5d-4f transition in $KAl_{1-x}PO_4Cl:Ce_x^{3+}$ $(0.1 \leq x \leq 5)$

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Abstract

A series of phosphors $KAl_{1-x}PO_4Cl:Ce_x^{3+}$ $(0.1 \leq x \leq 5)$was synthesized using a facile combustion method using urea as a fuel and their structural ,morphological and photoluminescence properties were investigated. The 5d levels corresponding to the $4f^1 \rightarrow 4f^0 5d^1$ transition of Ce^{3+} ions were identified .The 5d level spectroscopy of Ce^{3+} ion is very simple, which has only one electron in the 4f shell and exhibits strong absorption and efficient fluorescence from the allowed interconfigurational $4f^1 \rightarrow 4f^0 5d^1$ transition. In this work, we report the synthesis,X-ray powder diffraction (XRD), photoluminescence (PL) and scanning electron microscopy (SEM) of $K_{1-x}Al(PO4)Cl:Ce_x^{3+}$ $(0.1 \leq x \leq 5)$phosphors have been reported. Our work shows that $K_{1-x}Al(PO_4)Cl:Ce_x^{3+}$ $(0.1 \leq x \leq 5)$ has a strong absorption peak at 305 nm and gives emissions at 359 nm.

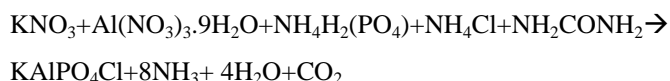**Keywords**— *phosphor; phosphate; scintillator; rare earth; UV*

Introduction

Rare earth doped with phosphate phosphor has a wide range on potential application. Most of the researchers have been extensively studied over it since last decade. Recently Shinde and co-workers had reported several rare earth activated phosphate phosphors [1-4]. Ce^{3+} ions play a significant role in the rare earth ions; commonly, they act as the blue-emitting phosphors due to the parity allowed electric dipole transition of 4f → 5d. Ce^{3+}activated phosphors commonly act as the blue-emitting phosphors as the result of their $4f_1$ configuration in solids shows efficient broad band luminescence which due to the 4f → 5d parity allowed electric dipole transition. The 4f →5d transitions of the Ce^{3+} ion have been widely investigated. Generally, the 5d → 4f emissions of the Ce^{3+} ion shift slightly to longer wavelengths which depend on the host composition, the crystal structure, or the lattice symmetry. In all of the hosts, phosphate has attracted extensive attention attributed to their stable physical and chemical properties, excellent thermal stability. The present $KAlPO4Cl:Ce^{3+}$ 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 [5]. 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 [6], co-precipitation [7,8], sol-gel [9,10] and combustion [11] are used to prepare these phosphors. 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 combustion method $Ca_3(PO_4)_2$ [12], $M_5(PO_4)_3F$ (M=Ba, Sr, Ca) [13] $Na_3Al_2(PO_4)_3$:RE (RE=Ce^{3+}, Eu^{3+} and Mn^{2+}) [14], The effect of Ce^{3+} rare earth ion 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

Phosphor powder samples with a nominal composition of $KAl_{1-x}PO_4Cl: Ce_x^{3+}$ ($0.1 \leq x \leq 5$) were prepared by a novel facile combustion method. The starting AR grade materials (99.99% purity) taken were Potassium nitrate (KNO_3), Aluminium nitrate ($Al(NO_3)_3.9H_2O$), Di-ammonium hydrogen phosphate ($NH_4H_2(PO_4)$), Ammonium chloride (NH_4Cl), Ammonium Cerium nitrate ($(NH_4)_2Ce(NO_3)_6$ and Urea (NH_2CONH_2) was used as fuel for combustion. 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. The mixture of reagents was mixed together to obtain a homogeneous solution. Ce^{3+} ion was introduce in the form of $(NH_4)_2Ce(NO_3)_6$ solution by dissolving $(NH_4)_2Ce(NO_3)_6$ into HNO_3 solution. The molar ratio of europium rare earth ion was changed in relation to $KAlPO_4Cl$ phosphor. The combustion method involves the dissolution of metal nitrate and combustion fuel then the heating of the solution (at ~ 650 °C). After heating, foam appeared followed by self-ignition and black smoke was observed to obtain the $KAl_{1-x}PO_4Cl: Ce_x^{3+}$ ($0.1 \leq x \leq 5$) powders. Chemical reaction is as follows:

