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Ce^{3+} and Eu^{3+} activtated $Na_2Sr_2Al_2PO_4F_9$ nanophosphor

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ABSTRACT

A halophosphate based nanophosphor has been synthesized by wet chemical method. XRD confirms the preparation of nanophosphor and this article presents the luminescence properties of Ce^{3+} and Eu^{3+} activated $Na_2Sr_2Al_2PO_4F_9$ under UV/NUV excitation. The photoluminescence spectrum comprises of a main peak in the range 270–350 nm with a shoulder in the range 350–370 nm, which may be ascribed to transitions from 5d–4f levels of cerium in the mixed host lattice ($Na_2Sr_2Al_2PO_4F_9$). In $Na_2Sr_2Al_2PO_4F_9$: Eu^{3+} nanophosphor, orange/red luminescence under the near ultraviolet excitation of 393 nm, attributed to the transitions from $^5D_0$ excited states to $^7F_{J\ (J=0–4)}$ ground states of Eu^{3+} ions. Copyright © 2011 VBRI press.

Keywords: Nanophosphors; wet chemical synthesis; white lighting; photoluminescence.

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Introduction

Efforts have been made on finding new materials with low phonon energy in order to reduce the multiphonon non-radiative deexcitation and improve cross-sections of the RE ions, being the fluoride based matrices are the common choices. In this direction, fluorophosphate glasses have received great attention and are the subject of intense research mainly because of their wide transmission range from UV to IR regions and capability of dissolving large amount of foreign ions, such as RE ions without clustering and quenching luminescent properties [**1, 2**]. Phosphates generally show a rather short wavelength of optical absorption edge. This makes them suitable as hosts to contain active rare earth (RE) ions. Recently, we have reported some novel halophosphate based phosphors [**3-7**]. Wet chemical method is relatively cost-effective, quick and can be easily exploited to prepare phosphors with enhanced optical properties. Preparation of complex fluorides involving several constituent fluorides is still not an easy task. The constituents may have vastly differing melting points, and loss of one or more constituents during crystal growth is inevitable. In modern years, some wet chemical methods for preparation of OH^- free fluorides have been described [**8, 9**]. Recently, rare earth based materials developed for wide application due to high potential characteristics of rare earth ions [**10-14**], therefore development of spectroscopic study of these materials is new challenges in the field of inorganic materials. Here, this work is advanced to the preparation of complex fluorides involving as many as triple components with Eu^{3+}/ Ce^{3+} rare earth ions.

Experimental

For preparing the nanocrystalline complex fluorides halophosphate phosphors, the wet chemical method is used; that is, constituent chlorides with stoichiometric ratios are dissolved in double-distilled deionised water in a glass beaker (Borosil) and are evaporated then till the mixture becomes anhydrous. Use of chlorides as starting materials helps preventing the hydrolysis. The $Na_2Sr_2Al_2PO_4F_9$ phosphors were prepared by a wet chemical method. NaCl, $SrCl_2.6H_2O$, Al $(NO_3)_3.9H_2O$, $NH_4H_2PO_4$, NH_4F analar grade were taken in a stoichiometric ratio and dissolved separately in double-distilled deionised water, resulting in a solution of $Na_2Sr_2Al_2PO_4F_9$. In the present investigation, materials were prepared according to the chemical formula $Na_2Sr_{2-x}Al_2PO_4F_9:Eu_x$. Diluted HNO_3 soluble in $Eu_2O_3/(NH_4)_2Ce(NO_3)_6$ was then added to the solution to obtain $Na_2Sr_2Al_2PO_4F_9:Eu^{3+}/ Ce^{3+}$. In this formula x-value indicates the concentration of impurity in the mole%. The mixture of reagents were mixed together to obtain a homogeneous solution. The molar ratio of europium RE ion was changed in relation to $Na_2Sr_2Al_2PO_4F_9$ phosphor. The compositions of the reagents were calculated using the total oxidising and reducing valencies of the components, which served as the numerical coefficients so that the equivalent ratio is unity. It is confirmed that no undissolved constituents were left behind and all the chemicals had completely dissolved in water. The compounds $Na_2Sr_2Al_2PO_4F_9:Eu^{3+}$ in their powder form were obtained by evaporating at 120^0C for 8 hrs. The dried samples were then slowly cooled to room temperature. The resultant nanocrystalline powder was crushed to fine particles in a crucible. The powder was used in further study. This method shows the advantage in using a simple experimental procedure and chemicals that are easily available, non-toxic and easily handled at ambient conditions of humidity and pressure.

