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The Self-activated Luminescence Properties of Blue-emitting $Sr_9Ga(PO_4)_7$

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The photoluminescence excitation and emission spectra of $Sr_9Ga(PO_4)_7$ were investigated. This phosphor can be efficiently excited by VUV–UV light and X-ray irradiation and presents bright blue luminescence. The excitation and emission spectra of $Sr_9Ga(PO_4)_7$ were compared with those of $ZnGa_2O_4$ and Eu^{2+}-doped (10 mol %) $BaMgAl_{10}O_{17}$. Under the same conditions, the light yield of X-ray excited luminescence of $Sr_9Ga(PO_4)_7$ is about 57% as large as that of scintillation crystal $Bi_4Ge_3O_{12}$. The luminescence is suggested to be from the self-activation center of the octahedral Ga–O groups in the $Sr_9Ga(PO_4)_7$ lattices.

The structure and application of β-$Ca_3(PO_4)_2$-related compounds have been extensively studied.[1,2] Ca-containing compounds $Ca_9M(PO_4)_7$ (M = Y, La–Lu, Bi, Fe, In, and Ga) are isotypic with β-$Ca_3(PO_4)_2$ (space group $R3c$).[3] These materials have been investigated for ferroelectric, catalytic, two-stage hydrogen oxidation, nonlinear-optical, and ion-conductive materials.[4] In recent years, the luminescence of rare earth (RE) or transition metal (Mn^{2+})-doped $Ca_9M(PO_4)_7$ have been also paid great attention as efficient phosphors for the applications in white light-emitting diodes.[5]

Sr-containing phosphates with formula of $Sr_9M(PO_4)_7$ have a structure closely related to β-$Ca_3(PO_4)_2$,[6,7] which depends on the kinds of M cations. For example, $Sr_{9+y}M_{1.52-y}(PO_4)_7$ (M = Mn, Fe, Co, Ni, and Cu)[8,9] has space group $R\bar{3}m$; however, $Sr_9M'(PO_4)_7$ (M′ = Sc, Cr, Ga, and In)[6] shows centrosymmetric or monoclinically distorted β-$Ca_3(PO_4)_2$-type structure (space group $I2/a$).

$Sr_9M'(PO_4)_7$ (M′ = Sc, Cr, Ga, and In) compounds have been paid great attention for structural studies and applications because the lattice contains the cations with highly disordered arrangements.[6,9] Different from the Ca compounds $Ca_9M(PO_4)_7$ with ferroelectric phase transition, the analogous strontium phosphates $Sr_9M(PO_4)_7$ possess antiferroelectric phase transition.[3] No second-harmonic generation (SHG) responses confirm that they are centrosymmetric.[6]

In this letter, the synthesis and the self-activated luminescence of $Sr_9Ga(PO_4)_7$ were reported. The photoluminescence excitation spectra were investigated in VUV–UV range excitation. The luminescence properties were investigated under UV and X-ray excitation. $Sr_9Ga(PO_4)_7$ presents bright blue luminescence, which was compared with a well-known scintillating crystal $Bi_4Ge_3O_{12}$. The luminescence mechanism was suggested on the basis of the luminescence properties and crystal structure.

$Sr_9Ga(PO_4)_7$ (SGP) was synthesized by a conventional solid-state reaction. The starting material was a stoichiometric mixture of $SrCO_3$ (Aldrich, 99.99%), $(NH_4)_2HPO_4$ (Aldrich, 99%), and Ga_2O_3 (Aldrich, 99.99%). First, the mixture was heated at 350 °C for 10 h. Then the powder obtained was thoroughly mixed and heated up to 850 °C for 5 h. After that, the sample was heated at 1050 °C in air for 10 h. The Mn^{2+}-doped compound was prepared by adding 5 mol % $MnCO_3$ (Aldrich, 99.99%) to $SrCO_3$ in the mixture and sintering in a reducing atmosphere at 1050 °C for 10 h. For a comparison the blue-emitting phosphors of $ZnGa_2O_4$ (ZGO) and Eu^{2+}-doped (10 mol %) $BaMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$) were also prepared. ZGO was heated in atmospheric air at 1300 °C. $BAM:Eu^{2+}$ was prepared in an reducing atmosphere at 1400 °C.

XRD data were collected on a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry using Cu Kα radiation ($\lambda = 1.5405$ Å). The UV-excited luminescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer with Monk–Gillieson type monochromators.

