

Intense White Luminescence from Combustion Synthesized $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: $\text{Yb}^{3+}/\text{Yb}^{2+}$ Single Phase Phosphor

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Abstract The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: $\text{Yb}^{3+}/\text{Yb}^{2+}$ single phase nano-phosphor has been synthesized through combustion route and its luminescence and lifetime studies have been carried out up to 20 K using 976 and 266 nm excitations. The samples heated in open atmosphere have shown the presence of Yb in Yb^{3+} and Yb^{2+} states. The 976 nm excitation results a cooperative upconversion emission at 486 nm due to the Yb^{3+} state and a broad band in the blue region and has been assigned to arise from the defect centers. The 266 nm excitation on the other hand results a broad emission band even from as-synthesized phosphor without doping of Yb, the width of which increases in presence of Yb due to the emission from Yb^{2+} ions formed in heated samples. The white emission covers almost whole visible region with bandwidth 190 nm. The ions in Yb^{2+} state has been found to increase with the increase in heating temperature up to 1,273 K. A back conversion of Yb^{2+} to Yb^{3+} has been observed for higher temperatures. Effect of boric and phosphoric acids as flux on the emission properties of Yb^{3+} and Yb^{2+} states have been examined and discussed. Quantum yield of emission has also been determined for different samples.

Keywords Nano-phosphor · Combustion route · Cooperative upconversion · Heat treatment · Fluxes

Introduction

Rare earth ions have been widely employed as luminescent ions, activators and sensitizers in phosphor materials for applications in fluorescent lamps, X-ray intensifying screens, cathode ray tubes etc. The upconverted luminescence from rare earth ions has also been investigated extensively because of their wide range of applications [1–3]. In recent years, phosphors have attracted attention of researchers due to their novel optical, electrical and electronic properties [4, 5, and references there in].

Solid state reaction processes have been commonly used for synthesis of phosphor materials, but these processes often results in poor homogeneity and require high heating temperatures. Moreover, the grain size of the phosphor materials prepared through this process is large in size (several tens of micrometers). Phosphors of smaller grain size are then obtained by grinding. This often introduces additional defects in the sample. The net result of this is the greatly reduced luminescence efficiency [6]. Several other chemical synthesis techniques, such as coprecipitation [7], sol-gel [8, 9], microwave [10], Pechini [11] and combustion [12–14] have been developed. All these methods use liquid phase and therefore the different components are accurately controlled and uniformly mixed.

Calcium aluminate is an important cement material and a number of studies related to mechanical and chemical stability, phase and crystal structure are reported in literature [15, 16]. The use of calcium aluminates in the preparation of luminescent materials though in past has been rare, but has become more frequent during the last 2 years. Recently we have prepared $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase phosphor of this material by combustion method [17]. The existence of several phases of calcium aluminate has added to the confusion and debate [18, 19]. One needs a zeolite

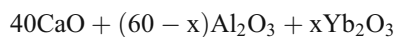
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form, in which oxide ions (O^{2-}) are trapped in a Ca–Al–O cage which is well known as an oxygen ion conductor [20]. The chemical formula of the unit cell of $Ca_{12}Al_{14}O_{33}$ phase is $[Ca_{24}Al_{28}O_{64}]^{4+} + 2O^{2-}$ that contains two free oxygen ions. These free oxygen ions are responsible for photoinduced conductivity and several other properties [21]. Though some physical and optical properties of this phase of Ca–Al–O has been studied in our previous work [17], however several other interesting properties of this crystal phase have to be dug out still especially, the optical properties of this phase with doping of rare earth ions. However, the synthesis of single phase $Ca_{12}Al_{14}O_{33}$ is difficult since it needs a very typical composition of CaO and Al_2O_3 .

Ytterbium is an important rare earth which can be used as luminescence centre as well as sensitizer. Investigations about Yb doped materials revealed the potential applications since Yb^{3+} gives laser emission in the near infrared region (920–1,060 nm) as well as very narrow and bright visible emission around 486 nm due to cooperative emission [22]. In general, Yb reside in the 3+ valence state, but in several crystal systems like calcium aluminates Yb stabilizes in 2+ valence state also. The broad emission from Yb^{2+} centres occur in blue green region due to the $4f5d \rightarrow 4f$ transition. Contrary to transitions within the levels of 4f configuration of the lanthanides, the $4f5d \rightarrow 4f$ transitions are sensitive to the nature of the host. For a particular concentration of Yb and heating temperature it gives intense broad white emission covering whole visible region. The aim of present work is to study fluorescence properties of Yb^{3+}/Yb^{2+} ions in $Ca_{12}Al_{14}O_{33}$ phase phosphor doped with different concentrations of rare earth and heated at different temperatures. The effect of boric and phosphoric acids as flux on the fluorescence emission of the samples at different temperatures has also been investigated. We have also determined the quantum yield of heated and the fluxed samples.

