



PHOTOLUMINESCENCE IN $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$

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Abstract

In the system of $\text{CaO-Al}_2\text{O}_3$, CaAl_4O_7 , $\text{CaAl}_{12}\text{O}_{19}$ and CaAl_2O_4 are more commonly studied. However, there is not much information available on the title compound $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$. Here we report the synthesis and luminescence for this compound. $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ phosphors activated with various dopants were prepared by combustion synthesis. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. PL characteristics were studied using a Hitachi F-4000 spectrofluorimeter, at room temperature, using 1.5 nm spectral slit width in the range of 200–700 nm. XRD pattern of the prepared compound matched well with the ICDD file 02-392. Characteristic luminescence of Pb^{2+} , Ce^{3+} , Eu^{2+} and Eu^{3+} was observed in the as prepared phosphors. Luminescence of Pb^{2+} , Ce^{3+} is in UV region of the spectrum while that of Eu^{2+} in the blue. Weak emission of Eu^{3+} was predominantly in the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition which is in the red region (611 nm).

Keywords: *aluminate; spinel; combustion synthesis; photoluminescence; phosphor.*

1.0 INTRODUCTION

There are several compounds in the system $\text{CaO-Al}_2\text{O}_3$. Out of these CaAl_4O_7 , $\text{CaAl}_{12}\text{O}_{19}$ and CaAl_2O_4 are more commonly studied. With the exception of pure phases, the system $\text{CaO-Al}_2\text{O}_3$ has four to five nearly stoichiometric compounds, which can be called as calcium aluminates. The existence of the phase C_{12}A_7 ($\text{C}=\text{CaO}$ and $\text{A}=\text{Al}_2\text{O}_3$) and also the melting points of different compounds vary from one source to another.

The first studies of this system [1,2], indicated the presence of four compounds: $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A), $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (C_5A_3), CaAl_2O_4 (CA) and $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ (C_3A_5). Lagerqvist et al. [3] studied the system by X-ray diffractometer and could identify $\text{Ca}_5\text{Al}_6\text{O}_{14}$ as $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C_{12}A_7) and $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ as CaAl_4O_7 (CA_2); and



reported a new compound $\text{Ca}_3\text{Al}_{32}\text{O}_{51}$ (C_3A_{16}). All four compounds were reported to melt incongruently, namely $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A) at 1541°C to a liquid of 45.1 mol % $\text{AlO}_{1,5}$; CaAl_2O_4 (CA) at 1604°C to a liquid of 66 mol % $\text{AlO}_{1,5}$; CaAl_4O_7 (CA_2) at 1765°C to a liquid of 80 mol % $\text{AlO}_{1,5}$; and $\text{CaAl}_{12}\text{O}_{19}$ (CA_6) at 1833°C to a liquid of 85 mol % $\text{AlO}_{1,5}$. However, there is not much information available on the title compound $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$. Calcium aluminates $\text{Ca}_3\text{Al}_2\text{O}_6$, CaAl_2O_4 , CaAl_4O_7 , and $\text{CaAl}_{12}\text{O}_{19}$ are of great importance in ceramics and cement industries [4]. The very alumina rich phases may be formed as very high-temperature condensates from the primitive solar nebula and thus are of special interest to cosmochemistry. Commercial calcium aluminate cements are known to contain various phases (major phases CA and CA_2 , minor phases C_{12}A_7 and $\alpha\text{-A}^+$). The monocalcium (CA) aluminates impart high mechanical strength and refractoriness to the cement, whereas rapid setting is mostly associated with C_{12}A_7 , which dissolves rapidly. The properties of these materials, namely, the rate of hydration of the aluminates and the product formed in the reactions among the fine constituents, are dependent on their composition and degree of crystallinity. Fumo et al. [5] prepared single aluminate powder CaAl_2O_4 (CA), CaAl_4O_7 (CA_2) and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C_{12}A_7) by using combustion synthesis to find their lattice parameter, powder density, crystal size and crystallinity degree.

Two of the main advantages of calcium treatment are not only the improvement of the castability but also the improvement of the final properties of the steels, machinability, toughness and surface quality. Zheng et al. [6] studied the effect of mineralizer on the structure and properties of calcium aluminates formation.

