## **B. TECH. PROJECT REPORT**

On

# Synthesis and Application of Orthovanadate Materials

BY

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## **Synthesis and Application of Orthovanadates**

#### A PROJECT REPORT

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#### **CANDIDATE'S DECLARATION**

We hereby declare that the project entitled "Synthesis and Application of Orthovanadate Materials" submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Metallurgy Engineering and Materials Science' completed under the supervision of Dr. Ajay Kumar Kushwaha (Assistant Professor, Discipline. of MEMS and Dr. Somaditya Sen, Discipline of Physics, IIT Indore is an authentic work.

Further, we declare that we have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student(s) with date

#### **CERTIFICATE by BTP Guide(s)**

It is certified that the above statement made by the students is correct to the best of our knowledge.

Signature of BTP Guide(s) with dates and their designation

## **Preface**

This report on "Synthesis and Application of Orthovanadate Materials" is prepared under the guidance of Dr. Ajay Kumar Kushwaha and Dr. Somaditya Sen.

This work presents the sol-gel synthesis and characterization of CeVO<sub>4</sub>, SmVO<sub>4</sub>, and LaVO<sub>4</sub>. These vanadate materials are known to be excellent host materials for  $Ln^{3+}$  ions. The comparison is made by performing XRD analysis, FESEM, XPS, EDX, and PL spectroscopy. Through this report, we aim to give a detailed idea of better materials for optoelectronic devices and try to fulfill the requirements as needed by the society these days for better results, and if the material is technically and economically sound and feasible.

We have tried to the best of our abilities and knowledge to explain the content in a lucid manner. We have also added figures and graphs to make it more illustrative.

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We wish to thank Dr. Ajay Kumar Kushwaha and Dr. Somaditya Sen for their kind support and valuable guidance. It is through their help and support by which we were able to complete the design of this technical report.

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We would like to express our special thanks of gratitude to our supervisor(s) Dr. Ajay Kumar Kushwaha and Dr. Somaditya Sen who gave us this golden opportunity to do this beautiful project on the topic 'Synthesis and Application of Orthovanadate materials' as well as our respected HOD Dr. Parasharam M. Shirage and the MEMS department DUGC, Dr. Santosh S. Hosmani, the doctorate students and other lab members who helped us a lot in gathering information, collecting data and guiding us from throughout the length of this project, despite their busy schedules, they provided us with ideas as to the direction to be pursued to make this project unique. This also helped us in doing exceptional research, and we came to know about new ideas and concepts we are really thankful to them.

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#### ♦ <u>Abstract:</u>

Cerium, Lanthanum, and Samarium orthovanadate particles (CeVO<sub>4</sub>, LaVO<sub>4</sub>, and SmVO<sub>4</sub>) were fabricated using the sol-gel combustion method. Fabricated CeVO<sub>4</sub>, LaVO<sub>4</sub>, SmVO<sub>4</sub> particles were sintered at different temperatures (600°C, 750°C, 900°C) to study the differences observed in the results of the different characterization techniques. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of synthesized LaVO<sub>4</sub>, SmVO<sub>4</sub>, and CeVO<sub>4</sub> particles and can provide information regarding unit cell dimensions (which changed with sintering temperature). Finely ground powder particles were used to obtain XRD data. The average bulk composition is determined by this technique. The morphological shape and the crystalline nature were examined by Energy-dispersive X-ray spectroscopy (EDX), Field Emission Scanning Electron Microscopy (FESEM) affirmed the presence of elemental composition and purity of fabricated samples. The morphological shape of the fabricated particles was observed to change with sintering temperature. Fourier Transformation Infrared Spectroscopy (FT-IR), excite vibrations of molecular bonds by absorption of infrared photons, was used to characterize the different bonds and types of vibrations present in the compounds. Spectra of the characteristic bands were produced that can be used as a fingerprint to identify and characterize the LaVO<sub>4</sub>, SmVO<sub>4</sub>, and CeVO<sub>4</sub>. Vibrational modes of LaVO<sub>4</sub>, SmVO<sub>4</sub>, CeVO<sub>4</sub> molecules can be easily determined by Raman spectroscopic technique, in spite of the fact that we can also observe rotational and other low-frequency modes of systems.

