu^{3+} occupies only one site in the lattice, namely the Ca^{2+} site of the investigated host lattice.

The evolution of the photoluminescence properties with the doping rate is depicted in **Fig. 5** for the phosphors $\text{Ca}_2\text{Ga}_2\text{SiO}_7$: x% Eu^{3+} (with x = 1, 2, 3, 4 and 5%) monitored at 393 nm. The emission intensity increases gradually with the doping rate without getting any concentration quenching. Consequently, the one parameter that prevents to increase the doping rate to enhance emission intensity is the solubility limit of Eu^{3+} in the host lattice because over 5% of Eu^{3+} ions, a unidentified secondary phase appears on XRD pattern.

Figure 5. Emission spectra monitored at 393 nm of $\text{Ca}_2\text{Ga}_2\text{SiO}_7$: x% Eu^{3+} (with x = 1, 2, 3, 4 and 5%) at room temperature. Inset: The CIE chromaticity diagram for sample $\text{Ca}_{2-3x/2}\text{Eu}_x\text{Ga}_2\text{SiO}_7$ (x = 0.1) excited at 393 nm.

The Commission Internationale de l'Eclairage (CIE 1931) chromaticity diagram was depicted in **Fig. 5** for the $\text{Ca}_2\text{Ga}_2\text{SiO}_7$: 5% Eu^{3+} phosphor excited at 393 nm. For all samples, the color coordinates (x,y) are located in the red region. Referring to the National Television System Committee (NTSC illuminant red = (0.67;0.33))²¹, the 5%-doped gallium melilite exhibit well comparable pure red CIE color coordinate (0.639, 0.358) which is due to the huge emission intensity of the $^5D_0 \rightarrow ^7F_{2,4}$ transitions.

Trivalent europium-doped $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ phosphors were successfully synthesized via solid-state route. Taking into account the charge balance, two Eu^{3+} ions substitute three Ca^{2+} ions in the samples. In these conditions, the maximal solubility limit is equal to 5% molar. The phosphors show intense emission peaks at 617 and 700 nm from the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions of Eu^{3+} . The dominant emission at 700 nm results in deep red-emission with CIE chromaticity coordinates of (0.637, 0.358). Hence, $\text{Ca}_{2-3x/2}\text{Eu}_x\text{Ga}_2\text{SiO}_7$ (x = 0.1) can be a potential candidate for red LEDs phosphor due to its high luminescence efficiency under UV irradiation and its high color purity.

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Author Contributions

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Notes

The authors declare no competing financial interests.

REFERENCES

- [1] Meyer, J.; Tappe, F. *Adv. Opt. Mater.* **2015**, *3*, 424-430.
- [2] Jüstel, T.; Nikol, H.; Ronda, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3084-3103.
- [3] Liu, Y.F.; Zhang, X.; Hao, Z.D.; Wang, X.J.; Zhang, J.H. *J. Mater. Chem.* **2011**, *21*, 6354-6358.
- [4] Annadurai, G.; Masilla Moses Kennedy, S. *J. Lum.* **2016**, *169*, 690-694.
- [5] Zhu, H.; Fang, M.; Huang, Z.; Liu, Y.; Chen, K.; Min, X.; Mao, Y.; Wang, M. *J. Lum.* **2016**, *172*, 180-184.
- [6] Saradhi, M. P.; Raveau, B.; Caignaert, V.; Varadaraju, U. V. *J. Solid State Chem.* **2010**, *183*, 485-490.
- [7] Xie, M.; Li, Y.; Li, R. *J. Lum.* **2013**, *136*, 303-306.
- [8] Skaudzius, R.; Katelnikovas, A.; Ensling, D.; Kareiva, A.; Jüstel, T. *J. Lum.* **2014**, *147*, 290-294.
- [9] Pulchalska, M.; Zych, E. *J. Lum.* **2012**, *132*, 2879-2884.
- [10] Jia, P.Y.; Lin, J.; Yu, M. *Mater. Res. Bull.* **2007**, *42*, 1556-1564.
- [11] Merkle, L. D.; Allik, T. H.; Chai, B. H. T. *Opt. Mater.* **1992**, *1*, 91-100.
- [12] Kaminski, A. A.; Verdun, H. R.; Mill, B. V. *Physica Status Solidi A : Applied Research* **1992**, *129*, K125-K130.
- [13] Jiao, M.; Lv, W.; Lü, W.; Zhao, Q.; Shao, B.; You, H. *ChemPhysChem.* **2015**, *16*, 817-824.
- [14] Kaminskii A. A.; Belokoneva, E. L.; Mill, B. V.; Sarkisov, S. E.; Kurbanov, K. *Phys. Status Solidi A* **1986**, *97*, 279-290.
- [15] R. D. Shannon, *Acta. Cryst.* A32 (1976)
- [16] a) J. Tauc, R. Grigorovici, A. Vancu, *Physica Status Solidi* 15 (1966) 627-637. b) E.A. Davis, N.F. Mott, *Philos. Mag* (1970) 22903.
- [17] Kresse, G.; Joubert, D. *Phys. Rev. B.* 1999, *59*, 1758-1775.
- [18] Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15-50.
- [19] Kresse, G.; Furthmüller, J. *Phys. Rev. B.* **1996**, *54* 11169-11186.
- [20] Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118* 8207-8215.
- [21] Dalal, M.; Taxak, B. V.; Iohra, S.; Sangwan, D.; Khatkar, S.P. *J. Lum.* **2015**, *161*, 63-70.

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Eu^{3+} -doped $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ red phosphors were successfully synthesized by solid-state reaction. In the melilite structure, Eu^{3+} ions are located in a noncentrosymmetric site, which leads to intense emission peaks at 617 and 700 nm arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions of Eu^{3+} . Moreover, the abnormally dominant emission at 700 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) results in deep red-emission with CIE chromaticity coordinates of (0.637, 0.358).