Crystal Structure: CaAl_4O_7 are isostructural with four formulae in the unit cell. In these compounds, all the Al atoms are tetrahedrally coordinated, with all O_4 tetrahedra sharing corners. The structure is represented in Fig.1. Looking at the Al array, it appears that half of the Al atoms (the eight Al1 atoms) are five connected, whereas the other half (the eight Al2 atoms) are six-connected. Since calcium can only transfer eight electrons, not all the Al atoms can be converted into pseudo-elements of the main group. This is the reason why, in this compound, the Al atoms show a higher and unusual connectivity which could be explained looking at the location of the O atoms. In the environment of Al1,

we see that three O atoms are situated close to the midpoint of three Al-Al contacts, as if the three valence electrons of aluminium would have formed three directed, two-center, two-electron bonds. It is clear that the other two contacts do not originate from this type of bond because the central Al atom would have ten electrons, thus violating the octet rule. Therefore, the two remaining bonds are formed with two Al atoms belonging to a triangle which has only one O atom at its center, just as if the Al₃ triangle corresponded to a three-center, two-electron bond. These two electrons would complete the octet of the central Al atom. In the case of Al₂, which is six-connected, the Al-Al bonding scheme can be explained in the same way. Here, there are two Al-Al contacts which have the O atom midway between them. This seems to indicate that Al₂ has used two valence electrons to form these two-center, two-electron bonds. The remaining four contacts take place with four Al atoms belonging to two different Al₃ triangles than those described above. In this way the Al₂ atoms also complete their octet. Thus there are eight electrons from calcium plus eight electrons from Al₂ which are involved in these three-center, two electron bonds. This would lead to eight bonding pairs, which is just the number of such O(Al)₃ triangles in the unit cell [7].

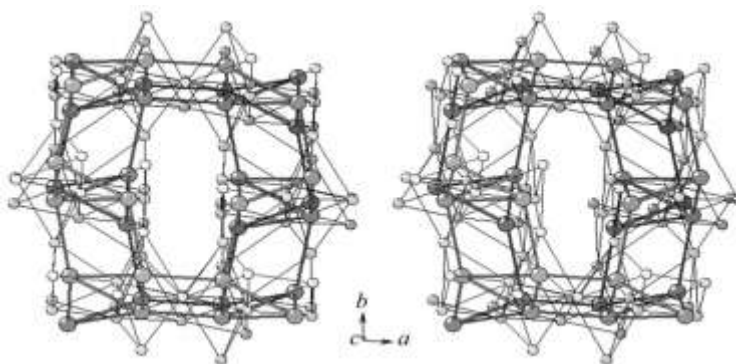


Fig. 1: Stereo pair showing the tetrahedral skeleton in CaAl₄O₇ at normal pressure. The Al-Al contacts are drawn to show the five-connectivity of the Al atoms. The O atoms lying at the center of Al₃ triangles are also seen.

2. EXPERIMENTAL

Host Ca₃Al₁₀O₁₈ was prepared by combustion synthesis with stoichiometric composition of calcium nitrate Ca(NO₃)₂·4H₂O, aluminium nitrate (Al(NO₃)₃·9H₂O and urea (NH₂·CO·NH₂) which acts as a fuel. All constituents

were mixed together. Due to presence of large crystallization water in aluminium nitrate, a thick paste was formed. A china dish containing the paste was inserted in a furnace heated to 500 C. Within minutes the mixture swelled, foamed and finally ignited, yielding a white fluffy powder which was collected after removing the dish from the furnace. Entire process completes within few minutes. Photoluminescence studies of $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ is carried out by doping various rare earth activators such as Ce^{3+} , Eu^{3+} etc. as well as ns^2 activator Pb^{2+} . For doping, the nitrate salt of the appropriate metal in the required quantity was added to the mixture. The stoichiometric ratio of Ca: Al: Urea is taken as 3:10:30.

3. RESULT AND DISCUSSION

Fig. 2. shows stick patterns deduced from the diffraction data obtained for the $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ samples prepared in this work. The patterns are compared with the major lines in the ICDD data file 02-0392. An excellent match is seen but with less relative intensity at low d-values compared to the standard data. Thus by X-ray diffraction pattern it is concluded that the compound $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ was prepared in one step by combustion synthesis without additional thermal treatment.