The lanthanides (Ce - Lu) are unique among the elements, in aqueous solutions trivalent state  $Ln^{III}$  ([Xe]4f<sup>n</sup>, n= 0-14) shown by the atoms and their derived ions. The 4f–4f transition is the result of the shielding of the 4f orbitals by the filled 5p<sup>6</sup> 6s<sup>2</sup> sub-shells.

The studies describing the synthesis of CeVO<sub>4</sub> particles by a simple sol-gel auto combustion method followed by the investigation of antifungal activities may be useful for the research activities to open a new horizon in the field of nanotechnology.

A sol-gel method was employed for the synthesis of LaVO<sub>4</sub>, SmVO<sub>4</sub>, and CeVO<sub>4</sub> samples. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Raman and PL spectroscopy were used to characterize the obtained samples. The characterization revealed that uniform microcrystals and pure Tetragonal Zircon phase of CeVO<sub>4</sub> and SmVO<sub>4</sub> and the Monoclinic Monazite phase of LaVO<sub>4</sub>.

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#### Abbreviations used:-

LVO	- LaVO <sub>4</sub>
LVO 600	– LaVO4 600°C
LVO 750	– LaVO4 750°C
LVO 900	– LaVO4 900°C
CVO	$-CeVO_4$
CVO 600	- CeVO <sub>4</sub> 600°C
CVO 750	$-CeVO_4750^\circ C$
CVO 900	- CeVO <sub>4</sub> 900°C
SVO	$-SmVO_4$
SVO 600	– SmVO4 600°C
SVO 750	- SmVO <sub>4</sub> 750°C
SVO 900	– SmVO <sub>4</sub> 900°C
Fig.	– Figure
PL	- Photoluminescence

#### Chapter -1

#### **1.1 Introduction:**

Research has always been fuelled by human curiosity and the search for materials or instruments to fill the needs of the household and industrial purposes. This thirst for something better will go on as long as humans exist, as even a highly efficient instrument or material could be replaced by a more efficient or cheaper material not very long into the future. Orthovanadates, are a distinct group of compounds with unique crystal structure and applications in multiple fields. In the family of inorganic materials, rare earth orthovanadates (RVO<sub>4</sub>) are an important compound [1,2]. A monoclinic monazite type and a tetragonal zircon type are the two polymorphs of the RVO<sub>4</sub> structure [2]. The ionic radii of rare earth elements influencing the phase of the individual RVO<sub>4</sub>. Since the monazite phase has a higher coordination number, the larger La prefers to crystallize in the monoclinic monazite phase, instead of the tetragonal zircon phase [2].

Rare-earth-activated luminescence, magnetic and Jahn-Teller phase transitions are various physical properties exhibited by LnVO<sub>4</sub> compounds. These compounds are the subject of various experimental and theoretical investigations [3-9]. For the oxidative dehydrogenation of propane, these can act as a potential catalyst [3]. Among the binary system, Ln<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> lanthanide orthovanadates are major compounds that have been characterized via crystallography.

Among rare earth orthovanadates (denoted by LnVO<sub>4</sub>), the compounds are found to exhibit multiple crystal structures, they primarily exist in Monoclinic Monazite (space group: P21 /n, Z=4) and Tetragonal Zircon (space group: I41 /amd, Z=4) at ambient temperature and pressure, this existence in two crystal structures is governed by the size of the A-site atom. However, a phase transition has been achieved via the application of high pressure and much research has been done to understand the conditions under which these transitions occur. Meanwhile research concluded an irreversible zircon to Tetragonal Scheelite (space group: I41 /a), among the orthovanadates with smaller A-site atoms which include HoVO<sub>4</sub> , EuVO<sub>4</sub> , TbVO<sub>4</sub> , SmVO<sub>4</sub> and LuVO<sub>4</sub> at high pressures ranging from 6 to 8 GPa and a reversible scheelite to fergusonite (space group: I41 /a) at even higher pressures[10] . A second reversible transition to an orthorhombic phase is observed in NdVO<sub>4</sub> and CeVO<sub>4</sub> at 18.1 and 14.7 GPa respectively [11]. Lanthanide orthovanadates are irreplaceable as catalysts, polarisers, solid-state protonic conductors, phosphors and low threshold laser hosts [12].

