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Effect of Synthesis Method on Photoluminescence Properties of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} Nanophosphor

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Abstract: We have synthesized a series of single-composition emission $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor by traditional solid state reactions and novel combustion method. Formation of compound was confirmed by X-ray diffraction analysis. The photoluminescence (PL) emission spectra were observed at 376 nm when excited around 322 nm for the various concentrations in both cases. The PL emission spectra of phosphors showed strong Ce^{3+} emission due to the $5d \rightarrow 4f$ transition of Ce^{3+} ions. The Ce^{3+} emission intensity in $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} prepared by combustion was higher than that of solid state reactions.

Keywords: Nanophosphor; Luminescence; Halophosphate

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Introduction

The applications of phosphor materials in different fields have resulted in its great growth. Halo-based phosphors, such as halophosphate phosphors have attracted tremendous attention due to their intense luminescence intensities, high emission efficiencies, simple preparation techniques and wide application fields in illumination and display [1-5]. The present $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor is not studied yet for its optical properties and application in scintillation. Ce^{3+} doping in phosphates results in emission spectra near ultraviolet (UV) region [6]. Recently, trivalent lanthanide dopants have received greater attention for fast and bright scintillators. In particular, Ce^{3+} is a favored dopant in many scintillators due to its allowed optical $5d{-}4f$ transition, which is relatively fast. Today, low temperature methods such as hydrothermal microwave [7], co-precipitation [8,9], sol-gel [10,11] and combustion [12] are used to prepare these phosphors. However, we synthesized $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor by both traditional solid state reactions and novel combustion method. Moreover, we investigate comparatively impact of synthesis method on the photoluminescence properties of same system. Orthophosphates have been extensively investigated, due to their structural diversity. This makes them suitable as hosts to accommodate active rare earth ions. The phosphate family symbolizes possibly one of the most attractive kinds of novel inorganic material, largely owing to the ability of the tetrahedral PO_4^{3-} group to bond with other structural units. Recently, Dhoble and coworker reported some phosphate phosphors prepared by both solid state method and combustion method $Ca_3(PO_4)_2$ [13], $M_5(PO_4)_3F$ (M=Ba, Sr, Ca) [14] $Na_3Al_2(PO_4)_3$:RE (RE=Ce^{3+}, Eu^{3+} and Mn^{2+}) [15], Dy^{3+}, Mn^{2+} or Gd^{3+} activated $NaCaPO_4$ [16], trivalent dysprosium activated $X_6AlP_5O_{20}$ (where X=Sr,

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Ba, Ca and Mg) [17].

The effect of rare earth ion (i.e., Ce^{3+}) in the above system and its effect on the luminescence behavior of the materials were not focused by the researchers before and hence material is considered as the main attempt in the present investigation.

Experimental

Ce activated $Na_2Sr_2Al_2PO_4Cl_9$halophosphate phosphor was prepared via combustion method and solid state method as well.

For Combustion Method: All starting AR grade materials (99.99% purity) taken were in nitrates form and urea was used as fuel for combustion. Materials were prepared according to the chemical formula $Na_2Sr_2Al_{2-x}PO_4Cl_9$:Ce_x. The mixture of reagents was mixed together to obtain a homogeneous solution. Ce ion was introduced in the form of $(NH_4)_2Ce(NO_3)_6$. The compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which served as the numerical coefficients so that the equivalent ratio is unity and the maximum heat liberated during combustion. After stirring for about 15 min, precursor solution was transferred to a furnace preheated to 500℃ and the porous products were obtained.

For Solid State Method: All starting AR grade materials (99.99% purity) taken were in carbonate/oxide form. The raw materials with stoichiometrical ratio were weighed and mixed in mortar sufficiently. In order to obtain the target compound with pure phase, the mixture was heated at 900℃ for 8 h in a covered alumina crucible then cooled down to the room temperature.

The prepared host lattice was characterized 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°, continue time 20 s, in the 2θ range from 10° to 120°, the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherrer's equation. The morphology of the samples were investigated on scanning electron microscopy (SEM). 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. All the measurements were conducted at room temperature.

Results and discussion

XRD and morphology of $Na_2Sr_2Al_2PO_4Cl_9$

Figure 1 shows the XRD pattern of $Na_2Sr_2Al_2PO_4Cl_9$ materials prepared by both solid state and combustion methods. The XRD patterns did not indicate presence of the starting constituents and other likely phases which are an indirect evidence for the formation of the desired compound. This result indicates that the final product was formed in crystalline and homogeneous form. The XRD spectra of prepared compounds cannot match the existing standards JCPDs file. However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds. These results imply that the prepared samples are not the simple physical mixtures of starting materials, but a new single-host $Na_2Sr_2Al_2PO_4Cl_9$ compound. Only intensities varies in both the cases otherwise peak position and phases are quite resemblance to each other.