$$KNO_3 + Al(NO_3)_3.9H_2O + NH_4H_2(PO_4) + NH_4Cl + NH_2CONH_2 \rightarrow KAlPO_4Cl + 8NH_3 + 4H_2O + CO_2$$

Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD), using a PAN-analytical diffractometer (Cu–Kα radiation) at a scanning step of 0.01°, continue time of 20 s and in the 2θ range 10–90°. The photoluminescence measurements of excitation and emission were recorded on a Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2g) 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 KAlPO4Cl: Ce $^{3+}$

Figure 1 shows the XRD pattern of $KAlPO_4Cl: Ce^{3+}$ materials prepared by 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 can- not match the existing standards JCPDs file. It was previously mention in *Akojwar et al.*[15] 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 $KAlPO_4Cl: Ce^{3+}$ compound.
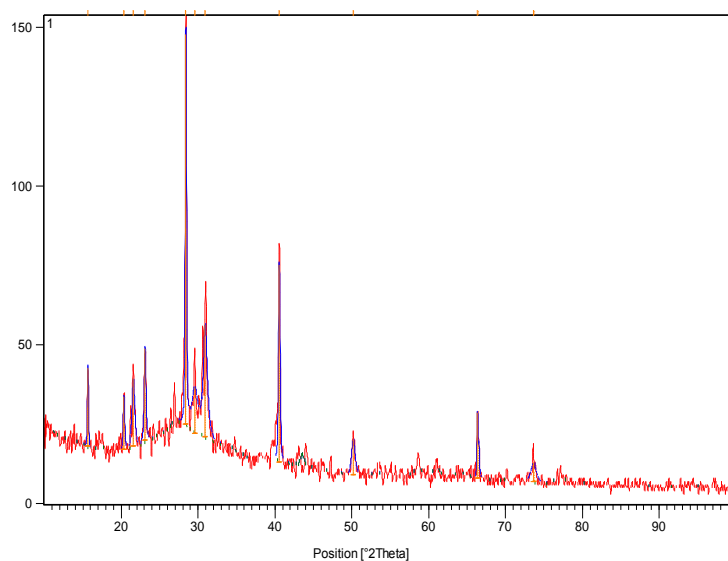

