



Synthesis, Characterisation and Luminescence in KAlP₂O₇: Bi

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Abstract:

KAlP₂O₇ phosphor activated with Bi was synthesized by using combustion synthesis. The phosphor was characterized by X-ray diffraction method and was found to possess monoclinic structure. Photoluminescence spectra shows intense emission of Bi³⁺ around 325 nm corresponding to transition ¹P₁ → ¹S₀ state. This emission lies in UV region. The excitation spectra shows a maximum at around 250 nm with a good overlap at 254 nm which insures the use of the material as a lamp phosphor in UV region. As Bi³⁺ emission matches with the 4f^N levels of the rare earth ion, energy transfer from Bi³⁺ to rare earth ions Gd, Eu, Dy and transition metal ions like Mn was studied in the sample KAlP₂O₇.

Introduction:

Luminescence science is very much alive. Luminescence is defined broadly as the generation of light in excess of that radiated thermally¹. Man's fascination with luminescence stems from when an otherwise invisible power is converted into visible light. The commercial importance of luminescence is ubiquitous, being manifest in lamps, displays, X-ray machines, etc.

Materials that generate luminescence are called phosphors. Commercial phosphors are mostly inorganic compounds prepared as powders (with grain sizes usually in the order of 20-200 nm) or thin films. The phosphor materials contain one or more impurity ions or activators (A), typically present in 0.01-100 mol % concentrations. The actual emission is generated on these activator ions. Typical activators are rare earth- or transition-metal ions, ions undergoing s-p transitions (like Bi³⁺), and molecular anions like the tungstate, vanadate or phosphate groups. Sensitizers (S) are useful if the activator ions cannot be excited, *e.g.*, because of forbidden transitions. In such cases, the exciting energy is absorbed by the sensitizers and subsequently transferred to the activator ions. Common to all these moieties is the not completely filled electron shell in at least one state (ground state, excited state) involved.

UV excited phosphors² lead to the possibility of developing a mercury-free fluorescent lamp. Quantum efficiencies in excess of unity (up to 140%) have been reported by GE and Philips research groups in Pr³⁺ activated fluorides. In addition, GE also reported quantum cutting of Pr³⁺ in oxides. Such multiphoton emission may be used to generate good overall conversion efficiency in fluorescent lamps or in plasma display panels where the ultraviolet radiation is provided by a xenon discharge (emitting between 147 and 200 nm) instead of the conventional mercury-based discharge (254 nm).





The combustion synthesis^{3,4} is an attractive synthetic procedure because of its capacity to yield products at 500°C which otherwise are prepared at temperatures as high as 1500°C or even more. The process is based on mixing stoichiometric proportions of component nitrates and a suitable fuel. The heat of exothermic reaction between the redox mixture elevates temperature of constituents to around 1500°C, the components are transformed into products. This process is safe, simple and instantaneous. It is time saving i.e. the whole synthesis lasts for 5 minutes. It is energy saving as exothermicity of the reaction is being used fruitfully for synthesis.

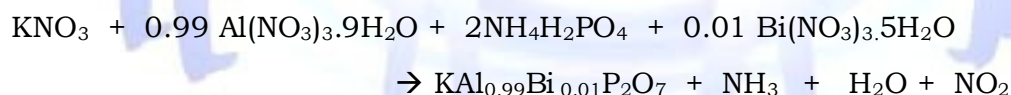
KAlP₂O₇ belongs to the system having structure M^IM^{III}P₂O₇ compounds, where M^I is a monovalent metal and M^{III} is a trivalent metal. KAlP₂O₇ has monoclinic structure. The compound was first characterized by d'Y Voire⁵ and later by Klyucharav and Skobla⁶. KAlP₂O₇ was prepared by them by firing method⁷ which involves high temperature of the order of 1100° C. We have prepared KAlP₂O₇ phosphor by combustion synthesis which is very easier, time and energy saving method.

Thus KAlP₂O₇ phosphor activated with Bi³⁺ was prepared by combustion method and luminescence was studied. Further, as Bi³⁺ emission matches with the 4f^N levels of the rare earth ions, energy transfer from Bi³⁺ to rare earth ions Gd, Eu, Dy and transition metal ions like Mn was studied in the sample KAlP₂O₇.

Experimental:

Stoichiometric compositions of the metal nitrates (Oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components which serve as the equivalence ratio is unity and the heat liberated during combustion is at a maximum.

For example : The preparation of KAl_{0.99}Bi_{0.01}P₂O₇ is described as follows:



We calculate weights of constituent compounds as follows.

1 gm of KNO₃ requires

$$= \frac{0.99 \times \text{molecular weight of Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}}{\text{molecular weight of KNO}_3} \\ = \frac{0.99 \times 375.13}{101.11} \\ = 3.7101197 \text{ gms of Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$$

Similarly, the required weights of NH₄H₂PO₄ and Bi(NO₃)₃ were calculated for 1 gm of KNO₃.

