# STUDY OF OPTICAL PROPERTIES OF CERIUM DOPED $NALI_2PO_4$PHOSPHOR SYNTHESIZED BY SOLID STATE METATHESIS

**A.M. Muke[1,†], Jaishri.S. Dhengre[2], Gunjan.M. Raut[2], V. Attatappa[1], Nilesh.V. Gandhare[2], S.V. Moharil[3]**

[1]Department of Physics, Avvaiyar Government College for Women, Karaikal-Puducherry
[2]Department of Chemistry, Nabira Mahavidyalaya, Katol- Maharashtra.
[3]Department of Physics, RTM Nagpur University, Nagpur- Maharashtra
**†Corresponding author's e-mail:** anil.muke@gmail.com

**Abstract:**
**Novel microwave assisted Solid StateMetathesis (SSM) synthesis technique was effectively used for synthesizing$NaLi_2PO_4$:xCe (x=0.01)phosphor. Simple household microwave oven with output power 900W was efficiently used in synthesis process. The Solid State Metathesis reaction is self-propagating type of reaction in which the formation of the high lattice energy by-product like NaCl is solely responsible for carrying the reaction. The metathesis reaction can be initiated by heating the reaction precursors by external sources of energy like microwave electromagnetic waves. Microwave heating is accompanied with several benefits over others routes like shorter reaction time, less consumption of potential energy, improved yield and product uniformity and controlled morphology with desired properties. The structure of $NaLi_2PO_4$:xCe of prepared phosphor was investigated and confirmed by using X-ray diffraction technique. Further, the optical properties specifically photoluminescence of Cerium doped $NaLi_2PO_4$ phosphor was examined.**

**Keywords: $NaLi_2PO_4$:Ce; Photoluminescence; Solid State Metathesis; Microwave**.

## 1. Introduction:

Since many decades, orthophosphates having general formula $ABPO_4$ (here A is monovalent cation and B is divalent cation) are being studied. These compounds form a large family of mono-phosphates with various structures. The relative size of the A and B ions play key role in deciding structure of these mono phosphates. These compounds have high thermal stability and are also known for being used as an efficient luminescent host[1]. The family of Phosphate compounds are commonly known as orthophosphatesand have raised its importance due to their wide applications specifically in the field of solid state lighting. They possess superior optical as well as ferroelectric properties and many intriguing features such as excellent thermal, mechanical, and chemical stability which make them unique for all the types of displays [2].Phosphate compounds have their unique characteristics such as they are capable of providing many crystal field environments which is generally imposed on emission centres. Phosphate material used as a phosphor which can be doped with rare earth ions also exhibit excellent thermal and charge stabilization [3]. Alongside, phosphate compounds are familiar as amultifunctional material. Recently, orthophosphates are being extensively studied because of their structural diversity. These characteristics of orthophosphates are responsible for establishing them as a best host materialwhich caneasily accommodate active rare earth ions.

In this paper, brief information aboutCerium doped $NaLi_2PO_4$ synthesized as a phosphor material is elaborated. Novel Solid State Metathesis using microwave oven is the key method of synthesis. Many researchers tried to synthesize various phosphate material using different methods. P.D. Sahare and Co-workers[4, 5] synthesized Ce doped $NaLi_2PO_4$ using solid state reaction, Bhuli Bai, et al synthesized $NaLi_2PO_4$ doped with 'Cu' [6] and $Eu^{3+}$ doped $NaLi_2PO_4$[7] using solid-state diffusion method. K.N. Shinde et al [8] also synthesized $NaLi_2PO_4$.Tb by solution combustion method and studied its luminescence properties. Before in 2011, same group of researchers successfully studied synthesis of $NaLi_2PO_4$.Eu by solid state reaction [3].

