

# Novel microwave initiated solid-state metathesis synthesis and characterization of lanthanide phosphates and vanadates, $LMO_4$ ( $L = Y, La$ and $M = V, P$ )

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## Abstract

A novel solid-state metathesis (SSM) approach represented by the reaction  $(LCl_3 + Na_3VO_4 \rightarrow LVO_4 + NaCl)$  ( $L = Y, La$ ) is proposed to synthesize technologically important rare-earth phosphates and vanadates. The SSM reaction, driven in the forward direction is facilitated by the formation of high lattice energy by-product like NaCl. The structural, thermal, optical, and chemical properties of synthesized powders are determined by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), and diffused reflectance (DR) spectra in the UV–vis range. The direct band gap of the synthesized materials was found out to be  $\sim 3.5$  eV for  $LaVO_4$ ,  $YVO_4$ ,  $YPO_4$  and  $\sim 2.6$  eV for  $LaPO_4$ .

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## 1. Introduction

Lanthanide metal oxides have received attention due to their potential applications in various fields such as phosphors, ion exchangers, sensors, and nonlinear optics (NLO) [1–5]. Lanthanide metal phosphates ( $YPO_4$  and  $LaPO_4$ ) have found applications either in the form of powders, coatings or dense sintered parts in fluorescent lamps, laminate composites, fiber–matrix composites or thermal protection coatings, to name a few. Similarly, yttrium ortho-vanadate ( $YVO_4$ ) has been extensively used as a red phosphor with several rare-earth metal ions as dopants in cathode ray tubes (CRTs) and color televisions in powder form [6–8].  $LaVO_4$  is well-known for catalytic as well as magnetic, luminescent and solid-state protonic conducting properties [9–11].

Synthesis of the technologically important  $LMO_4$  ( $L = La, Y$  and  $M = P, V$ ) has been well reported in the literature.  $LVO_4$

( $L = La, Y$ ) has been synthesized by high temperature solid-state reaction [12], mechanochemical [13,14], precipitation [15,16], hydrothermal [8,17], and micro-emulsion methods [17,18], etc. Similarly,  $LPO_4$  ( $RE = La, Y$ ) phosphates have been synthesized by solid-state reaction [19,20], mechanochemical [21,22], precipitation [23,24], hydrothermal [25,26] and micro-emulsion methods [27,28]. In general it has been observed that the chemical composition, grain size, morphology of particles as well as the associated properties of the materials are strongly influenced by the method of compound preparation. Therefore, it is important to tailor the method of synthesis for  $LMO_4$  ( $M = V, P$ ) compounds to have the desired optimum properties.

There are several disadvantages of the above mentioned syntheses that need to be overcome. For example, synthesis of phosphovanadate materials by ball milling, where longer grinding time is applied, result in damage of the crystal particle size which causes lower luminescent efficiency. Normally, high temperature solid-state reactions produce relatively large grain size materials in addition to oxygen defect color centers. In the precipitation reaction, proper care in regulating pH has

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to be taken in order to avoid the hydroxide of the respective phase formation. Hydrothermal synthesis, in general, needs longer reaction time. Sol–gel and reverse micellar synthesis methods are expensive, complex and the yield is a concern. Therefore, a simplified method that can overcome the disadvantages, like long-reaction time, high temperature treatment requirement, complicated processing, use of expensive equipment, or poor yield is desired. We propose a novel solid-state metathesis reaction driven by microwave energy as a method of synthesis for these materials.

Solid-state metathesis (SSM) method of synthesis is emerging as a viable alternative method of synthesis of inorganic solids and has been successfully employed in the preparation of oxides, chalcogenides, oxide superconductors, metal halides, nitrides, etc. [29–38]. We have recently shown the room temperature synthesis of  $Zn_3(PO_4)_2$  by solid-state metathesis method [39]. The metathesis reaction, which is a self-propagating type of reaction, where the formation of the high lattice energy by-product like NaCl drives the reaction in the forward direction, can be initiated by heating the reaction precursors by external sources of energy like using nichrome wire heating, and microwave electromagnetic waves, etc. There are several advantages in microwave heating which include the potential for energy saving, shorter processing time, improved product uniformity, yields and controlled microstructure with desired properties and formation of novel materials. Accordingly, we have chosen solid-state metathesis reactions driven by microwave energy as our synthetic approach.

