

Preparation, X-ray analysis and Photoluminescence investigation of $\text{MgAl}_6\text{O}_{10}$ doped with Ce^{3+} and Tb^{3+} using Combustion Synthesis

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Abstract- In the system $\text{MgO-Al}_2\text{O}_3$, three compounds MgAl_2O_4 , $\text{MgAl}_6\text{O}_{10}$ (also expressed as- $\text{Mg}_{0.4}\text{Al}_{2.4}\text{O}_4$) and $\text{MgAl}_{26}\text{O}_{40}$ are well known. Importance of the first two is well established. Magnesium aluminate (MgAl_2O_4) spinel is a technologically important material due to its interesting thermal properties. The MgAl_2O_4 ceramics also find application as humidity sensors. Apart from the luminescence studies, the interest in MgAl_2O_4 is due to various applications such as humidity-sensing and PEM fuel cells, TL/OSL dosimetry of the ionizing radiations, white light source. Interest in the $\text{MgAl}_6\text{O}_{10}$ has aroused due to possible use as a substrate for GaN growth. Attempt was made to synthesize these compounds by the combustion synthesis using metal nitrates as oxidizer and urea as a fuel. Compounds MgAl_2O_4 and $\text{MgAl}_6\text{O}_{10}$ were formed in a single step, while $\text{MgAl}_{26}\text{O}_{40}$ was not formed by this procedure. Activation of $\text{MgAl}_6\text{O}_{10}$ by rare earth ions like Ce^{3+} , Eu^{3+} and Tb^{3+} and ns^2 ion Pb^{2+} could be achieved. Excitation bands for $\text{MgAl}_6\text{O}_{10}$ are at slightly shorter wavelengths compared to those reported for MgAl_2O_4 .

Keywords- aluminate; spinel; combustion synthesis; photoluminescence; phosphor.

1. INTRODUCTION

ICDD records contain files with three different chemical formulae in the system $\text{MgO-Al}_2\text{O}_3$, viz. MgAl_2O_4 , $\text{MgAl}_6\text{O}_{10}$ (also expressed as- $\text{Mg}_{0.4}\text{Al}_{2.4}\text{O}_4$) and $\text{MgAl}_{26}\text{O}_{40}$. The magnesium-aluminum spinel, MgAl_2O_4 in particular, has been comprehensively studied due to notable properties like high melting point (2135 C [1] and interesting thermal and optical properties [2]. MgAl_2O_4 can crystallize in the “normal” or “inverse” spinel structure. Luminescence of several $3d^n$ activators such as Ti^{3+} [3], Mn^{2+} [4], Cr^{3+} [5, 6], as well as $4f^n$ ions like Eu^{3+} [7,8], Tb^{3+} [9,10], Dy^{3+} [11] has also been studied in this host. Apart from the luminescence studies, the interest in MgAl_2O_4 is due to various applications such as humidity-sensing and PEM fuel cells [12]. A variety of methods have been employed in synthesis of MgAl_2O_4 . These include combustion synthesis [13], co-precipitation [14], citrate sol-gel [15, 16], flame spray pyrolysis [16], hydrothermal synthesis [17, 18], Molten Salt Synthesis [19] etc. Not many studies have been carried out on the remaining formulae $\text{MgAl}_6\text{O}_{10}$ and $\text{MgAl}_{26}\text{O}_{40}$. Interest in the former has aroused due to possible use as a substrate

for GaN growth [20, 21]. Several aluminates can be easily prepared by combustion synthesis [22, 23]. It will be interesting to see whether various compounds in the system $\text{MgO-Al}_2\text{O}_3$ system can be prepared by the combustion synthesis.

2. EXPERIMENTAL

Various Mg-aluminates were prepared by combustion synthesis. The detailed description of the methods can be found in the original works of Patil and co-workers. Ingredients used were Magnesium Nitrate ($\text{Mg}(\text{NO}_3)_2$), Aluminium Nitrate, ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), as oxidizer and Urea ($\text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2$) which acts as a fuel. All constituents in the stoichiometric ratios were mixed together. The china dish containing the mixture was inserted in a furnace preheated to 500C. 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. For doping, the nitrate salt of the appropriate metal in the required quantity was added to the mixture. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence spectra at room temperature were

recorded in the range 220-700 nm on Hitachi F-4000 spectro- fluorimeter with spectral slit widths of 1.5 nm.