Many routes are available for the preparation of LnVO<sub>4</sub> systems like solid-state reactions and precursor routes. Because luminescent lanthanide ions have many applications presently, attention focuses on:[13] (i)continuous use for the engineering of lamp phosphors in the lighting industry,[14] (ii) their potential to give electroluminescent materials for organic light-emitting diodes and optical fibres for telecommunications, [15] and (iii) their ability to produce functional complexes for biological assays [16, 17] and medical imaging purposes [18].

Lanthanum orthovanadate LaVO<sub>4</sub> has attracted much interest from the researchers from the last decade both from a fundamental point of view and from the prospect of applications due to its surface catalytic properties. Firstly, Ropp and Carroll reported the preparation of nanocrystalline LaVO<sub>4</sub> [19] where the reaction of  $La^{3+}$ and  $VO^{2+}$  occurs with NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub>. LaVO<sub>4</sub> is at odds with the rest of the lanthanide orthovanadates in that it exists in the monazite phase, whereas the rest exists in the zircon phase in ambient conditions. The  $Ln^{3+}$ ions in the lattice in the zircon and monazite phase have a coordination number of 8 and 9 respectively. The oddity in the crystal structure of LaVO<sub>4</sub> is accredited to the larger size of  $La^{3+}$  (as larger ions prefer to have higher coordination numbers) when compared to the rest of the Ln<sup>3+</sup> ions. The 3d electron configuration of La<sup>3+</sup> (3d<sup>10</sup>) is reported to exhibit antiferromagnetic at certain temperatures range below room temperature down to 140K. Therefore, the interplay of orbital, spin and vibrational motions of  $V^{5+}$  and  $La^{3+}$  ions may lead to a sequence of phase transitions involving changes in the structural, magnetic and optical properties of this compound [20]. In order to reveal such phenomenon in monazite LaVO<sub>4</sub>, low-temperature synchrotron X-ray diffraction measurements were carried out to study structural phase transition in this material along with Raman and photoluminescence studies at room temperature to characterize the structure-property relationship and its potential applications. Past research on LaVO<sub>4</sub> was mostly linked to the stabilization of its metastable zircon state by doping other rare earth elements such as; Eu, Dy, Sm, Tb, Yb, Er [21]. In another study with a similar  $La_{1-x-y}Eu_yCa_xVO_4(0 < x, y < 0.2)$ , it was synthesized, characterized, and its properties with increasing Ca and Eu were studied [22].

Tetragonal zircon-type structure shown by cerium orthovanadate (CeVO<sub>4</sub>) which belongs to space group  $I4_1/amd$  [23–26]. By application of pressure zircon-type CeVO<sub>4</sub> transformed into a metastable monazite-type CeVO<sub>4</sub>. However, the transformation of stable monazite to a metastable zircon is not observed.

The compound exhibits unique electronic [26–28], optical [26–30], magnetic [26–30], catalytic [29, 30], and luminescent [29, 30] properties. It has extensive possible applications in different fields, like oxidative catalyst [27, 30, 31, 33], gas sensors [27, 31, 32], luminescence [27, 30], electrochromic material [29, 33], and components of solid oxide fuel cells (SOFCs) [31, 32, 33]. Previous methods of cerium orthovanadate synthesis were reported: hydrothermal method [1, 2, 33], microwave-assisted synthesis [29, 31], sonochemical method [2, 30], and sol-gel [25]. Ce is the borderline element among the lanthanides in that it exists at the boundary where the phase changes from monazite in LaVO<sub>4</sub> to zircon for the rest occurs.

For lanthanides, we get configurational f-f transitions because the emission is due to transitions inside the 4f shell as the closed  $5s^2$  and  $5p^6$  shells shield the partially filled 4f shell and shielding it in a better way.