Several complementary methods were used to characterize the prepared phosphor. The prepared host lattice was characterised for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01^0, continue time 20 s, in the 2u range from 10 to 80^0. The photoluminescence (PL) measurement of excitation and emission were recorded on the Shimadzu RF5301PC Spectrofluorophotometer. The same amount of sample (2 g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

Results and discussion

As a member of orthophosphates, $Na_2Sr_2Al_2PO_4F_9$ boggildite (monoclinic) crystal structure with JCPDS file no. 01-084-0497 was first described by Hawthorne [**15**]. The **fig. 1** shows the $Na_2Sr_2Al_2PO_4F_9$ has a monoclinic crystal structure (Buchwaldite). XRD pattern for $Na_2Sr_2Al_2PO_4F_9$ phosphor is shown in **Fig. 2**. The peak positions in **Fig. 2** match well with those of the standard pattern (JCPDS 01-084-0497) for $Na_2Sr_2Al_2PO_4F_9$, which confirms that the synthesized sample is single phase. The XRD pattern did not show presence of the constituents like, NaCl, $SrCl_2.6H_2O$, Al $(NO_3)_3.9H_2O$, $NH_4H_2PO_4$ or NH_4F and other likely phases which is an indirect evidence for the formation of the desired compound. These results show that the final product was formed in nanocrystalline and homogeneous form. No differences in the XRD patterns were observed when phosphors were doped with different amounts of Ce^{3+} and Eu^{3+}. The average structural unit distance was estimated from the full width at half maximum of the diffraction peak by the Scherrer equation [**16**]:

$$D = k\lambda/\beta \cos\theta \quad \text{--------} \ (1)$$

where D is the mean crystallite diameter, k (0.89) is the Scherrer constant, λ is the X-ray wavelength (1.5406 Å), and β is the full width half maximum (FWHM) of $Na_2Sr_2Al_2PO_4F_9$ diffraction peak (0.0041 Å). The average crystallite size calculated using the most intense reflection at 2θ=32.74° is 35.26 nm.

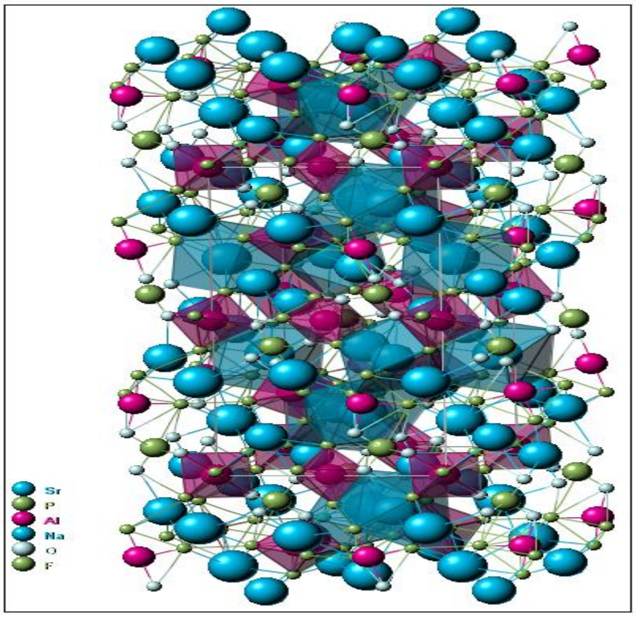

Fig. 1. Boggildite crystal structure of $Na_2Sr_2Al_2PO_4F_9$ [**15**].