Experimental

Samples doped with Yb_2O_3 were prepared through combustion method exactly in the same way as described in our earlier work [17]. The purity of the chemicals $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ and Yb_2O_3 used is 98, 98, and 99.99% respectively. The different compositions used were:



where $x=0-5.0$ mol%.

It was observed that fluorescence emission has maximum bandwidth (complete visible region) and highest intensity for 2 mol% concentration of Yb_2O_3 . Therefore for further studies we have used this particular composition of rare earth.

To produce crystallization in the as-synthesized foamy samples, batches were heated at different temperatures. The crystal structure and the phase purity of the samples were analyzed with the powder X-ray diffraction (XRD) measurements using $CuK\alpha$ radiation (1.5406 \AA) with nickel filter. The luminescence measurements were carried out by exciting the samples with 266 nm from pulsed Nd: YAG laser and with 976 nm from a diode laser. A closed cycle helium cryostat (Model 202S, Advanced Research Systems, USA) was used to cool the sample to 20 K. An iHR320, Horiba Jobin Yuon, spectrometer was used to disperse and detect the signal.

Results and discussion

Structural characterization

The phase diagram of CaO– Al_2O_3 complex has been discussed by Chatterjee and Zhmoidin [23] and it is clear from their study that $Ca_{12}Al_{14}O_{33}$ phase forms at the lowest temperature amongst the other phases of calcium aluminate. X-ray diffraction (XRD) patterns of the as-synthesized as well as samples heated for 2 h at different temperatures viz. 1,073 K, 1,273 K and 1,473 K in air are shown in Fig. 1. No apparent crystallinity is observed in the as-synthesized sample as well as samples heated at 1,073 K and seems purely amorphous in nature. However, for temperatures above

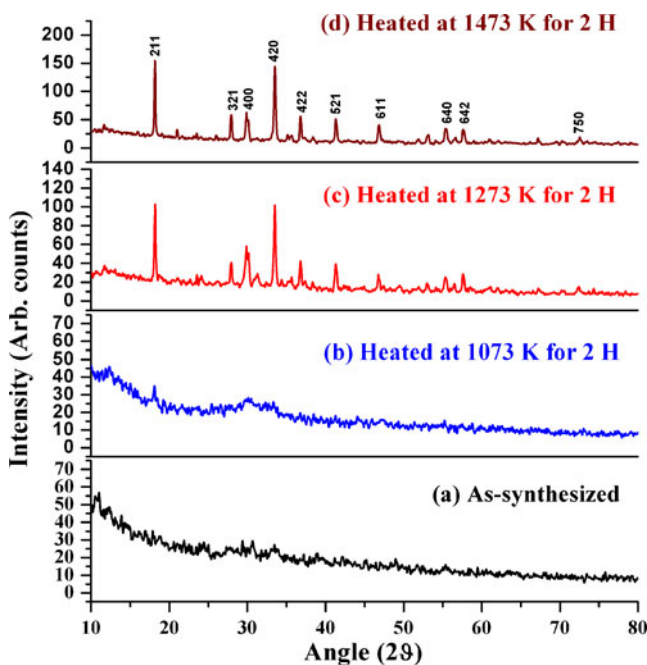


Fig. 1 X-ray diffraction pattern of $Ca_{12}Al_{14}O_{33}$: 2.0 mol% Yb^{3+} , heated at different temperatures for 2 h: **a** As-synthesized; **b** heated at 1,073 K; **c** heated at 1,273 K; **d** heated at 1,473 K

1,073 K crystalline feature starts appearing and using JCPDS data the single phase of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ has been ascertained at $\geq 1,273$ K. Doping with rare earth ions is seen to have no effect on the phase of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase is cubic with a cell parameter $a=11.982\text{\AA}$ and belongs to I43d space group. The crystallite size is determined from selecting three most intense peaks using Gaussian peak fitting and found in the 40–50 nm range. Only a small increase in crystallite size is observed on increasing the heating temperature.