Fig.1 : X-ray diffraction (XRD) patterns of KAlPO$_4$Cl: Ce^{3+} phosphor powder

It is clearly seen that the grains prepared by combustion method are irregular in shape of particles with a size of about 1-5 μm. This shows that the combustion reactions of the mixtures took place well. The particles possess foamy like morphology formed from highly agglomerated crystallites, The particles of $KAlPO_4Cl$ with agglomeration prepared by combustion method were irregular in grain size of about 1-5 μm seen in SEM image
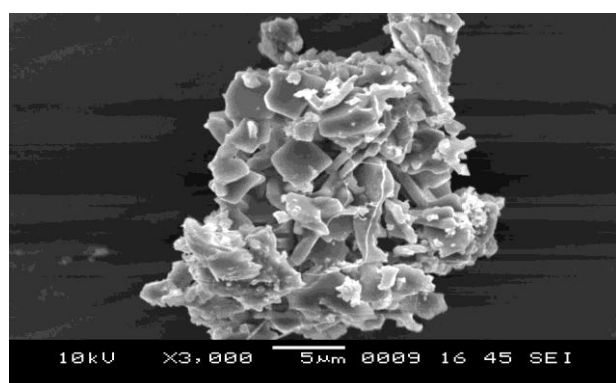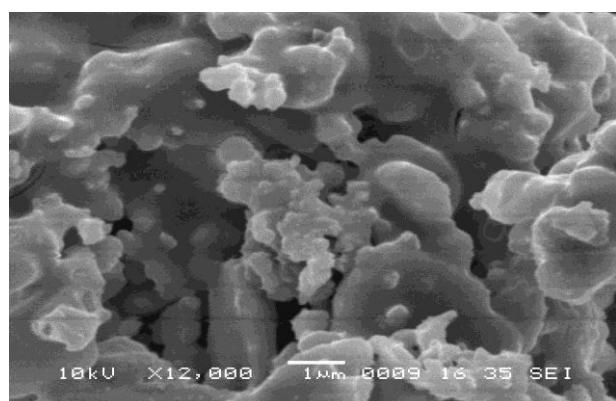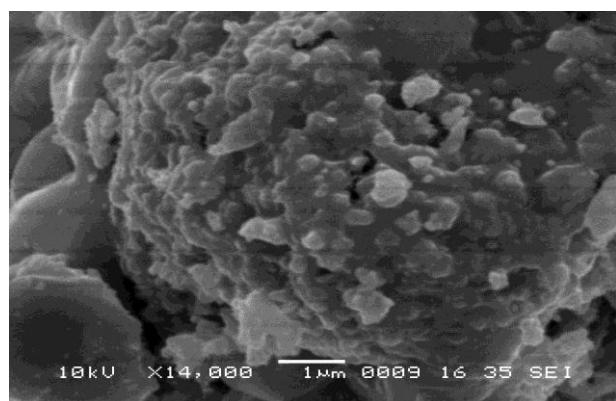

fig. (a)

fig. (b)

fig. (c)

Fig. 2. SEM images of $KAlPO_4Cl$: Ce^{3+} phosphor powders prepared by facile combustion method.

PL Properties of $KAlPO_4Cl$: Ce^{3+}

PL excitation spectra of $KAlPO_4Cl$: Ce^{3+} phosphor shows broad band at 305 nm with λ_{em} = 359nm fig.(4).The PL emission spectra of Ce^{3+} ions in $KAlPO_4Cl$ phosphate phosphor with different concentration under excitation at 305 nm wavelength of light. Single broad band peaks are observed in the range of 325 nm to 475 nm peaking at 359 nm which are assigned to the 5d-4f transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions the peak intensity of 359 nm peak decreases and maximum intensity is observed for 0.3mol% of Ce^{3+} ions. This indicates that the $KAlPO_4Cl$ lattice is more suitable for lower concentration of Ce^{3+} ion. The asymmetric emission spectra in fig.(4) show that Ce^{3+} has more than one emission centre in the lattice. The peak centre of 1 mol % and 0.3 mol % varies in the Ce^{3+} concentration range of 0.1-5 mol % . the observation of two emission bands is in agreement with result of two crystallographic sites available for Ce^{3+} in $KAlPO_4Cl$.[16,17] *Tang et al* . [18]. Ce^{3+} is a very good candidate as activator as well as sensitizer, for studying the behavior of 5d electrons. 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 $^2F_{7/2}$ [19]. 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 ^2F_j 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 variation of PL emission intensity observed may be due to cross-relaxation between Ce^{3+} ions (in this process, an excited ion transfers only a part of its energy to another ion) in cases of heavy concentration of Ce^{3+} Fig. (4). The emission intensities increase with an increase of Ce^{3+} content up to x = 0.3 and