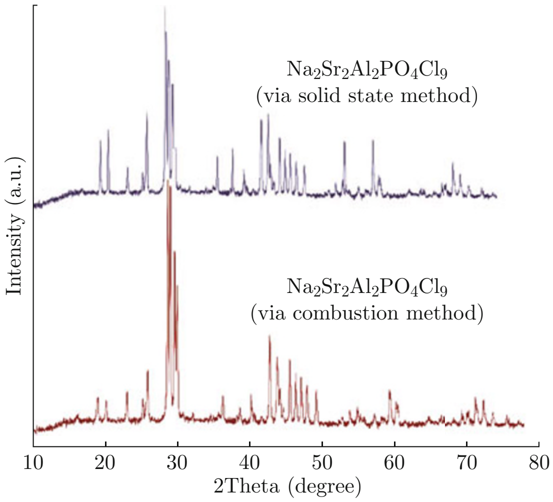

Fig. 1 X-ray diffraction (XRD) patterns of $Na_2Sr_2Al_2PO_4Cl_9$ host prepared by both solid state (purple line) and combustion methods (red line).

It is clearly seen that the grains prepared by combustion method are irregular in shape of particles with a size of about 0.5-1 µm. This shows that the combustion reactions of the mixtures took place well. The typical morphological images are presented in Fig. 2(b). The particles possess foamy like morphology formed from highly agglomerated crystallites, whereas, in Fig. 2(a) an average crystallite size is in sub-micrometer range and the particles of $Na_2Sr_2Al_2PO_4Cl_9$ with agglomeration prepared by solid state method were uniform in grain size of about 2-5 µm seen in SEM image.

$Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} prepared by Solid state method

As all the results were related to PL of Ce^{3+}, general features of the emission are mentioned first. The $5d$-level spectroscopy of Ce^{3+} is very simple. In the excited state, the $4f$ shell is empty and there is only one single $5d$ electron interacting with the crystalline environment. In the ground state, Ce^{3+} ion has the (Xe) $4f^1$ configuration, which results in only two $4f^1$ energy levels, $^2F_{5/2}$ and $^2F_{7/2}$. The spatially diffuse $5d$ electron orbital extends outward from the ion to overlap the neighbouring ligand ions, and is more strongly influenced by their motion. In consequence, the optical properties depend strongly on the structure of the host crystals. Both absorption and emission have a usually broadband character, showing splitting characteristic of ^2Fj states. As the position of the $5d$ band itself depends on the host, not only the Stoke's shift but also the spectral positions of both the excitation and emission bands are host-dependent. In phosphate, the emission is expected to be in the UV region. Figures 3 and 4 show the PL excitation and emission spectra of Ce^{3+} ions in $Na_2Sr_2Al_2PO_4Cl_9$ phosphor prepared by solid state method of different concentrations under light excitation at a wavelength of 320 nm. The splitting peaks are observed at 355 nm and 376 nm, which are assigned to the $5d$-$4f$ transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions, the peak intensity of both peaks increases and maximum intensity is observed at 1 mol% of Ce^{3+} ions (Fig. 4). This indicates that the $Na_2Sr_2Al_2PO_4Cl_9$ lattices are more suitable for higher concentrations of Ce^{3+} ions. Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits is known to take place generally through multipolar interactions, such as dipole-dipole or dipole-quadrupole interactions [18-20]. The Ce^{3+} ion can be used as a sensitizer as well as an activator, depending on the splitting of $5d$ excited levels by the crystal field symmetry.

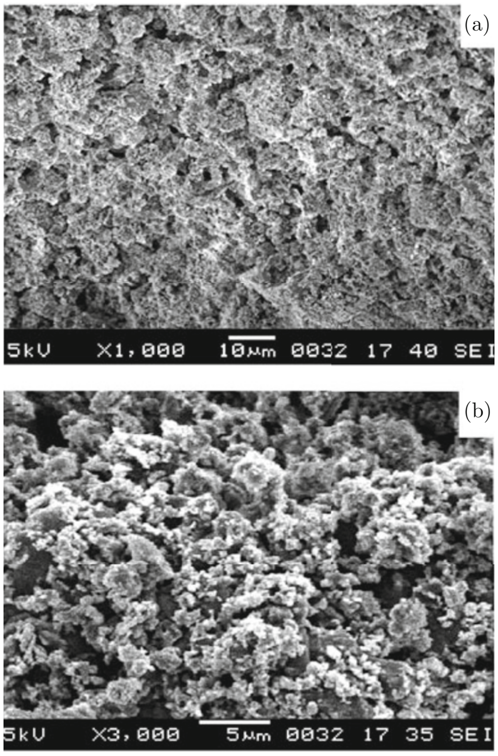

Fig. 2 SEM images of $Na_2Sr_2Al_2PO_4Cl_9$ prepared by (a) solid state method and (b) combustion method.