Disturbance in the electronic configurations of the trivalent lanthanide ions but only to a limited extent is created by the ligands in the first and second coordination spheres. This shielding property is accountable for the specific properties of lanthanide luminescence, especially for the long lifetime and narrowband emission of the excited states.  $Ce^{3+}$  ion emits intense broadband emission, and this particular case is because of allowed f-d transitions. The ligand environment of the  $Ce^{3+}$  ion can cause significant variation in the position of the emission. Based on the method of excitation, various types of luminescence can be defined , for example , photoluminescence [in which electromagnetic radiation by irradiation after excitation creates emission] , electroluminescence [in which electrons and holes recombine under the influence of electric field and thus creates emission], chemiluminescence [in which chemical reaction produces non thermal light], triboluminescence [in which on applying mechanical stress to crystals or by fracture of crystals can produce emission]. Minimal amounts of radiation were absorbed by direct excitation in the 4f levels since the molar absorption coefficient ( $\varepsilon$ ) of most of the transitions in absorption spectra of trivalent lanthanide ions are smaller than 10 L mol<sup>-1</sup> cm<sup>-1</sup>. Weak light absorption results in weak luminescence because the luminescence is not only proportional to the luminescence quantum yield but also to the amount of light absorbed. From the so-called antenna effect [or sensitization], the problem of weak light can be overcome.



Figure: 1 Vanadate (3-) is a vanadium oxo anion that is a trianion with formula  $VO_4^{3-}$  in which the vanadium is in the +5-oxidation state and is attached to four oxygen atoms.



Figure2:- Crystal structure of LVO, SVO, and CVO.

Photocatalysis by solar energy has played an important role [34,35] in solving global energy and environmental crises. Many areas like air purification, wastewater treatment, water splitting to produce hydrogen gas, and other environmental problems[29,35,36] have used this type of photocatalysis. Lanthanide orthovanadates can act as photocatalysts which can be used for the degradation of dyes and organic compounds [37]. For the degradation of methylene blue, rare earth orthovanadates can act as a photocatalyst that was reported by Mahapatra et al. [24] and Selvan et al. [2].

Because rare-earth compounds have unique electronic structures and numerous transition modes involving 3d and 4f shell of lanthanide they can be used widely in many practical applications [37,44]. In cathodoluminescence and lithium-ion batteries, as well as thermo-phosphors, scintillators, photocatalysis materials, and as a laser-host material, these are a number of important applications of rare-earth orthovanadates.[45] In shorter-wavelength photo-electric devices, especially for photo-detectors, ultra-violet laser diodes, and phosphor host materials vanadate group materials are very useful materials [46,47]. Lanthanide-doped lanthanum orthovanadates (LaVO<sub>4</sub>) have been widely studied for various applications, like solar cells [49], laser host materials [48], and thin-film phosphors [50].

They crystallize in the tetragonal zircon- type structure (space group: I41/amd, Z = 4).[51], with LaVO<sub>4</sub> as an exception. Transformations to denser phases [52-54] for these compounds is easily done under moderate compression. Particularly, the tetragonal scheelite-type structure (space group: I41/a, Z = 4) is transformed by the compounds with small rare- earth cations while the monoclinic monazite-type structure (space group: P21/n, Z = 4) is transformed by the large cations. These phase transformations have enticed a lot of attention [55-58] because of their fascinating technological applications, geophysics, and geochemistry. These factors made it quite avoidable that the material can depict some of the optoelectronic properties.

#### **1.1.1 Introduction to XRD:**

X-rays produced in powder X-ray diffraction can be used to investigate and quantify the crystalline nature of materials by making use the coherently scattered X-rays from the planes of atoms within the material. Single crystal XRD has the limitation that all possible orientations of the crystal can't be identified, hence the requirement of polycrystalline powder XRD. The intensity of the peaks of the XRD is dependent on the type of atom and their position in the crystal. The position of the peaks however, is completely dependent on the cell parameters. Measurement of crystalline content of materials; also the identification of crystalline phases present (including the quantification of mixtures in favorable cases) and well as the percentage of different phases, if present can be quantified; it can also be used; determine the spacing between lattice planes and the length scales over which they persist; study preferential ordering and epitaxial growth of crystallites. In essence, it probes length scales from approximately sub angstroms to a few nm and is sensitive to ordering over tens of nanometres.