Though all above traditional methods are being used for synthesis of phosphates, till they are associated with certain lacunas. In case of high temperature solid-state reaction, it is time consuming and dissipates enormous quantity of heat. Despite of above drawbacks, solid state reaction still produces relatively large grain size materials. In the precipitation reaction, it is extremely essential to regulate pH value which on ignorance form crystallization of the hydroxide of the concerned phase formation. Hydrothermal synthesis technique is also associated with prolonged reaction time. At the same time, Solegel and reverse micellemethods of synthesis are considered to be more expensive and complicated. Therefore, to overcome these multiple difficulties, simplified technique of synthesis is desired. Here we propose a novel Solid-State Metathesis reaction driven by microwave energy is more preferable over all above traditional synthesis techniques. The method nowadays is emerged as a viable alternative method of synthesis for inorganic phosphors and is being successfully employed in the preparation of wide range of phosphor families[9]. The solid-statemetathesis reaction, which is assumed to be self-propagating type of reaction, in which the formation of the high lattice energy by-product like NaCl is solely responsible for carrying the reaction. The metathesis reaction can be initiated by heating the reaction precursors by external sources of energy like microwave electromagnetic waves. Microwave heating is accompanied with several benefits over others routes like shorter reaction time, less consumption of energy, improved yield and product uniformity and controlled morphology with desired properties.

In this work, Solid State Metathesis which is followed by combustion reaction is carried using simple household microwave oven with 900 W output power.Many compounds like $CaSO_4$.Eu [10], (Ba,Sr)$SO_4$.Eu [11], $CaCO_3$.Tb[12] were prepared by this novel method. The microwave mediated synthesis techniqueand Solid StateMetathesis driven by microwave energy was earlier reported by P. Parhi and researchers in 2008 for synthesis of some phosphates and vanadates[9] using novel microwave assisted solid state metathesis.

## 2. Experimental:

The analytical reagent grade chemicals were preferred for synthesis of $NaLi_2PO_4$.Ce. LiCl.Ce(1%) powder was first prepared by dissolving $Li_2CO_3$and $Ce_2O_3$ in concentrated HCl solution with stoichiometric proportion. Here the ratio of Li:Ce was accurately maintained 99:1. The excess acid was distilled off in a closed assembly. LiCl.Ce (1%) powder so obtained was thoroughly mixed for 30-40 minutes with $Na_3PO_4$powder using mortar and pestlein the proportion compatible with the metathesis reaction.

$$\mathbf{Na_3PO_4+2LiCl.Ce(1\%)\rightarrow NaLi_2PO_4.Ce(1\%)+2NaCl}$$

The high lattice energy of NaCl in above reaction is wholly responsible for driving the reaction in the forward direction resulting into formation of product. The resulting mixture was transferred in to crucibleand then was immediately placed in a domestic microwave oven operating at 2.45 GHz with 900 Woutput power. The mixture was irradiated with microwaves for maximum 10 minutes. After ensuring the completion of combustion process in microwave oven, the crucible was safely removed from the oven. The products obtained wererepeatedly washed with extremely pure distilled water to remove the unreacted $Na_3PO_4$ and/or LiCl, and NaCl formed in the metathesis. The filtrate was then dried on a hot plate at $90^o$ C overnight. The insoluble matter was used for further experiments. X-ray diffraction patterns were recorded on Philips PANalyticalX'pert Pro diffractometer. Photoluminescence (PL) spectra in the spectral range 220–700 nm was recorded on Hitachi F-4000 spectro-fluorimeter with a spectral slit width of 1.5 nm.

## 3. Results and discussion:

Figure 1 shows X-Ray Diffraction pattern of prepared $NaLi_2PO_4:Ce^{3+}$phosphor compared with standard JCPDS data. The peak positions in the diffraction pattern of ourprepared sampleare compared with the standard data available in the literature (JCPDS # 80-2110) [1, 3, 13].Some additional peaks with low intensitywhich may be corresponding to undissolved impurity phases are also observed. From X-ray diffraction pattern it is also revealed that, the final product formed by solid state metathesis using microwave has good crystallinity and homogeneity. Compound formed as $NaLi_2PO_4$ has an orthorhombic crystal structure with its lattice parameter given by a=0.69nm, b = 1nm and c = 0.4938 nm. It wasalso highlighted here that the small amount of doped cerium hasno effect on the resultant phase structures. There is no clear indication regarding presence of characteristic peaksoriginating due to $Ce^{3+}$ ion. This clarifies thatthe addition of $Ce^{3+}$ ion into the$NaLi_2PO_4$as a host does notalter the original crystal structure of thehost matrix.