3. RESULT AND DISCUSSION

This Figure 1 and Figure 2 show stick patterns deduced from the diffraction data obtained for the $MgAl_2O_4$ and $MgAl_6O_{10}$ samples prepared in this work. The patterns are compared with the major lines in the ICDD data file 82-2424 and ICDD data file 87-0345 respectively. An excellent match is seen. Both $MgAl_2O_4$ and $MgAl_6O_{10}$ and is thus formed in one step by the combustion procedure. No high temperature annealing was required.

Diffraction data obtained for the $MgAl_{26}O_{40}$ samples prepared in this work, however did not match with the major lines given by Jagodzinski. The obtained pattern was found to match with ICDD file 81-2266 for $\alpha-Al_2O_3$. It is thus seen that the compounds $MgAl_2O_4$ and $MgAl_6O_{10}$ are formed in a single step by simple combustion synthesis just by taking the constituent nitrates in the stoichiometric ratios, while

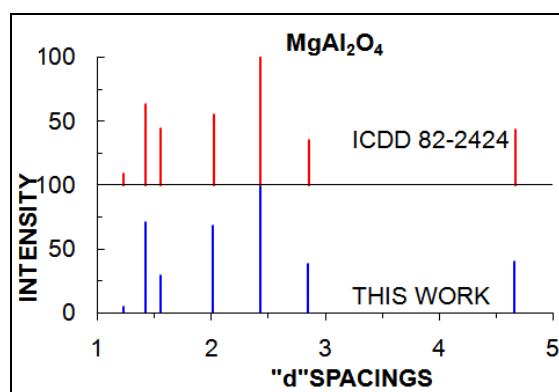


Fig. 1. Stick XRD pattern of $MgAl_2O_4$ compared with ICDD 82-2424

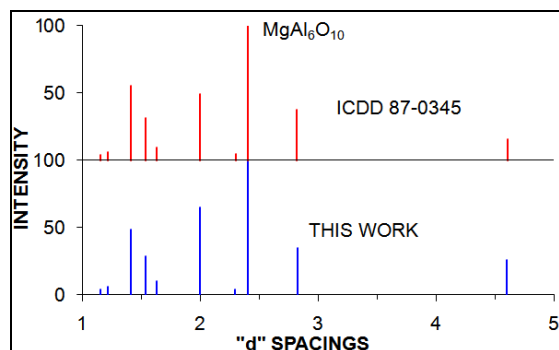


Fig.2. Stick XRD pattern of $MgAl_6O_{10}$ compared with ICDD 87-0345

$MgAl_{26}O_{40}$ is not formed by this procedure. Though luminescence studies have been carried out frequently for $MgAl_2O_4$, there are no data on PL in $MgAl_6O_{10}$ host.

3.1. Rare-earth activators

3.1.1. Ce^{3+}

The 5d-level spectroscopy of Ce^{3+} is very simple. The 4f shell is empty and there is only one single 5d electron interacting with the crystalline environment. The Ce^{3+} ion has the [Xe] $4f^1$ configuration, which results in only two $4f^1$ energy levels: the $^2F_{5/2}$ ground state and $^2F_{7/2}$ excited state. These energy levels are approximately 2000 cm^{-1} apart. At higher energy, the $4f^05d^1$ bands can be found. The energy of the bands is strongly dependent on the host lattice. The $4f^1$ ground state is separated about 51,000 cm^{-1} from the excited $5d^1$ configuration. In a crystalline environment, the 5d configuration may split by as much as 25,000 cm^{-1} into at most five distinct 5d states. In addition, the average energy of the five 5d levels may shift downwards by 22,000 cm^{-1} . The redshift of the first f-d-transition in Ce^{3+} when introduced in a crystalline host is a result of two mutually independent contributions: (1) The centroid shift, defined as the lowering of the average energy of the Ce^{3+} 5d configuration relative to the value for Ce^{3+} as a free ion. (2) The total crystal field splitting; defined as the energy difference between the lowest and highest 5d level. The $4f^05d^1-4f^1$ emission is parity-allowed with a decay time of 3–50 ns. Both absorption and emission have a usually broad band character, showing splitting characteristic of 2F_J states. As the position of 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.