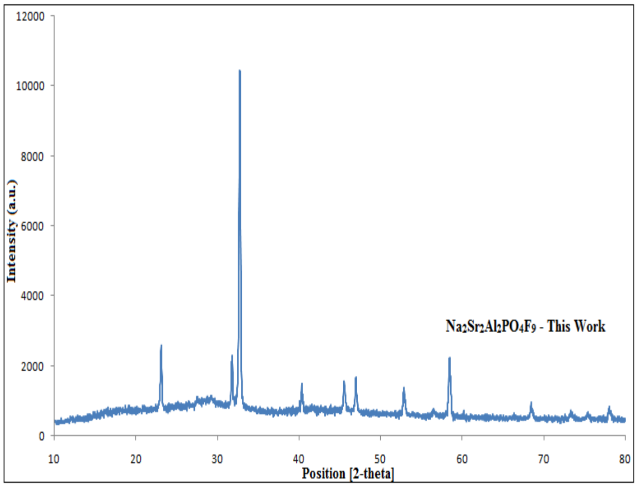

Fig. 2. XRD of $Na_2Sr_2Al_2PO_4F_9$ host lattice.

Photoluminescence properties of $Na_2Sr_2Al_2PO_4F_9:Ce^{3+}$

Ce^{3+} is a very good candidate as activator as well as sensitizer, for studying the behavior of 5d electrons. Ce^{3+} has only one outer electron and only two spin- orbital splitting 4f states ($^2F_{5/2,\ 7/2}$). Thus, its excited state energy structure is simpler than that of the other trivalent rare-earth ions. Photoluminescence excitation spectra of $Na_2Sr_2Al_2PO_4F_9:Ce^{3+}$ phosphor shown in **Fig. 3**. The broad band is observed peaking at 252 nm with a prominent shoulder at 270 nm (λ_{emi} =317 nm). **Fig. 4** shows the PL emission spectra of Ce^{3+} ions in $Na_2Sr_2Al_2PO_4F_9$ phosphor with different concentrations under the same excitation (i.e. 252 nm) wavelengths of light. Two emission peaks are observed from 317 nm to 355 nm, which are assigned to the 5d-4f transition of Ce^{3+} ions. The highest intensity observed at 317 nm due to $^2D(5d) \rightarrow {}^2F_{7/2}(4f)$) transition between two peaks. The concentration of Ce^{3+} ion increases the corresponding intensity of all peaks and at higher concentration (1 mol %) of Ce^{3+} ion. This indicates a change of the surrounding of the Ce^{3+} ions at higher concentration in the $Na_2Sr_2Al_2PO_4F_9$ lattice. The intensity of Ce^{3+} emission at 317 nm is greater than other observed peaks. Variations observed in PL emission intensities, may be cross relaxation between Ce^{3+} ions in the case of heavy concentration of Ce^{3+}. The Ce^{3+} ion can be used as sensitizer as well as an activator, depending on the splitting of 5d excited levels by the crystal field symmetry. Much work has been done on the Ce^{3+} to different activator ions in different host lattice.

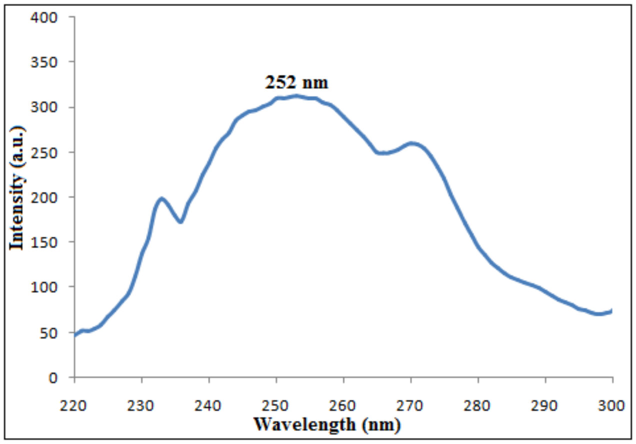

Fig. 3. Excitation spectrum of $Na_2Sr_2Al_2PO_4F_9:Ce^{3+}$ when monitored at 317 nm.