The samples for analysis are usually in the form of fine powders, but diffraction can also be obtained from surfaces, provided they are relatively flat and not too rough. Moreover, the materials can be of a vast array of types, including inorganic, organic, polymers, metals or composites and are useful in almost all research fields, e.g. metallurgy, pharmaceuticals, earth sciences, polymers and composites, microelectronics and

nanotechnology. Powder XRD can also be applied to study the pseudo crystalline structure of mesoporous materials and colloidal crystals provided that the particle size is within ideal range.

#### **1.1.2 Introduction to FESEM:**

FESEM (Field Emission Scanning Electron Microscope) is a microscope that works with electrons in place of visible ligh as in the case of the optical microscopes. These electrons are discharged by a field emission source. The object is scanned by electrons adhering to a zig-zag movement pattern. A FESEM is used to visualize very small morphological details of the material or entire or fractionated objects. Biology, chemistry, and physics are fields were this technique is applied to observe structures that may be in the nanometer size range.

A high electric field is applied to accelerate the electrons emitted by the field emission source. Within the high vacuum column, these so-called primary electrons are focussed and directed by electric lenses to produce a narrow scanning beam that bombards the object. As a result, secondary electrons are emitted from each spot on the object. Surface structure of the object is obtained from the angle and velocity of these secondary electrons . A detector is used to capture the secondary electrons and produces an electronic signal. This signal is amplified and converted into a video scan-image that can be seen on a monitor or to a digital image that can be saved and processed further.

#### 1.2 Objective:-

In existing and future technologies rare-earth orthovanadates play an important role in the field of material science. A while back a significant amount of research has been done on these materials and they have attracted attention because of their wide application in alternative green technologies. [59]

1. Orthovanadates are best- fit for laser-host materials. [60]

**2.** Orthovanadates are favorable materials for biomedical applications such as controlled delivery of the drug into the body of humans [61] because they exhibit properties like luminescence, chemical stability, and non-toxicity.

**3.** In the course of the last few years, various studies have been done on orthovanadates to investigate their visible light response [64], luminescence properties [62,63] and their photocatalytic activity [64].

**4.** As shown in Figure 3, where the 4 and 9-fold coordination exhibited by  $V^{5+}$  and the La<sup>3+</sup> ions respectively and VO<sub>4</sub> polyhedra share corners and edges with the LaO<sub>9</sub> ones. Thus, the monazite-type structure (space group P21/n, Z = 4) shown by LaVO<sub>4</sub>[65] (Figure 3)

**5.** We aim to characterize the compounds LaVO<sub>4</sub>, SmVO<sub>4</sub>, and CeVO<sub>4</sub>, to see how their characteristics vary with temperature so as to maximize the properties which are sought after.

**6.** Ce existing on the borderline of the different phases exhibited by La (space group: P21/n, Z=4) and the rest of the lanthanides (space group: I41/amd, Z=4), considering the extreme conditions under which the phase transitions occur Ce could be a prospective factor for bringing about an easier phase transition, and Sm being photoluminescent could be used in place of Yttrium, for LASER based applications.



Figure: - 3 Crystal structures of LaVO4(at low and high pressure). The green dodecahedra signify La in nine-coordination with O and the red tetrahedra signify the VO4 tetrahedra.

#### Chapter - 2

#### 2.1. Experimental/Methodology:-

The sol-gel process (gelation): In this process polycondensation reaction occur which causes a liquid state to change into a gel state. A sol is a stable dispersion of amorphous or crystalline colloidal particles(of typical size few nm.) or polymers in a solvent. A gel consists of a three-dimensional continuous network of the sol particles, which encloses a liquid phase. In a colloidal gel, agglomeration of colloidal particles builds a network whereas, in a polymer gel, aggregation of sub-colloidal particles make a polymeric substructure. Covalent bonding, Van Der Waal- and H-bondings are formed during gelation.



Figure4:- Transformation of Sol into Gel depicted through the diagram.