The VUV excitation spectra were measured at the VUV spectroscopy station at the Beijing Synchrotron Radiation Facility of the Institute of High Energy Physics. A 1 m Seya–Namioka monochromator and an Acton Spectra-308 monochromator were used for the measurement of excitation and emission spectra. The signal was detected by a Hamamatsu H5920-01 photon counter. The pressure of the sample chamber was lower than 1×10^{-3} Pa. The X-ray excited luminescence (XEL) spectra were measured by using an X-ray-excited spectrometer, FluorMain, where an F-30 movable X-ray tube (W anticathode target) was used as the X-ray source.

Figure 1a shows the X-ray powder diffraction patterns of $Sr_9Ga(PO_4)_7$. The sample shows the pure phase. The XRD peaks on the pattern are indexed according to the PDF2 card number No. 53-0180 ($Sr_9Ga(PO_4)_7$) in the International Centre for Diffraction Data (ICDD) database. The sharp peaks in each XRD pattern indicate good crystallizability of the sample.

Figure 1b shows the schematic views of $Sr_9Ga(PO_4)_7$ structure with double cell along [100] direction. $Sr_9Ga(PO_4)_7$ is structurally related to β-$Ca_3(PO_4)_2$ with a type of monoclinic superstructure (space group $I2/a$). In β-$Ca_3(PO_4)_2$ structure, Ca^{2+} ions are distributed between five crystallographic sites, four of them Ca(1), Ca(2), Ca(3), and Ca(5) are completely filled, the Ca(4) site is only half-occupied. The stability of a structure with half-occupied Ca(4) position makes it possible to assume the existence of a crystal structure, where Ca(4) is fully occupied or completely empty.

In $Sr_9Ga(PO_4)_7$, (Sr1, Sr2, Sr3), (Sr4, Sr5), Sr6, and Ga sites correspond to the (Ca1, Ca2), Ca3, (Ca4, Ca6), and Ca5 sites in β-$Ca_3(PO_4)_2$, respectively. And Sr6 is vacant. The asymmetric unit contains five Sr, one Ga, four P, and 14 O sites. Sr^{2+} ions are coordinated to either eight or nine oxide ions. Ga^{3+} ions occupy an octahedral site surrounded by Sr1, Sr2, Sr3, and P.[6] The isolated GaO_6 octahedrons are arranged in one-dimensional [100] direction, which are separated from one another by infinite chains of strontium cations located in a distorted environment.

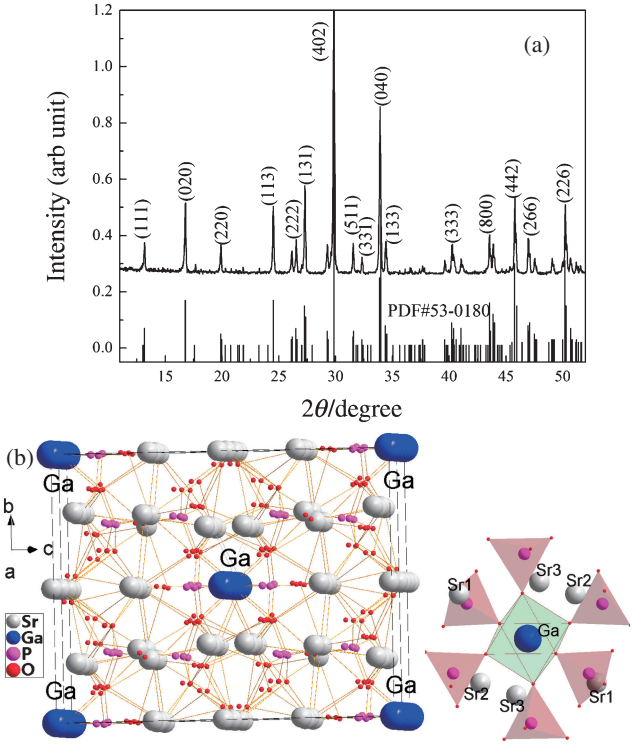

Figure 1. (a) XRD pattern of $Sr_9Ga(PO_4)_7$ compared with the corresponding standard JCPDs cards No. 53-0180. (b) The schematic views of the structures along [100] direction.

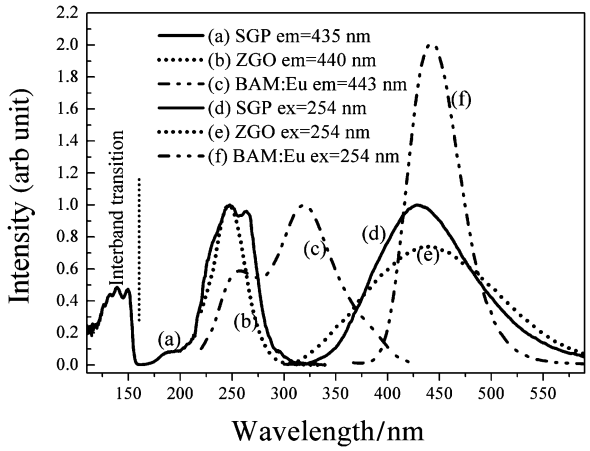

Figure 2. The normalized excitation spectra of SGP (a), ZGO (b), and BAM:Eu^{2+} (c); and the absolute emission spectra of SGP (d), ZGO (e), and BAM:Eu^{2+} (f) measured under the same conditions. For the excitation spectrum of SGP the synchrotron radiation VUV light was used for 110–300 nm, and Xe lamp was used for longer wavelengths.