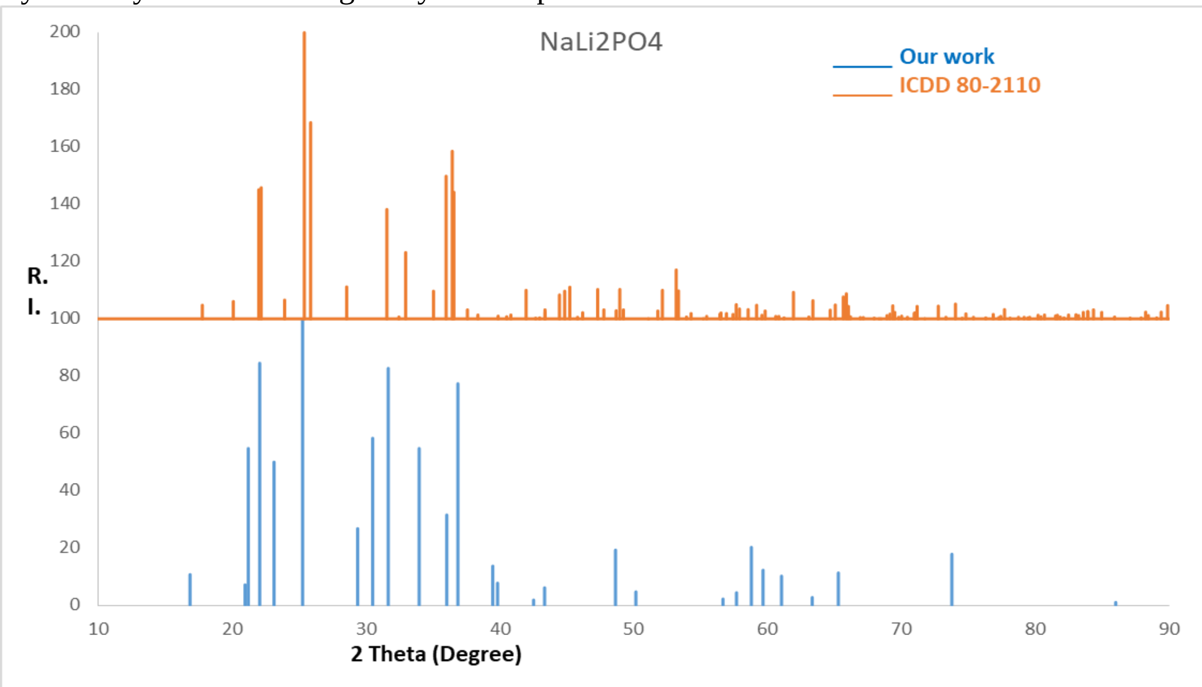


Fig. 1: X-ray diffraction pattern of $NaLi_2PO_4$: $Ce^{3+}$phosphor matched with JCPDF file No. 80-2110