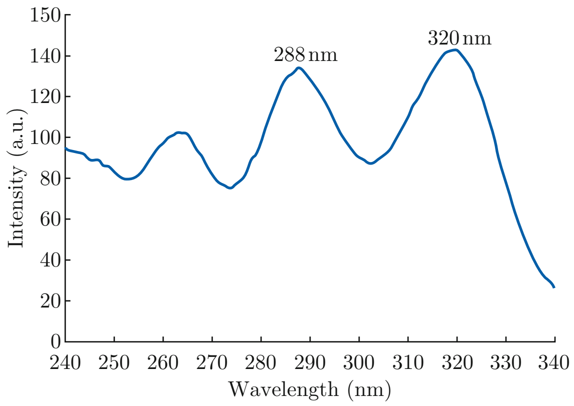

Fig. 3 PL excitation spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} monitored at 376 nm (prepared by Solid state Method).

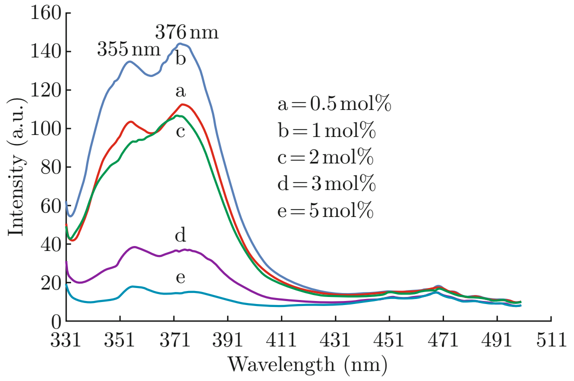

Fig. 4 PL emission spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} excited at 320 nm (prepared by Solid state Method).

The PL emission spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} (1 mol%) phosphor show Ce^{3+} emission at 376 nm due to $5d$-$4f$ transmission of the Ce^{3+} ions. The Ce^{3+} ion can be used as a sensitizer as well as an activator, depending on the splitting of $5d$ excited levels by the crystal field symmetry.

The basic mechanism for scintillation in a Ce-doped material is that an incident ray will produce a large number of electron-hole $(e-h)$ pairs in the host material that transfer to the Ce site. The emission of light then corresponds to a $5d$-$4f$ transition on the Ce site from the Ce $[Xe]4f^05d^1$ excited state, usually referred to as $(Ce^{3+})*$, to the Ce^{3+} ground state [Xe]$4f^1$ $5d^0$ (see Fig. 5). Trapping mechanisms on the host, such as self-trapped excitons, hole traps, or electron traps, can quench or reduce the transfer of energy to the Ce site. A necessary condition for scintillation and luminescence is that the Ce $4f$ and $5d$ levels must be in the gap of the host material. If the Ce $4f$ level lies in the valence band of the host or the $5d$ level is in the conduction band, there will be no Ce-activated scintillation or luminescence. Our theoretical calculations for the prediction of candidate scintillator materials are based on studies of the Ce $4f$ and $5d$ levels relative to the valence-band maximum and conduction-band minimum of the host material, respectively [21].

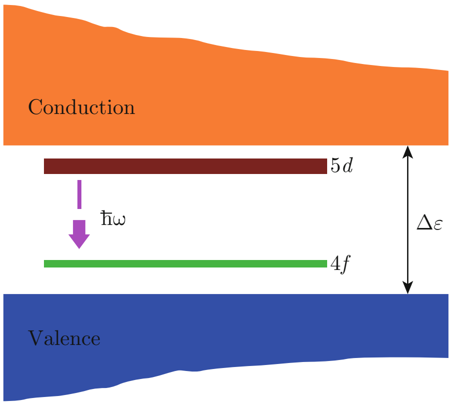

Fig. 5 Schematic diagram for a Ce-activated scintillator showing the positions of the Ce $5d$ and $4f$ levels relative to the conduction and valence band of the host material.

$Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} prepared by combustion method

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 and emission spectrum of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor shown in Figs. 6 and 7 respectively. Figure 7 shows the PL emission spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor with different concentrations under the same excitation (i.e., 322 nm) wavelengths of light. Two emission peaks are observed from 350 to 376 nm, which are assigned to the $5d$-$4f$ transition of Ce^{3+} ions. The highest intensity observed at 376 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 $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} lattice. The emission intensity is related to the concentration of the Ce^{3+} activator ions. With the increase of the concentration of the activator ion, the luminescent centre increases and the emission intensity is enhanced. The highest luminescent intensity was obtained at a cerium concentration of 1 mol%, and lower or higher cerium contents result in a substantial decrease in emission intensity. The luminescence spectra depict the concentration of the activated elements, which increases as a result of the concentration quenching effect. At high concentration the clustering of activator atoms may change a fraction of the activator into quenches, and may induce the quenching effect; this decreases the emission intensity. The quenching concentration is about 1 mol%. The oxygen vacancies might serve as a sensitizer for the energy transfer to the rare earth ion, due to the strong mixing of charge transfer states, resulting in highly enhanced luminescence [22]. However, excess oxygen vacancies in the host would inevitably destroy the crystallinity, leading to quenching of luminescence [22]. There is no PL observed in the host material. This signifies that the incorporation of Ce^{3+} ion into the $Na_2Sr_2Al_2PO_4Cl_9$ lattice causes a significant change to the PL properties compared with the host matrix.

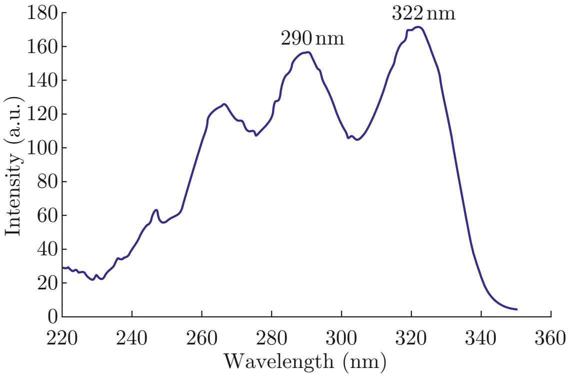

Fig. 6 PL excitation spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} monitored at 376 nm (prepared by combustion Method).

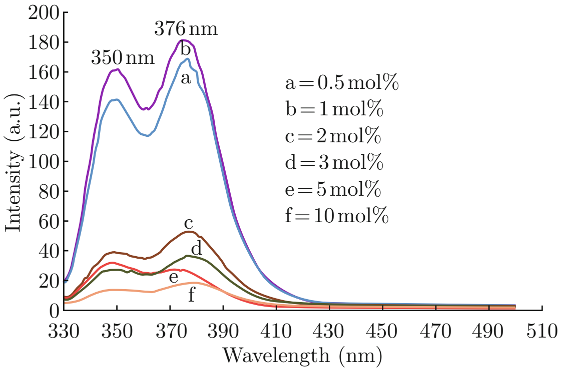

Fig. 7 PL emission spectra of $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} excited at 322 nm (prepared by combustion Method).

Above both results report the Ce^{3+} PL spectra of $Na_2Sr_2Al_2PO_4Cl_9$ very similar to each other. The positions of emission and excitation bands are very close. We have also observed excitation spectrum for $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} prepared by solid state method (Fig. 3) that is almost identical to that for $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} prepared by combustion method. The emission band for $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} (Fig. 6) is located at slightly longer wavelength of 322 nm. A shoulder around 290 nm is observable. The changes may be due to different synthesis method consequently local higher concentration or different local environment in the precipitated powders.

Conclusions

From the results presented here novel $Na_2Sr_2Al_2PO_4Cl_9$:Ce^{3+} phosphor involving as many as three constituents can be prepared by both traditional solid state and novel combustion method described here and formation of compound is confirmed by XRD. Strong luminescence of Ce^{3+} can be observed in the as prepared powders without any further heat treatment. Peak position (at 376 nm) is not influenced by different concentrations of Ce^{3+} and only relative intensities vary when excited around 322 nm. Only intensity varies may be due to different synthesis method. Present phosphor shows the near UV emission for development of energy transfer based co-activated advanced phosphors for lamp industry and scintillation. Besides, full understanding of the nature of the competing processes and the dynamics of holes trapping by Ce^{3+} is still one of the challenging subjects in scintillation mechanism research.

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