Luminescence studies

Upconversion studies (by 976 nm excitation)

Under NIR excitation, the doped samples give two emission bands in the visible region, a sharp emission band at 486 nm and the other broad emission bands around 525 and 542 nm. The 486 nm emission can be easily assigned to the cooperative upconversion emission from Yb^{3+} ions. However, the appearance of the broad emission bands at 525 and 542 nm are a matter of curiosity. Figure 2 compares the upconversion spectra of the samples heated at different temperatures. The intensity of the emission bands depends on the temperature of the sample. The emission intensities of the bands initially increase with the increase in heating temperature up to 1,273 K and finally decrease with rise in temperature further, though heating at higher temperature improve the crystalline structure and eliminates quenching centers to a good extent.

The characteristic absorption of Yb^{3+} ion is associated with ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition around 976 nm. The absorp-

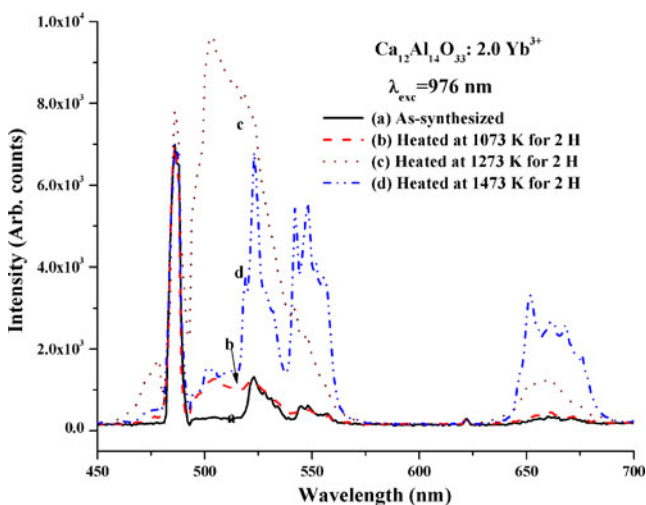


Fig. 2 Emission spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} heated at different temperatures for 2 h on excitation with 976 nm wavelength; **a** As-synthesized; **b** heated at 1,073 K; **c** heated at 1,273 K; **d** heated at 1,473 K

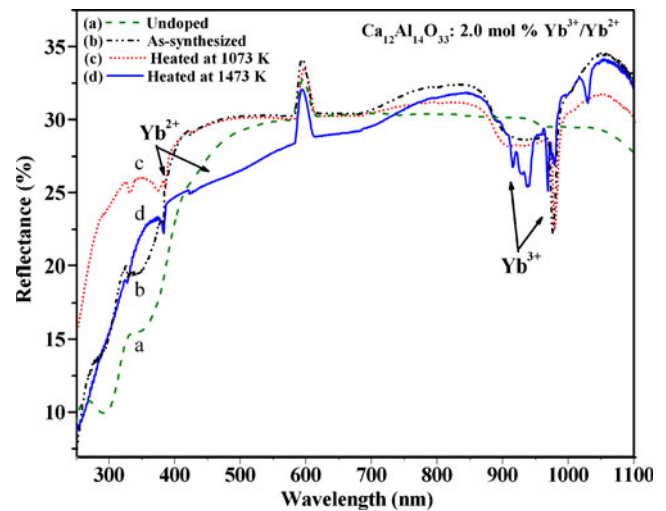
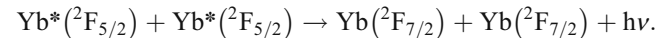


Fig. 3 Absorption spectra of sample $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} : **a** undoped; **b** As-synthesized; **c** heated at 1,073 K; **d** heated at 1,473 K

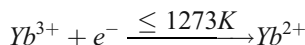
tion of 976 nm photons results an emission at 486 nm which is twice the energy of the incident photon, suggesting that it is the result of the radiative relaxation of an excited $\text{Yb}^{3+}-\text{Yb}^{3+}$ pair. Such emission band is named cooperative emission and described as:



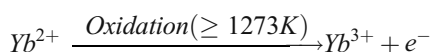
The discrete bands at 525 and 542 nm in Fig. 2 are the characteristic ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions of Er^{3+} which is due to the presence of trace impurity of Er^{3+} in the sample. This trace impurity exists in the raw material having high purity [see data sheet of Alfa Aesar, Stock no. 11192]. Similarly a weak band observed at 657 nm is due to ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ band of Er^{3+} ion. These bands result due to energy transfer from Yb^{3+} to Er^{3+} . It is interesting to note that Er^{3+} does not appear in absorption spectrum of the sample (due to its negligibly small quantity). Thus presence of traces (below absorption detection limit) of Er^{3+} in a sample can be detected by adding traces of Yb in the sample. The undoped sample gives no emission on 976 nm excitation. The intensities of Er^{3+} bands decrease as we go from room temperature to 1,273 K however it appears bright again at 1,473 K.