There are few reports of synthesis of  $LMO_4$  ( $L = La, Y$  and  $M = P, V$ ) using microwave [40,41]. However, such reactions have either been carried out in pH adjusted solutions, ionic liquid-based solutions involving complex steps or pre-treatment like ball milling of the reactants before subjecting to microwave energy [41–47]. Microwave mediated synthesis of  $LaVO_4$  is not reported in the literature. Also, solid-state metathesis driven by microwave energy has not been reported, so far, for both  $LaVO_4$  and  $YVO_4$  compounds. The synthesis approach is characterized by high yield, less reaction time, use of less-expensive capital equipment as well as producing products with controlled morphology. In addition, to probe the driving force for the metathesis reactions we have calculated the enthalpy ( $\Delta H$ ) and free energy changes ( $\Delta G$ ) associated with the reactions. The synthesized products have been characterized for structure–property relationship which included the measurement of optical band gap for these materials.

## 2. Experimental

$Na_3VO_4$ ,  $LaCl_3 \cdot 7H_2O$ ,  $YCl_3 \cdot xH_2O$ , and  $Na_3PO_4$  obtained from Alfa Aesar, USA were employed for the preparation of the title compounds. Preparation of  $YVO_4$  powder was carried out by grinding  $Na_3VO_4$  and hydrated  $YCl_3$  in a molar ratio 1:1 in a pestle mortar followed by treating the reactants in a domestic microwave (2.45 GHz, operating at 1100 W power) for 10 min. The final product was obtained by washing the powder

with 50 ml of deionised water and acetone and drying the product in an oven at 80 °C. XRD patterns of the synthesized sample were recorded. Preparation of  $LaVO_4$  was carried out similarly by reacting hydrated  $LaCl_3$  and  $Na_3VO_4$ .  $YPO_4$  and  $LaPO_4$  were synthesized by the procedure mentioned above. The amorphous product obtained in both cases was subjected to further heat treatment to get the desired crystalline product.

Powder X-ray diffraction (XRD) measurements were carried out with Scintag X2 diffractometer with  $Cu K_{\alpha}$  radiation and Peltier detector. A scan rate of 1 °/min with a step size of 0.02° was employed to obtain the XRD spectra. Search match analysis was performed using Bruker EVA software. SEM characterization was performed on the JSM-6500F, a field emission system with the In-Lens Thermal Field Emission Electron Gun (TFEG). Diffuse reflectance spectra were recorded in the wavelength range 250–2500 nm using Varian Associates Cary 500 double beam spectrophotometer equipped with Praying mantis. Employing Aluminum mesh (1.1Abs) as a rear beam attenuator compensated the reflection losses in the Praying mantis. Compressed polytetrafluoroethylene (PTFE) was used for standard calibration (100% reflectance). X-ray photoelectron spectroscopy (XPS) experiments were performed on a Physical Electronics 5800 spectrometer. This system has a monochromatic  $Al K_{\alpha}$  X-ray source ( $h\nu = 1486.6$  eV), hemispherical analyzer, and multichannel detector. A low energy (30 eV) electron gun was used for charge neutralization on the non-conducting samples. DSC was carried out with modulated differential scanning calorimeter with liquid nitrogen accessory (TA Instruments, Model DSC 2920). The samples were hermetically sealed in Al pans and heated from room temperature to 600 °C at a ramp rate of 10 °C/min.

## 3. Results and discussion

Fig. 1 shows the XRD of the as-synthesized products. XRD of the product before washing showed the presence of NaCl (marked with \* in Fig. 1a). The presence of NaCl confirmed the reaction has proceeded in a metathetic pathway, as established in the literature. The metathesis reaction is represented as follows:



The high lattice energy of NaCl drives the reaction in the forward direction enabling the product formation. Fig. 1b shows the XRD pattern of  $YVO_4$  after washing. Comparison of the XRD pattern with the standard JCPDS confirmed the single-phase nature of the compound.  $YVO_4$  crystallizes in the tetragonal system with  $a = 7.12$  Å,  $c = 6.289$  Å, space group  $I4_1/amd$ . XRD of  $LaVO_4$  after washing confirms (Fig. 1c) single-phase nature of the compound in comparison with JCPDS in Ref. [48].  $LaVO_4$  crystallizes in the monoclinic system with  $a = 7.047$  Å,  $b = 7.286$  Å,  $c = 6.725$  Å and  $\beta = 104.85^\circ$ , space group  $P2_1/n$ . Synthesis of  $LPO_4$  ( $L = La, Y$ ) was performed similar to the vanadate synthesis described above using

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