Figure 3 (curves a and b) shows luminescence of Ce^{3+} in $MgAl_6O_{10}$. In $MgAl_6O_{10}$, Ce^{3+} emission is observed (Fig.3, curve a) in form of a broad band with maximum around 397 nm and a shoulder at about 410 nm. The excitation spectrum contains the most prominent band around 327 nm (Fig.3, curve b) and several minor bands characteristic of splitting in crystal environment.

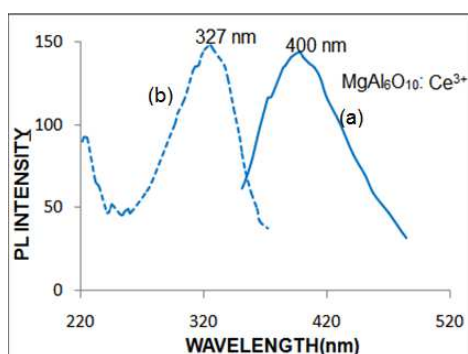


Fig. 3: PL Spectra of Ce^{3+} ions (1 mol %) in $\text{MgAl}_6\text{O}_{10}$
 a) Ce^{3+} emission for 327 nm excitation
 b) Ce^{3+} excitation for 400 nm emission

3.1.2. Tb^{3+}

Results on PL of Tb^{3+} are shown in Fig. 4 (curves a and b). UV excited luminescence of Tb^{3+} can be observed only if f-d excitation band is located in this region or if there is energy transfer from host which absorbs in UV region to one of the levels of $4f^8$ configuration of Tb^{3+} . Emission results from f-f transitions. In most hosts the f-d excitation band is located in deep UV region. $\text{MgAl}_6\text{O}_{10}:\text{Tb}^{3+}$ emission (Fig. 3, curve c) consists of typical lines around 488, 542.6, 587 and 622 nm corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions. There are some weak lines superposed over background corresponding to transition from higher $^5\text{D}_3$ level. The excitation spectrum (Fig. 3, curve d) consists of a prominent band around 247 nm corresponding to the transition from the ground state $^7\text{F}_6$ of $4f^8$ configuration to the excited state of $4f^75d^1$ configuration. These spectra are distinct from those reported for $\text{MgAl}_2\text{O}_4:\text{Tb}^{3+}$. Particularly, the excitation band for $\text{MgAl}_2\text{O}_4:\text{Tb}^{3+}$ is located around 260 nm and strong lines at longer wavelengths corresponding to f-f transitions could be observed. These differences have been interpreted on the basis of the differences in the crystal structures.

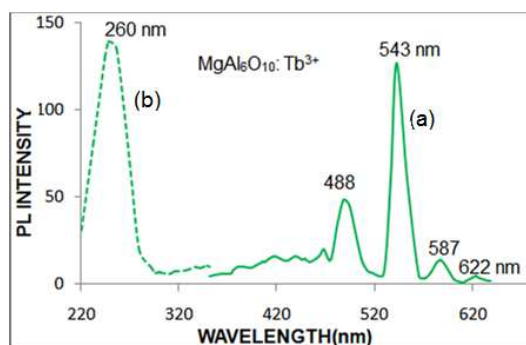


Fig. 4: PL Spectra of Tb^{3+} ions (1 mol %) in $\text{MgAl}_6\text{O}_{10}$
 a) Tb^{3+} emission for 248 nm excitation
 b) Tb^{3+} excitation for 543 nm emission

4. CONCLUSION

Thus out of three compounds in $\text{MgO}-\text{Al}_2\text{O}_3$ system, two viz. MgAl_2O_4 and $\text{MgAl}_6\text{O}_{10}$ could be successfully prepared by one step combustion synthesis. The remaining phase, $\text{MgAl}_{26}\text{O}_{40}$ could not be synthesized. Activation of $\text{MgAl}_6\text{O}_{10}$ by rare earth ions like Ce^{3+} and Tb^{3+} could be achieved. Excitation bands for $\text{MgAl}_6\text{O}_{10}$ are at slightly shorter wavelengths compared to those reported for MgAl_2O_4 .

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