The observation of new broad band near 500 nm in the spectrum is interesting. There may be two possibilities behind this broad emission. One: the emission is from Yb^{2+} state of Yb and the second is that it may be from the defect centers caused by the doping of Yb^{3+} ions. To verify this we recorded the UV/Vis./NIR absorption spectra of all the four samples (see Fig. 3). Bands due to Yb^{2+} ionic state of Yb were observed clearly in sample heated at 1,273 K. The samples heated at other temperature did not show any characteristic peak due to Yb^{2+} state. Thus it appears that the as-synthesized sample contains excess of Yb^{3+} , which on

976 nm excitation transfers its energy to trace present Er^{3+} to give emission in green and red regions. As we heat the sample, a part of the Yb^{3+} is converted into Yb^{2+} . As a result of this the emission from Er^{3+} is reduced. At 1,273 K the concentration of Yb^{2+} is maximum and due to the less number of Yb^{3+} ions available for induction, the Er^{3+} emission is negligibly small and emission of Yb^{2+} is optimum. At still higher temperature (1,473 K), a part of Yb^{2+} is again converted to Yb^{3+} . The Yb^{3+} thus formed transfers energy to Er^{3+} again to give intense green and red bands. Thus Yb^{3+} and Er^{3+} are complimentary to each other. The conversion process can be stated as [24]:



But at higher temperature, Yb^{2+} ions oxidized and again convert to Yb^{3+} as:



The temperature at which the reaction rate is optimum depends on the ion and the host matrix.

A broad upconversion emission band has also been reported to arise in this wavelength region from the defect centers by previous workers [25–28]. It appears that a part of the intensity is due to Yb^{2+} and a small contribution is from defects near 500 nm. The defects in the host lattice arise when Ca^{2+} ion is replaced by a Yb^{3+} ion. The charge neutrality requires that the Yb^{3+} ion changes its valence into Yb^{2+} and a hole is created in the sample. The resulting color center may be responsible for a part of broad emission seen in the upconversion spectrum.

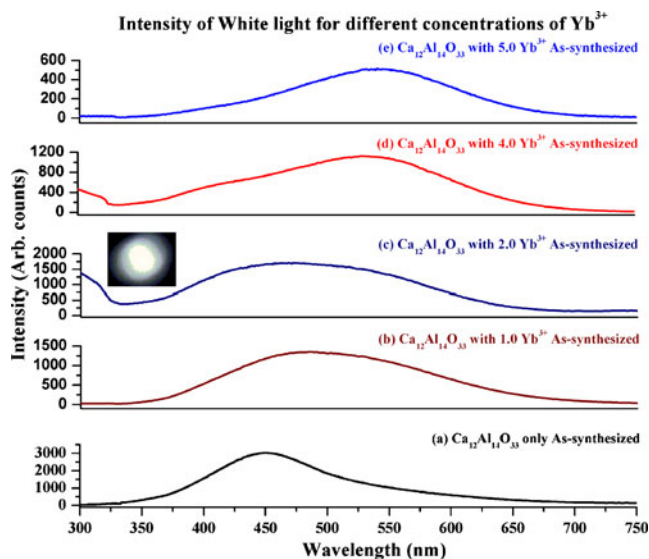


Fig. 4 Emission spectra of as-synthesized sample $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ doped with different concentrations of Yb^{3+} on 266 nm excitation, photograph of total emission of sample $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} (in inset 4c)

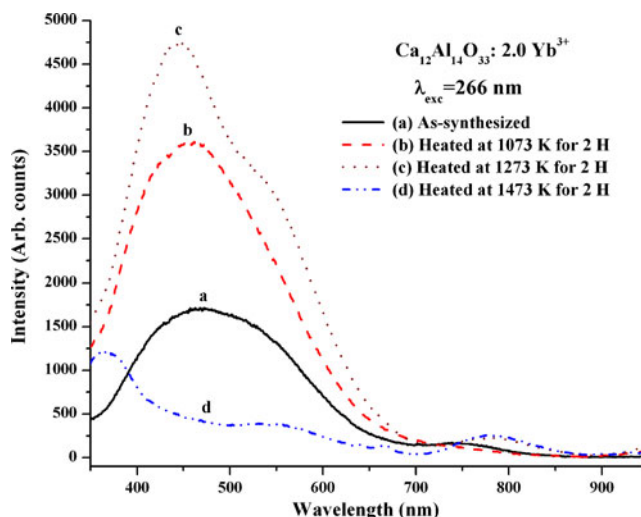


Fig. 5 Emission spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} sample heated at different temperatures for 2 h on 266 nm excitation: **a** As-synthesized; **b** heated at 1,073 K; **c** heated at 1,273 K; **d** heated at 1,473 K