Figure 2 presents the photoluminescence excitation (a) and emission (d) spectra of $Sr_9Ga(PO_4)_7$. The excitation spectrum by monitoring at 435 nm consists of two separated absorption bands centered at 145 and 254 nm. The high-energy band 145 nm is assigned as the host bands, viz., the transition from valence band to conduction band or the absorption due to near exaction in the host. The onset of absorption at about 152 nm implies that the band gap of $Sr_9Ga(PO_4)_7$ is about 8.16 eV, which is very similar to the value of the absorption edge of $[PO_4]^{3-}$ molecule. Under the excitation of 145 nm the emission spectrum keeps the same profile as that under the 254-nm excitation as shown in Figure 2.

The excitation and emission spectra of SGP were compared with those of the well-known blue-emitting phosphors ZGO and BAM:Eu^{2+} as shown in Figure 2. SGP and ZGO have similar profile of excitation spectra. BAM:Eu^{2+} shows the main excitation at 254 and 330 nm bands attributed to 4f–5d transition of Eu^{2+} ions.

The emission spectrum excited by 254 nm shows bright blue luminescence with the maximum wavelength at 435 nm (Figure 2d). The ZGO sample shows a strong broad blue luminescence with a peak at 440 nm (Figure 2e) resulting from the self-activated transition of regular O_h Ga–O groups.[10] On the emission spectrum of BAM:Eu^{2+}, one emission band peaking at 420 nm (Figure 2f) is observed from the $4f^65d \rightarrow 4f^7$ ($^8S_{7/2}$) transitions in Eu^{2+} ions. The ratio of luminescence intensity of SGP to those of ZGO and BAM:Eu^{2+} is 1:0.95:1.31. The CIE (Commission International de l'Eclairage 1931) coordinate of $Sr_9Ga(PO_4)_7$ was calculated to be ($x = 0.193$, $y = 0.218$) in the blue region.

Usually, the photoluminescence in self-activated, non-lanthanoid oxides often come from the delocalization of electrons in various defect levels or energy states lying within the band gap of the materials. Bharathy et al.[11,12] also suggested another mechanism in the photoluminescence investigation of Sr_3NaMO_6 and $Sr_3Li_6M_2O_{11}$ (M = Nb and Ta). It has been suggested that upon an excitation of 250 nm, an electron is promoted from the valence band or HOMO (a large highest occupied molecular orbital) to the conduction band or LUMO (a lowest unoccupied molecular orbital). There is a nonradiative transfer from the LUMO + n energy state to an intermediate low lying LUMO state. A radiative transfer from this intermediate state to the valence band gives rise to the emission.[11,12]

As a self-activated blue emitting phosphor, the excitation and emission spectra of $ZnGa_2O_4$ are well known, i.e., there is a broad excitation band with the maximum at 254 nm and the blue luminescence band centered at 432 nm.[10] It has been concluded that the excitation and fluorescence bands in $ZnGa_2O_4$ are originated from self-activation center of the octahedral Ga–O groups.[10]

As the present results in $Sr_9Ga(PO_4)_7$, the self-activated excitation and emission band, and the crystallographic surroundings of Ga^{3+} ions in the lattices are very similar to those in the reported $ZnGa_2O_4$ phosphor. Meanwhile, no luminescence could be detected in $Sr_9M(PO_4)_7$ (M = Sc, Cr, Fe, and In) in this experiment. Consequentially, it could be suggested that the absorption band at 254 nm and the fluorescence at 432 nm in $Sr_9Ga(PO_4)_7$ are from the self-activation center of the octahedral Ga–O groups in the lattices. Certainly, the lattice defects might play an important role on the luminescent performance of $Sr_9Ga(PO_4)_7$ because the formations of lattice defects such as, oxygen vacancies, cation vacancies, excitons, etc., are possible to be created in the solid-state reaction at high temperature. Further work on illuminating the detailed luminescence mechanism of $Sr_9Ga(PO_4)_7$ is needed and now underway.