Photoluminescence properties of $Na_2Sr_2Al_2PO_4F_9:Eu^{3+}$

Fluorescence spectra of Eu^{3+}-doped $Na_2Sr_2Al_2PO_4F_9$ were measured at room temperature (**Fig. 5** and **6**), the following emission transitions are observed: $^5D_0 \rightarrow {}^7F_1$ at 593 nm and $^5D_0 \rightarrow {}^7F_2$ at (619 nm). Between them, the $^5D_0 \rightarrow {}^7F_1$ transition is the strongest. Due to the magnetic dipole transitions $^5D_0 \rightarrow {}^7F_1$ and electric dipole transitions $^5D_0 \rightarrow {}^7F_2$, this phosphor exhibits orange colour emission.

According to the Judd-Ofelt theory, the magnetic dipole transition is permitted. But the electric dipole transition is allowed exceptionally on the condition that the europium ion occupies a site without an inversion centre and is sensitive to local symmetry. Consequently, the $^5D_0 \rightarrow {}^7F_1$ transition should be relatively strong when the Eu^{3+} ions occupy inversion center sites, while the $^5D_0 \rightarrow {}^7F_2$ transition must be relatively weak [**17**].

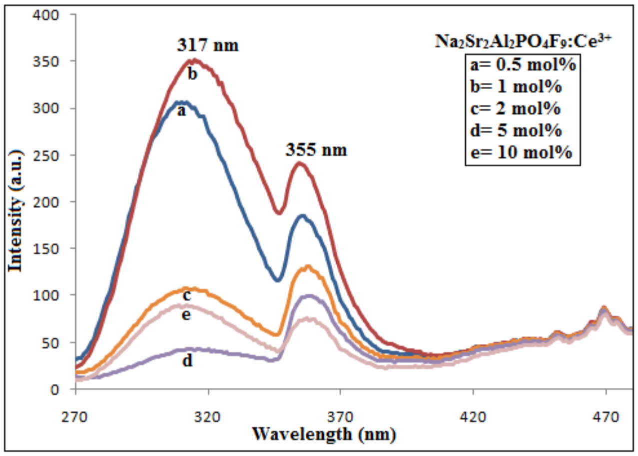

Fig. 4. Emission spectra of $Na_2Sr_2Al_2PO_4F_9:Ce^{3+}$ when excited at 252 nm.

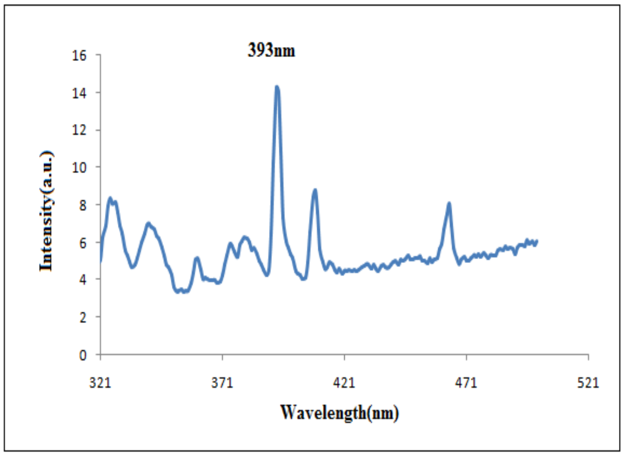

Fig. 5. Excitation spectrum of $Na_2Sr_2Al_2PO_4F_9:Eu^{3+}$ when monitored at 593 nm.

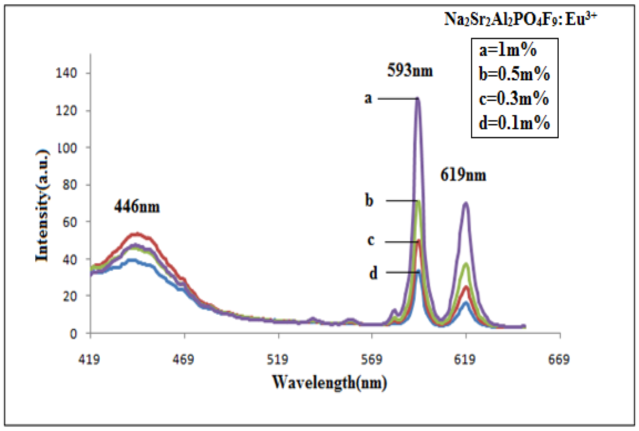

Fig. 6. Emission spectra of $Na_2Sr_2Al_2PO_4F_9:Eu^{3+}$ when excited at 393 nm.