**Figure 5:- Flowchart explaining the Sol - Gel Transformation** 



Figure 6:- The Experimental Setup as performed by us for Sol-Gel process

#### Polymeric sols: Gelling via condensation

Porous structures, thin fibers, dense powders, thin films, and many more shapes of the material may be prepared by using the sol-gel method

LaVO<sub>4</sub> (hereafter called LVO), SmVO<sub>4</sub> (SVO) and CeVO<sub>4</sub> (CVO) samples were prepared via sol-gel method using Lanthanum (III) oxide (La<sub>2</sub>O<sub>3</sub> of purity 99%), Cerium (III) nitrate (Ce(NO<sub>3</sub>)<sub>3</sub> of purity 99.9%), Samarium (III) oxide (Sm<sub>2</sub>O<sub>3</sub> of purity 99.9%), and Vanadium (V) oxide (V<sub>2</sub>O<sub>5</sub> of purity 99.9%) from Alfa Aesar. Citric acid and Ethylene glycol are added to the mixture, which serves the purpose of gelling agent and drying agent respectively. In a separate solution, a mixture of citric acid and ethylene glycol was prepared. These two chemicals, when heated form monomers which thereafter combine to form a polymeric gelling agent that serves as a gelling agent and a fuel for a combustion process. Heating at a temperature of about (~50° C) ensures homogeneous attachment of the precursor ions to the polymeric chains. After the dehydration of the gels due to continuous heating, the polymeric chains break, providing the much-needed energy required to form the chemical bonds between the ions. Such a process where the ions are homogeneously mixed before the gels are formed hence, yields excellent chemical homogeneity of the desired formula. The process is suitable to incorporate a wide range of elements with different proportions with ease maintaining phase singularity within the limitations of the natural solubility limit of the solid solution. The annealing time is comparatively low. The size of the particles can be controlled, and a low-temperature crystallization is attainable. The process is economical and straightforward and requires simple processing equipment.

The burnt gel powders were generally dark in color and required heating at 450°C for 6 hours in ambiance to remove the remaining carbon and nitrogenous compounds present in the powder. The obtained product was finely ground and sintered at 600°C, 750°C, and 900°C and reground after each heating cycle. The LVO samples will be termed as LVO600, LVO750, and LVO900 according to the sintering temperature. Similarly, for SVO and CVO samples.

A small amount of powder is used for X-Ray diffraction (XRD) and the XRD pattern of all these samples were obtained using Bruker D2 Phaser diffractometer from (2Theta =  $10^{\circ}$  to  $90^{\circ}$ ) using Cu K $\alpha$  radiation ( $\lambda$  = 1.54184 Å). The operating voltage and the current; 30kV and 10mA respectively are kept as standard. It gives the information about the phase purity of crystalline material and gives the information of the unit cell dimension.

The FESEM (Field Emission Scanning Electron Microscope) and EDX (Energy-dispersive X-ray spectroscopy) of the samples were done using JEOL JSM-7610FPlus FESEM and Oxford X-MaxN 20

machines to obtain particle size, shape and to identify the surface morphology and EDX to confirm the fraction of the elements present.

The Raman spectroscopy of LaVO<sub>4</sub>, SmVO<sub>4</sub>, and CeVO<sub>4</sub> sintered at 600°C, 750°C, and 900°C were performed using HORIBA Scientific LabRAM HR evolution by taking a small amount of sintered powder. Information related to the chemical structure, phase and polymorphy, crystallinity and molecular interactions was provided by this characterization method. Interaction between light and chemical bonds within materials is the basis of this experiment.

The Fourier Transform Infrared spectroscopy of the samples was done using the PerkinElmer Spectrum Two FT-IR spectrometer to determine the functional groups present and the types of vibration present in the functional groups therein.

Photoluminescence spectroscopy was performed to estimate the defect states within the bandgap using a Dongwoo Optron DM 500i spectrometer with a metal-vapor He-Cd laser source (excitation wavelength 325 nm).

#### Chapter - 3

#### **3.1. Results and Discussion:**

#### 3.1.1 X Ray Diffraction (XRD):

XRD patterns of the LVO, SVO, and CVO samples (in fig. 8, 10, 9) were recorded to analyze the effect of sintering temperature on the crystalline phase of the samples. The samples were observed to be in the tetragonal zircon (I4<sub>1</sub>/*amd*, Z=4) phase for SVO and CVO samples while LVO was in monoclinic monazite (P2<sub>1</sub>/*n*, Z=4) phase. Rietveld refinement was performed on the XRD data to obtain the lattice parameters (Table. 1). The lattice parameters of the monoclinic LVO were observed to be almost constant with increasing sintering temperature (Fig. 11); however, it is worth mentioning that the lattice parameter c decreases nominally from 6.7227Å (LVO600) to 6.7223Å (LVO750), and thereafter increases to 6.7273Å (LVO900). For the tetragonal SVO, lattice parameters decrease with increasing temperature (as shown in Fig. 11) and in CVO, however, the lattice parameters increase slightly from CVO600 to CVO750, then vehemently decreases on further heating (Fig. 11).