Following method was used for the calculation of the amount of urea (fuel) required for each of three nitrates.

For a trivalent oxidizer, say M(NO₃)₃·xH₂O (where M is a metal),

Oxidizing valency for Metal is (+3 x 1) = 3





For O is $(-2 \times 3) \times 3 = -18$

The net valency becomes $= -15$

For fuel $H_2N-C-NH_2$, the valency is -6

So 1 mole of oxidizer requires $15/6$ moles of urea. Thus depending upon the cation valency (+3 for $Al(NO_3)_3 \cdot 9H_2O$, $Bi(NO_3)_3$ and +1 for KNO_3), the multiplying factor is $15/6$ and $5/6$ respectively. Thus total weight of urea is calculated. Weighed quantities of $Al(NO_3)_3 \cdot 9H_2O$, KNO_3 , $Bi(NO_3)_3$ and urea (of AR grade) were added and the mixture is crushed together for 30 minutes (dry method) to form a thick paste. The resulting paste is transferred into a china crucible (3" J brand) and introduced into a muffle furnace maintained at $500 \pm 10^\circ C$. The mixture undergoes dehydration and then decomposes with the liberation of NH_3 and NO_2 . The process being highly exothermic continues and the liberated gases swell the mixture into large volume. Large exothermicity results into a flame changing the mixture into gaseous phase. Flame temperature as high as $1600^\circ C$ converts the vapour phase oxides into phosphates. The crucible is then taken out of the furnace and the foamy product is crushed into a fine powder.

Thus $KAlP_2O_7$ with different impurities Bi and Gd, Eu, Dy, Mn etc. were prepared using combustion synthesis. The compounds so prepared were identified using XRD technique. PL characteristics were obtained using Hitachi-4000 spectrophotometer. The Results are discussed as below.

Results and discussion :

$KAlP_2O_7 : Bi$

Fig.1 shows PL spectra for $KAlP_2O_7:Bi$. Intense emission of Bi^{3+} is observed around 325 nm corresponding to transition $^1P_1 \rightarrow ^1S_0$ state. This emission lies in UV region. The excitation spectra shows a maximum at around 250 nm with a good overlap at 254 nm which insures the use of the material as a lamp phosphor in UV region. PL intensity was studied by varying the concentration of Bi^{3+} with the intention of studying the effect of concentration on the intensity of emission. Table1 shows the emission intensity of $KAlP_2O_7 : Bi$ with different concentration of Bi^{3+} .

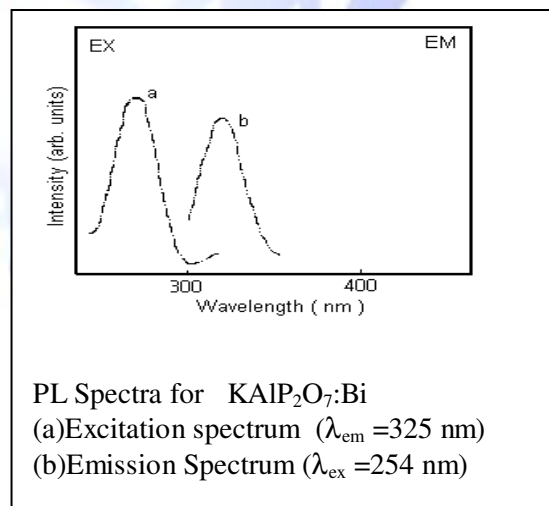


Table1:PL Emission of $KAlP_2O_7:Bi$ with different concentrations

Formula	$\lambda_{ex}(nm)$	$\lambda_{em} (nm)$	Intensity
$KAl_{0.99}Bi_{0.01}P_2O_7$	254	325	575
$KAl_{0.95}Bi_{0.05}P_2O_7$	254	325	400





It is observed that the PL intensity decreases with increasing the concentration of Bi^{3+} in the host, this means that for Bi^{3+} , there is a concentration quenching at room temperature.

As Bi^{3+} emission matches with the $4f^N$ levels of the rare earth ions, energy transfer from Bi^{3+} to rare earth ions could take place. Therefore energy transfer from Bi^{3+} to rare earth ions Gd, Eu, Dy and transition metal ions like Mn was studied in the sample KAlP_2O_7 .

Table 2 shows emission intensities of $\text{KAlP}_2\text{O}_7:\text{Bi}$ sample doped with rare earth ions Gd, Eu, Dy and Mn.