Also, according to Rambabu et al. and Yu et al., the transition $^5D_0 \rightarrow {^7F_1}$ displayed more intensity (1u.a) than $^5D_0 \rightarrow {^7F_2}$ transition (0.44 u.a) due to the localized energy transfer [**17, 18**]. The intensity of these emission transitions are usually used to gauge the quality of the luminescent material. The highest intensity of $^5D_0 \rightarrow {^7F_1}$ transition indicates that Eu^{3+} ions have centro-symmetrical environment in *P*21/*n* structure. Due to the little difference between ionic sizes of Eu^{3+} ion (94.7 pm) and Sr^{2+} ion (112 pm), we presume that Eu^{3+} ions can occupy Sr^{2+} ion sites, which causes a characteristic crystal splitting of the energy levels. The transitions are found to be split into components depending on the host matrix composition. Due to the dependency between $^5D_0 \rightarrow {^7F_1}$ emissions and the crystal field, $^7F_1$ associated with one site symmetry can split into three Stark lines in the crystal field and the $^5D_0 \rightarrow {^7F_2}$ transition of Eu^{3+} can split into, at most, five lines in the crystal field [**19**]. In this case, the photoluminescence excitation spectra of the prepared Eu activated $Na_2Sr_2Al_2PO_4F_9$ phosphor has shown in **Fig. 5**.The prominent excitation band at 393 nm may be due to the f-f transitions of Eu^{3+} ion. The PL excitation spectrum is broad and maximizes at 393 nm in the LED phosphors excitation region. The PL emission spectrum (λ_{exc} = 393 nm) consists of the intense peak at 593 nm (orange) that can be ascribed to $^5D_0 \rightarrow {^7F_1}$ transition of Eu^{3+} ion and other peaks at 619 nm which can be associated with the $^5D_0 \rightarrow {^7F_2}$ transition of Eu^{3+} ion shown in **Fig. 6**. The 593, 619 nm emission of Eu^{3+} ion in host of $Na_2Sr_2Al_2PO_4F_9$ material was very applicable as an orange/red phosphor for the solid state lighting. The excitation of this phosphor is 393 nm is far away to Hg excitation as well as this excitation is main characteristic of solid state lighting (in the range near UV region) in the lamp industry.

Conclusion

$Na_2Sr_2Al_2PO_4F_9{:}Eu^{3+}$ and $Na_2Sr_2Al_2PO_4F_9{:}Ce^{3+}$ high potential halophosphate based nanophosphor has been synthesized by wet chemical method. The XRD pattern of prepared phosphor is well match with the standard pattern (JCPDS 01-084-0497) for $Na_2Sr_2Al_2PO_4F_9$, which confirms that the synthesized sample is single phase. The average structural unit distance was estimated from the full width at half maximum of the diffraction peak by the Scherrer equation and the average crystallite size calculated using the most intense reflection at 2θ=32.74° is 35.26 nm. The photoluminescence spectrum shows the main peak in the range 270–350 nm with a shoulder in the range 350–370 nm, which may be ascribed to transitions from 5d–4f levels of Ce^{3+} ion in the mixed host lattice ($Na_2Sr_2Al_2PO_4F_9$). Orange/red emission observed in $Na_2Sr_2Al_2PO_4F_9$: Eu^{3+} nanophosphor due to transitions from $^5D_0$ excited states to $^7F_{J\,(J=0-4)}$ ground states of Eu^{3+} ions under the 393 nm and it is more favorable of solid state lighting. The effect of rare earth ion in the above system and its effect on the luminescence behaviour of the materials were not focused by the researchers before and hence material is considered as the main attempt in the present investigation.$Na_2Sr_2Al_2PO_4F_9{:}Ce^{3+}$ phosphor shows the near UV emission for development of energy transfer based co-activated advanced phosphors for lamp industry.

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