Fluorescence studies with 266 nm excitation

On excitation with UV radiation, an intense broad emission is observed from the samples with and without Ytterbium. This emission is different from the emission obtained on 976 nm excitation. It emits broad emission even without Yb with its maxima near 445 nm. Figure 4 shows the effect of Yb^{3+} ion concentration on the emission intensity in as-synthesized samples. The emission broadens and covers whole visible region on addition of Yb^{3+} . The optimum emission has been observed for 2.0 mol% Yb^{3+} doped sample. It is also observed that the shape and the intensity of the emission band is dependent on the preparation conditions like temperature, time and environment. These conditions define the ratio of Yb^{3+} and Yb^{2+} ions in the prepared sample. The emission color has been found to depend on the concentration of ytterbium ions and changes from bluish white to greenish yellow as the concentration varies from zero to 5 mol%. The effect of heat treatment at different temperatures on the emission intensity has been shown in Fig. 5 for 2.0 mol% Yb^{3+} concentration. The emission intensity increases with heat treatment and is optimum at 1,273 K, similar to the situation observed in upconversion emission on 976 nm excitation. The continuum emission covers the whole visible region (380–700 nm) with the FWHM ~ 190 nm and results an intense white emission.

From the Gaussian fit of the emission band it is evident that emission structure involves superposition of two bands one centred at 445 nm and the other at 550 nm. The band at 445 nm is due to host and the one at 550 nm is due to Yb^{2+} . The two bands show different behavior with the doping

concentration of ytterbium and initially thought to arise from different levels of Yb^{2+} . Yb^{2+} is known to give (Henke et al. [29]) three overlapping emissions at 480, 500 and 570 nm in YAlO_3 matrix. These emission wavelengths of the bands are host dependent and we feel that the band at 550 nm is due to Yb^{2+} . The other band is due to host because it appears even in the absence of Yb. Also the correlation between the absorption and the emission spectra support this statement. The lifetimes of 440 and 550 nm bands are 230 and 270 μs respectively at 20 K temperature (Fig. 6) which clearly indicates that the bands arise from two different species. The decay curves at 440 and 550 nm are single exponential having no rise time. We also measured the quantum yield for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} samples as-synthesized and heated at different temperatures. These values are given in Table 1. It is also clear from this Table that the quantum yield is maximum for 2 mol% Yb^{3+} sample heated at 1,273 K.

Addition of flux (H_3BO_3 and H_3PO_4)

The effect of addition of H_3BO_3 and H_3PO_4 as fluxes has been studied on the up and downconversion emissions. It is found that these fluxes significantly affect the emission properties of the phosphor [30–36]. Figure 7a compares the upconversion spectra of the samples with and without fluxes excited with 976 nm diode laser. It is observed that addition of H_3BO_3 increases the intensity of upconversion emission band from Yb^{2+} states and suppresses the bands due to Er^{3+} . On the other hand, if we add phosphoric acid as a flux to the sample, the emission intensity of Er^{3+} bands has been found to increase with Yb^{3+} . On excitation with 266 nm radiation, the emission from sample fluxed with H_3BO_3 has again been found to increase two to three times. The H_3PO_4 on the other hand quenches the fluorescence intensity to almost zero (Fig. 7b).

A probable reason behind the increase in emission intensity on addition of H_3BO_3 is the activation energy of

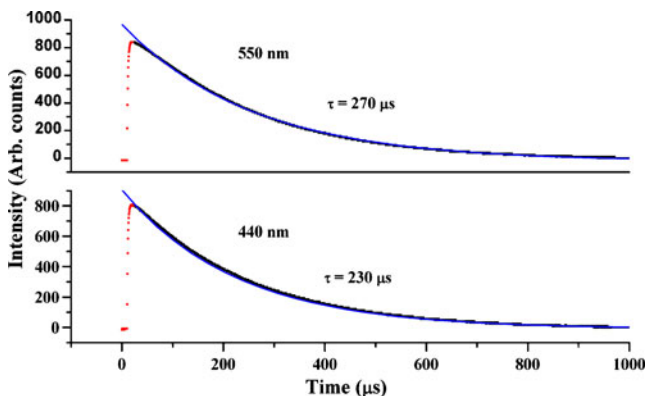


Fig. 6 The decay curve of 550 and 440 nm bands of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} on excitation with 266 nm radiation