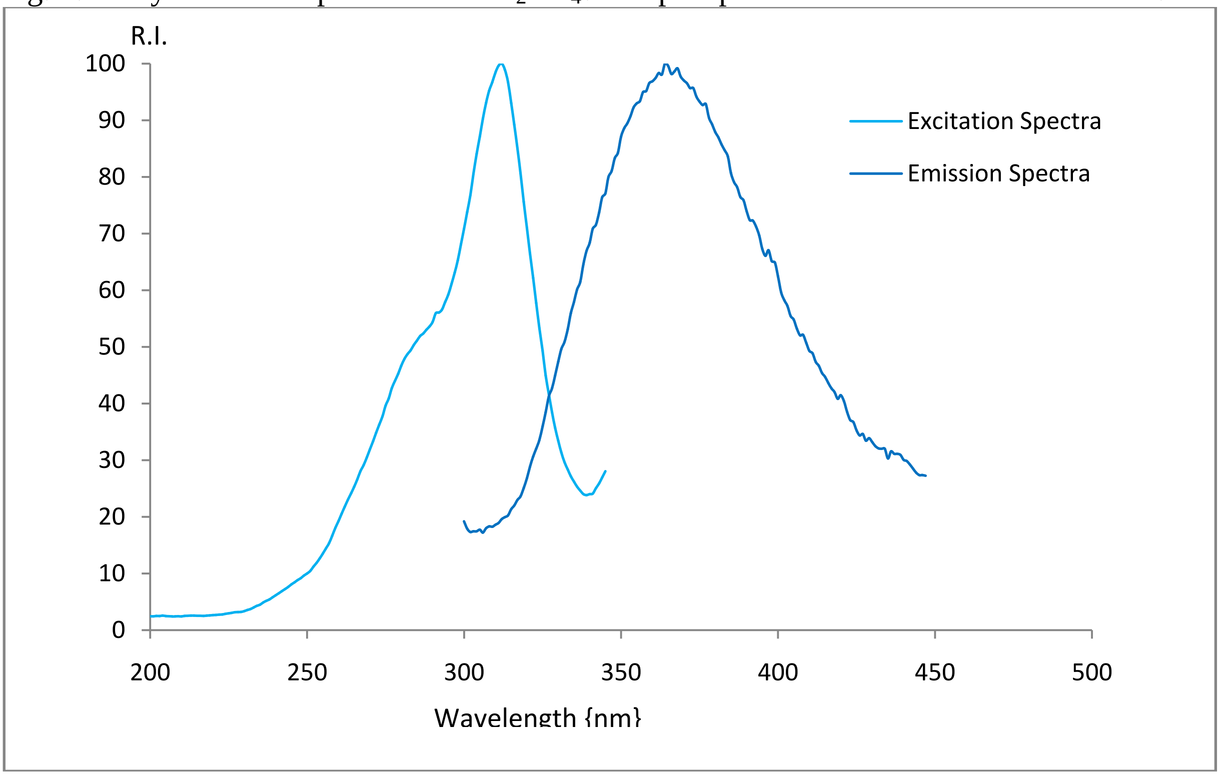

Fig. 2: PLE and PL spectra of a $Ce^{3+}$ doped $NaLi_2PO_4$ phosphor

Fig. 2 shows the PLE and PL spectra of a $Ce^{3+}$ doped $NaLi_2PO_4$ phosphor excited at 312nm which were captured at room temperature.The $Ce^{3+}$ ion doped in $NaLi_2PO_4$host is an efficient luminescence centre with a fastresponse. It has one electron cited in the 4f electronic state that which gets transferred to theempty 5d energy levelafter exciting itby means of electromagnetic radiations of suitable energy. Subsequent de-excitation is seen by an allowed 5 d–4 felectric dipole transition having a decay time of approximately 30 ns.Emission due to$Ce^{3+}$is usually seen in the form of two overlapping bands [14]. The PL emission of the $Ce^{3+}$activator ion is broad and is mainly the effect of 4f-5d allowed transitions as explained above. It can be inferred from the emission curve that our PL spectrum consists of only one peak centred at around 365 nm which is attributed to the typical electric dipole transitions of $^5d_1$to the $^4f1$ ($^2F_{7/2}$).

## 4. Conclusions

The Orthophosphate $NaLi_2PO_4:Ce^{3+}$ phosphor was successfully synthesized by novel technique of synthesis called as solid state metathesis using microwave oven. The X-Ray Diffraction pattern of so prepared sample $NaLi_2PO_4$ was in good agreement with the JCPDS standard file with card no.# 80-2110. Some extra peaks found in XRD of sample was inferred to be due to unreacted parts of the reaction. PL excitation spectra of$NaLi_2PO_4:Ce^{3+}$ is broadand is mainly the effect of 4f-5d allowed transitions. Solid-state metathesis (SSM) is an emergent method of synthesis and had found competent and viable alternative method of synthesis of inorganic phosphors. The method has been successfully employed in the synthesis of phosphates as a luminescent material.

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