then decreases by further increasing the Ce^{3+} content. The decrease is primarily because the energy absorbed by Ce^{3+} is released as a non-radiation transition instead of are light emission. Perhaps this is due to concentration quenching effect.(Fig.5)
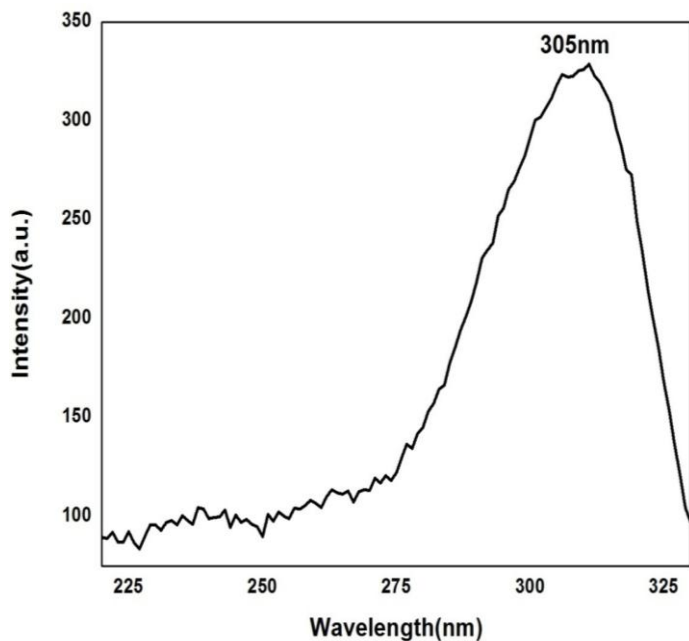

Fig. 3. Excitation spectrum of KAlPO₄Cl: Ce³⁺ phosphor powder monitored at 359 nm.
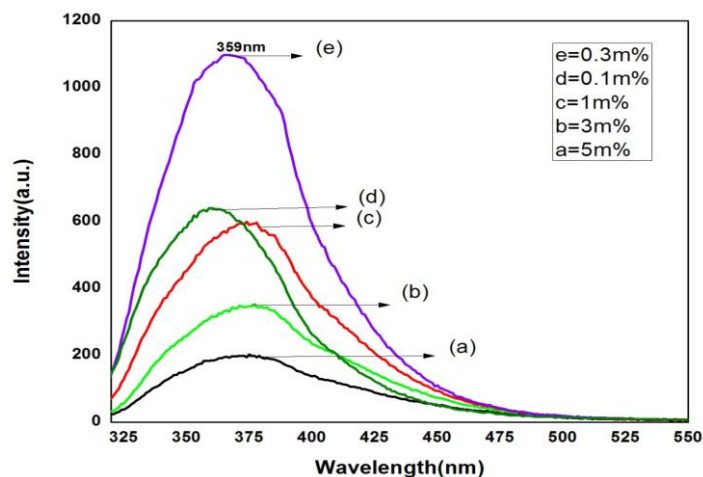

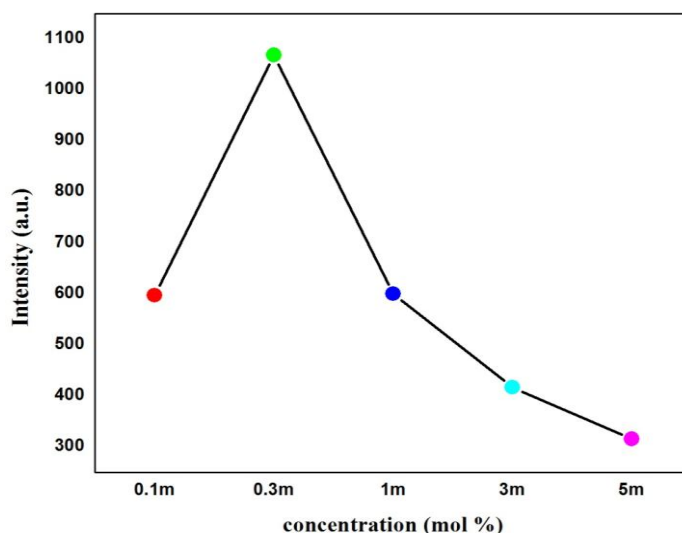**Fig. 4. Emission spectra of KAl$_{1-x}$PO₄Cl: Ce$_x$³⁺ (0.1 ≤ x ≤ 5) phosphor powder when excited at 305 nm.**

Fig. 5. Concentration of Ce in emission spectra of KAl$_{1-x}$PO₄Cl: Ce$_x$³⁺ (0.1 ≤ x ≤ 5) phosphor powder with respect to intensity