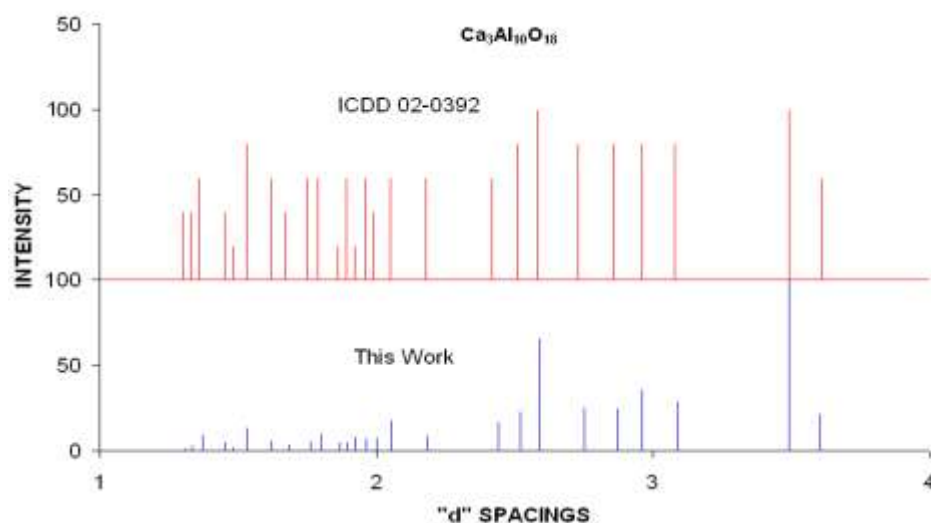


Fig. 2: XRD pattern of $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$

Fig.3(a) shows the emission (solid line) and excitation (dashed line) photoluminescence spectra of the $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ samples doped with Ce^{3+} and Pb^{2+} .

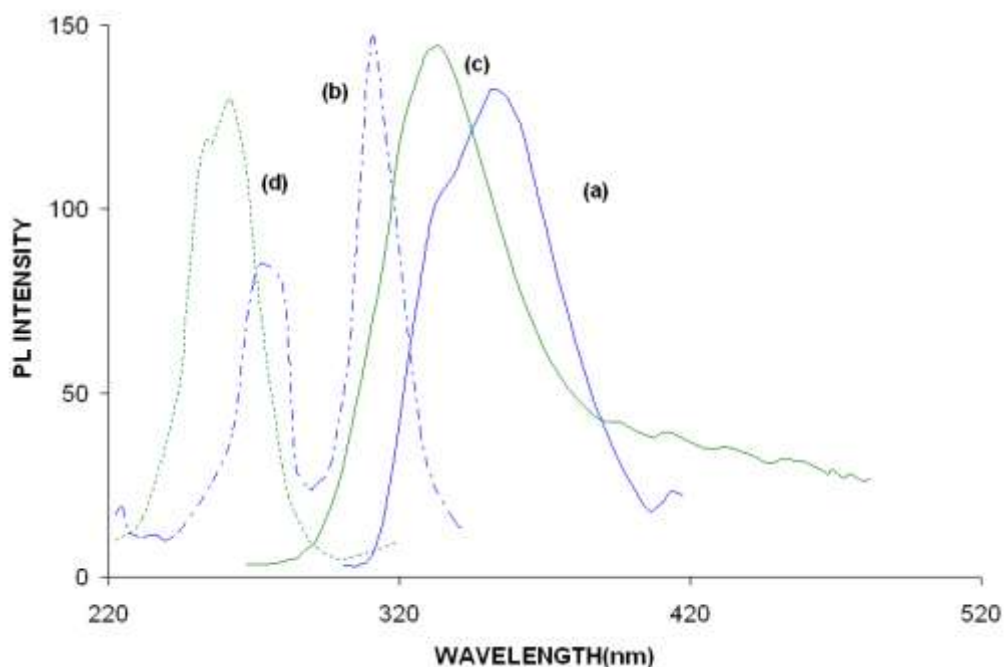


Fig. 3(a): PL Spectra of $\text{Ca}_3\text{Al}_{10}\text{O}_{18}:\text{Ce}^{3+}$

& $\text{Ca}_3\text{Al}_{10}\text{O}_{18}:\text{Pb}^{2+}$

a) Ce^{3+} emission for 274 nm excitation

b) Ce^{3+} excitation for 360nm emission

c) Pb^{2+} emission for 263 nm excitation

d) Pb^{2+} excitation for 335nm emission

The doping concentration of the samples was nominally 1 mol %. The excitation spectra (curve b) were obtained by monitoring emissions peak for Ce^{3+} (i.e. 360 nm). The emission spectra (curve a) were measured upon excitation at 274 nm. Same emission was observed when the sample was excited with 314 nm.