Figure 3 shows the XEL spectra of $Bi_4Ge_3O_{12}$, $Sr_9Ga(PO_4)_7$, and $Sr_9Ga(PO_4)_7$:Mn^{2+} 5 mol % under the same conditions. By comprising the integral emission intensities, the light

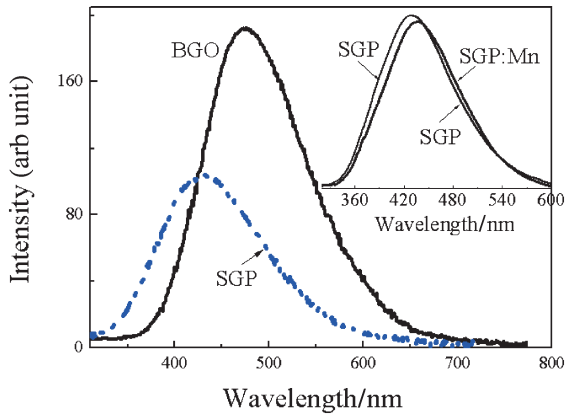

Figure 3. The X-ray excited luminescence spectra of $Bi_4Ge_3O_{12}$ (BGO), $Sr_9Ga(PO_4)_7$ (SGP), and SGP:Mn^{2+} 5 mol % (inset) powders measured under the same conditions.

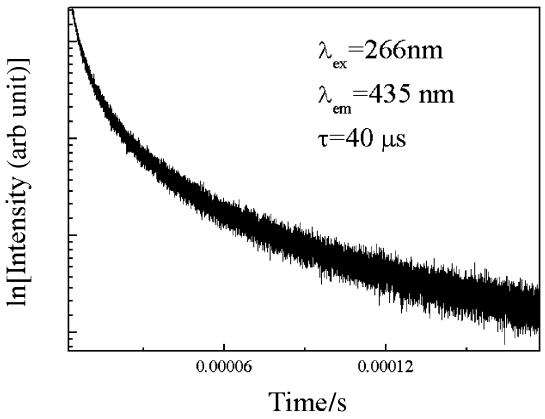

Figure 4. The luminescence decay curve of 435 nm in $Sr_9Ga(PO_4)_7$ under the excitation of 266 nm laser at 300 K.

yield of $Sr_9Ga(PO_4)_7$ is about 57%, as large as that of $Bi_4Ge_3O_{12}$ powders. Duan et al. have reported that the light yields of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, and α-$YBa_3(BO_3)_3$ powders are about 15%, 50%, and 50%, as large as that of $Bi_4Ge_3O_{12}$ powders.[13] The results in our experiments indicate that $Sr_9Ga(PO_4)_7$ could be considered as an effective potential XEL material or scintillator.

It is interesting to note that no obvious Mn^{2+} emission was observed in SGP:Mn^{2+} except for the small decrease of intensity (95.3% of pure SGP) and red shift of the spectra (Figure 3). This is different from the commonly reported results in Mn^{2+}-doped self-activated phosphors. For example, the red (655 nm from Mn^{2+}) and green (530 nm from self-activated luminescence) can be observed in the emission plectra of Mn^{2+}-doped $ZnGa_2O_4$ (excitation under 254 nm).[10]

Figure 4 shows the decay curve of $Sr_9Ga(PO_4)_7$ under the excitation of 266-nm laser at 300 K. The emission shows a nonexponential decay, which can be fitted by the equation:

$$\tau_{ave} = \frac{\int_{-\infty}^{\infty} tI(t)dt}{\int_{-\infty}^{\infty} I(t)dt} \quad (1)$$

where $I(t)$ is the luminescence intensity, t is the time. By fitting the curves in eq 1, the average decay time of $Sr_9Ga(PO_4)_7$ is calculated to be about 40 μs.

$Sr_9Ga(PO_4)_7$ was prepared by conventional solid-state reaction. The excitation spectrum shows two separated absorption bands centered at 145 and 254 nm. The band gap energy of $Sr_9Ga(PO_4)_7$ is about 8.16 eV. Under the excitation of UV light, $Sr_9Ga(PO_4)_7$ shows bright blue luminescence (peaked at 435 nm) with CIE coordinates of ($x = 0.193$, $y = 0.218$) and the luminescence lifetimes of 40 μs. $Sr_9Ga(PO_4)_7$ can be also efficiently excited by X-ray. The light yield of $Sr_9Ga(PO_4)_7$ is about 57%, as large as that of $Bi_4Ge_3O_{12}$ powders. $Sr_9Ga(PO_4)_7$ could be as an effective potential XEL material or scintillator. The luminescence mechanism of $Sr_9Ga(PO_4)_7$ can be assigned to the self-activation center of the octahedral Ga–O groups in the lattices.

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