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 mate rial 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. 6) [20]. 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].
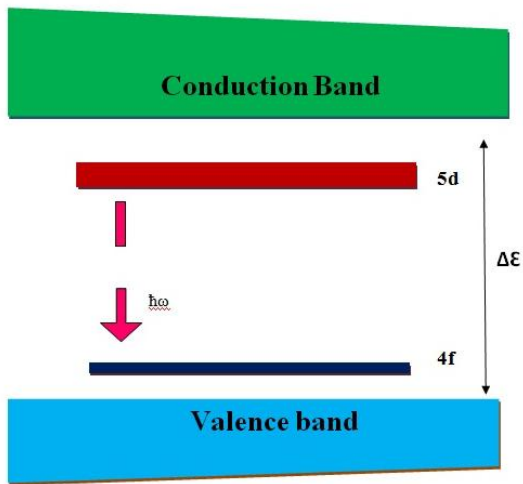
Fig. 6 Schematic diagram for a Ce-activated scintillator showing the positions of the Ce 5d and 4f levels relative to the conduction and valence band of the host material.
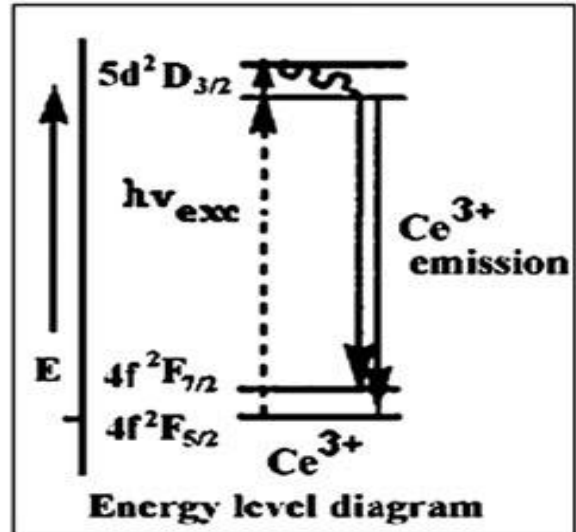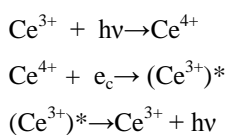

Figure 7. Energy level diagram of Ce^{3+}.

In the 5d→4f transition of Ce^{3+} ion, 4f is the lowest excited charge transfer state and t_1g is the molecular orbital of the surrounding ligand. Hence, Ce^{3+} ion was excited in this lattice at 307nm to check for its suitability for scintillating mechanism application. As shown in Fig. 7, the emission occurs from the lowest component of the 5 d configuration to the two-crystal field split levels ($^2F_{5/2}$ and $^2F_{7/2}$) of the 4f ground state [19]. As the concentration of Ce^{3+} ion increases to 0.3mol%, the PL intensity also increases, due to more Ce^{3+} ions in the KAlPO$_4$Cl: Ce^{3+} lattices. The 325–450nm PL emission was dominant at 0.3mol% Ce^{3+} ions. The observed Ce^{3+} emission in this phosphor can be used in scintillators according to an energy transfer process explained by Lempicki et al. [23] and Wojtowicz et al. [24,25]. According to this process, Ce^{3+} captures primary excitation energy (hυ) and becomes Ce^{4+}. After capturing a free electron (e_c) from the conduction band, Ce^{4+} will be converted to an excited Ce^{3+} ion or $(Ce^{3+})^*$. Relaxation to the ,ground state will be accompanied by emission of the scintillation photon hv. This process can be summarized as follows:

$$Ce^{3+} + hv \rightarrow Ce^{4+}$$
$$Ce^{4+} + e_c \rightarrow (Ce^{3+})^*$$
$$(Ce^{3+})^* \rightarrow Ce^{3+} + hv$$

Conclusions

From the results presented here novel KAlPO$_4$Cl :Ce3+ phosphor prepared by 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 359 nm) is not influenced by different concentrations of Ce^{3+} and only relative intensities vary when excited around 305 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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