Table 1 Quantum yield of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} phosphor sample in different conditions

Sample ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0mol% Yb^{3+})	Quantum yield (%)
1. As-synthesized	4.16
2. Heated at 1,273 K for 2 h	6.1
3. Heated at 1,273 K for 2 h with boric acid	7.8
4. Heated at 1,273 K for 2 h with phosphoric acid	1.16

Yb^{3+} to Yb^{2+} conversion. When Yb^{3+} replaces Ca^{2+} , the crystal lattice undergoes distortion and the phosphor involves the higher energy barrier in this process. But when the phosphor has been added with boric acid (H_3BO_3), B_2O_3 has higher reaction activation energy, which effectively reduces the energy barrier considerably

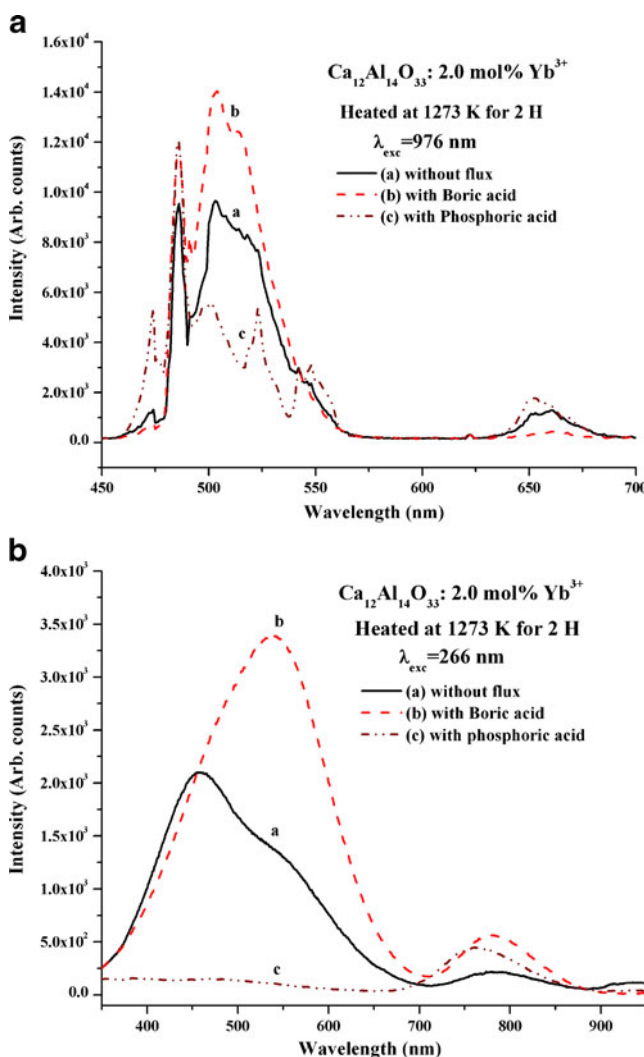


Fig. 7 Emission spectra of sample $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 2.0 mol% Yb^{3+} , with boric and phosphoric acids heated at 1,273 K for 2 h excited: **a** with 976 nm and **b** with 266 nm wavelength

and makes more Yb^{3+} ions enter into the crystal lattice. Thus the luminescent ion centers become large which results an enhancement in intensity [37]. The emission from the host in presence of Yb^{2+} covers almost whole visible region and give intense white emission.

Conclusions

The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}:\text{Yb}^{3+}/\text{Yb}^{2+}$ single phase nano-phosphor has been synthesized through combustion method. The process involves a low temperature self-propagating ignition route, which is safe, simple and rapid for the production of fine homogeneous powder. Heat treatment of the samples in air has shown the presence of Yb^{3+} and Yb^{2+} states. The 976 nm excitation has generated a cooperative upconversion emission at 486 nm due to the Yb^{3+} state and a broad upconversion band in the blue-green region from the Yb^{2+} centers. The 266 nm excitation on the other hand results intense Stokes emission from both the host and the Yb^{2+} centers. A thermo-induced conversion of Yb^{2+} state to the Yb^{3+} has also been marked at higher heating temperatures. The synthesized phase has good fluorescence and upconversion emission and is suitable for white luminescence applications.

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