Table 2: PL emissions in KAlP_2O_7

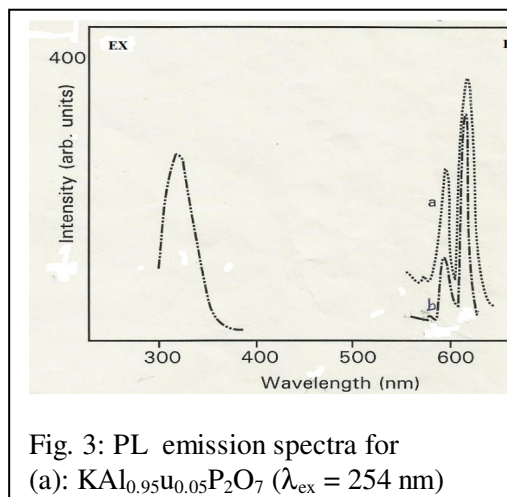
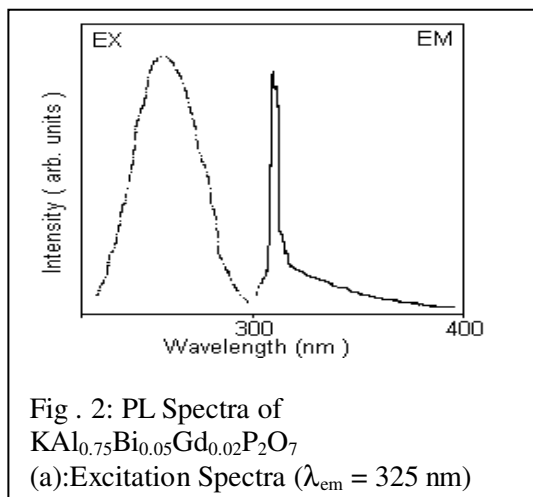
Sample No.	Formula	λ_{ex} (nm)	λ_{em} (nm)	Intensity
A	$\text{KAl}_{0.75}\text{Bi}_{0.05}\text{Gd}_{0.02}\text{P}_2\text{O}_7$	256	311	1300
			325	150
B	$\text{KAl}_{0.95}\text{Eu}_{0.05}\text{P}_2\text{O}_7$	254	595	30
			614	43
C	$\text{KAl}_{0.98}\text{Bi}_{0.01}\text{Eu}_{0.01}\text{P}_2\text{O}_7$	254	325	600
			614	40
			594	15
D	$\text{KAl}_{0.85}\text{Bi}_{0.1}\text{Eu}_{0.05}\text{P}_2\text{O}_7$	254	325	160
			610	145
			595	50
E	$\text{KAl}_{0.948}\text{Bi}_{0.05}\text{Dy}_{0.002}\text{P}_2\text{O}_7$	254	325 emission No Dy	
F	$\text{KAl}_{0.98}\text{Bi}_{0.01}\text{Mn}_{0.01}\text{P}_2\text{O}_7$	260	325	150
	$\text{KAl}_{0.9}\text{Bi}_{0.09}\text{Mn}_{0.01}\text{P}_2\text{O}_7$		No Mn emission	

From the table, it is observed that:

a

b





1. Moderate energy transfer from $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ leading to efficient Gd^{3+} emission at 311 nm with a sharp peak is observed in the sample $\text{KAl}_{0.75}\text{Bi}_{0.05}\text{Gd}_{0.02}\text{P}_2\text{O}_7$ (sample A in the table 2). This emission lies in UV region of the spectrum. The excitation and emission spectra are shown in Fig 2. The excitation peak is observed at 256 nm which shows a good overlap with the Hg line (i.e. 254 nm). Sufficient absorption and efficient emission in UV region of the spectrum would help the phosphor to use as lamp phosphor in UV region. A shoulder of emission spectrum for Bi^{3+} at 325 nm shows that Bi^{3+} emission is not completely quenched. This means that complete energy transfer from $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ has not taken place.
2. Very strong Bi^{3+} emission was observed in the sample $\text{KAl}_{0.98}\text{Bi}_{0.01}\text{Eu}_{0.01}\text{P}_2\text{O}_7$ but energy transfer from $\text{Bi}^{3+} \rightarrow \text{Eu}^{3+}$ was not found to be efficient. (Fig.3)
3. Dy^{3+} and Mn^{3+} emissions were not observed in the samples $\text{KAl}_{0.948}\text{Bi}_{0.05}\text{Dy}_{0.002}\text{P}_2\text{O}_7$ and $\text{KAl}_{0.98}\text{Bi}_{0.01}\text{Mn}_{0.01}\text{P}_2\text{O}_7$ respectively.

Conclusion:

Combustion synthesis was found to be an efficient method to prepare the KAlP_2O_7 sample. Intense emission of Bi^{3+} was observed in $\text{KAlP}_2\text{O}_7 : \text{Bi}$. Moderate energy transfer from $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ was observed in the sample $\text{KAl}_{0.75}\text{Bi}_{0.05}\text{Gd}_{0.2}\text{P}_2\text{O}_7$. As emission lies in UV region with the good overlap at 254 nm, the phosphor can be used as UV lamp phosphor in lamp industry.

References:

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