Fig. 3(a) also shows the PL emission (curve c) and excitation (curve d) spectra for Pb^{2+} doped (1mol %) $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$. Emission of moderate intensity is observed in the form of a rather broad band around 335 nm. The excitation band around

263 nm is much narrower. For Pb^{2+} the lowest excited state $^3\text{P}_0$ and $^3\text{P}_1$ are responsible for the luminescence features.

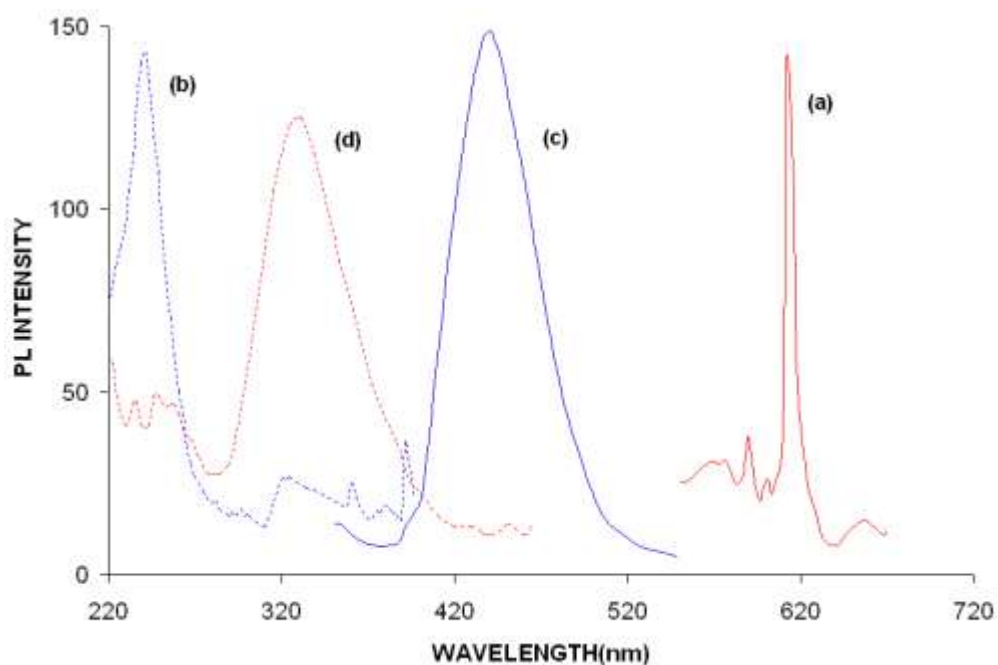


Fig. 3(b): PL Spectra of $\text{Ca}_3\text{Al}_{10}\text{O}_{18}:\text{Eu}^{3+}$

& $\text{Ca}_3\text{Al}_{10}\text{O}_{18}:\text{Eu}^{2+}$

a) Eu^{3+} emission for 242 nm excitation

b) Eu^{3+} excitation for 611 nm emission

c) Eu^{2+} emission for 332 nm excitation

d) Eu^{2+} excitation for 440 nm emission

Europium can act as an activator in two forms, viz. Eu^{2+} and Eu^{3+} . Fig. 3(b) (curve a & curve b) shows photoluminescence emission and excitation spectra of $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ samples doped with Eu^{3+} . The doping concentration of the samples was 1 mol %. Excitation spectra of synthesized material contain broad band attributed to ligand to metal $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$. Upon excitation at 242 nm the Eu^{3+} doped calcium dialuminates exhibit red photoluminescence with the main component peaking around 611 nm and the spectra consists of characteristics lines due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions.



Fig. 3(b) (curve c & curve d) shows photoluminescence spectra for Eu^{2+} in $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$. For the excitation of 332 nm the emission for Eu^{2+} is found to be around 440 nm. Eu^{2+} emission arises from the lowest band of $4f^65d^1$ configuration to $^8\text{S}_{7/2}$ state of $4f^7$ configuration. The excitation arises from the transition from $^8\text{S}_{7/2}$ state of $4f^7$ configuration to the states belonging to the $4f^65d^1$ configuration.

4. CONCLUSION

Results on luminescence in $\text{Ca}_3\text{Al}_{10}\text{O}_{18}$ are reported for the first time. Eu^{3+} , Tb^{3+} , Ce^{3+} and Pb^{2+} doped phosphors are successfully prepared and characteristic luminescence was observed.

5. REFERENCES

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