#### 3.1.2 FESEM and EDX:

FESEM studies revealed micrometer sizes of all samples, which increased with sintering temperature from 600 to 900 °C. In case of LVO, the particle size was observed to increase from an average of ~1-2 $\mu$ m (600 °C) to ~6-7 $\mu$ m (750 °C) to ~9-10 $\mu$ m (900 °C). For SVO, the sizes changed from ~2  $\mu$ m (SVO600) to 2.7  $\mu$ m (SVO750) to ~7  $\mu$ m (SVO900). For CVO, the sizes changed from ~.3  $\mu$ m (CVO600) to 3.3  $\mu$ m (CVO750) to ~2.9  $\mu$ m (CVO900) ( as shown in Table. 2). Some morphological changes were observed with heating for the three different series of samples. LVO particles (Fig. 12) adhere to an almost spherical shape at low temperatures but develop some sharp edges or faces when heated at 900 °C. For SVO (in fig. 13), cylindrical-shaped elongated particles are observed at 600 °C (with an average length of ~900nm and width of ~200nm) which gradually transforms into an almost elliptical shape at 750 °C (with an average grain size of ~0.8 $\mu$ m) and thereafter to a cubical shape at 900 °C (with an average grain size of ~2.3 $\mu$ m). Almost spherical shape CVO particles (Fig. 14) at 600 °C, but it develops some sharp edges or faces when heated at 900 samples, which are in agreement with the XRD studies. EDX results (Fig. 15-19) are consistent with the proposed atomic weight percentage (wt %) during synthesis.

36 Raman modes  $\Gamma = 18A_g + 18B_g$  of the exhibited 69 optical modes  $\Gamma = 16B_u + 17A_u + 18A_g + 18B_g$  have been discussed in the monoclinic monazite phase of LVO [69]. However, only 26 modes have been detected experimentally (Table. 3). Raman spectra of these LVO samples (Fig. 20) were in agreement both in the lower frequency range (270-490cm<sup>-1</sup>) and higher frequency range (760-900cm<sup>-1</sup>) with previously published data [68]. The stretching in the VO<sub>4</sub> units in LVO is responsible for the lower frequency modes [70]. Peaks below  $\omega$ <230cm<sup>-1</sup> can be surmised to be due to external lattice vibrations. The most prominent peak at ~860 cm<sup>-1</sup> and the other 6 high-frequency modes are associated with V-O stretching mode, Ag [70]. The Raman modes in tetragonal SVO (Fig. 21) and CVO (Fig. 22) are markedly different from monoclinic LVO. To describe the zircon structure, a primitive cell can be chosen with two formula units. 12 atoms are contained in this primitive cell at the center of the Brillouin zone (BZ), giving rise to 36 phonon branches. They decompose in the irreducible representations of  $D_{4h}$  symmetry as follows.  $\Gamma = (2A_{1g}+B_{1u}) + (4B_{1g}+4A_{2u}) + (A_{2g}+2B_{2u}) + (A$  $(B_{2g}+A_{2u})$  +  $(5E_g+5E_u)$ . In the tetragonal SVO and CVO phase, there are 12 Raman modes  $(\Gamma = 2A_{1g} + 4B_{1g} + B_{2g} + 5E_g)$ ; among these, the A and B modes are non-degenerate, the E modes are doubly degenerate, among which are 2 acoustic modes ( $\Gamma_{acoustic}=A_{2u}+E_{u}$ ) and 5 silent modes ( $\Gamma_{silent} = A_{2g} + A_{1u} + B_{1u} + 2B_{2u}$ ). In SVO, 9 modes out of 12 were visible (Table. 4). In CVO, 11 out of 12 are visible (Table. 5) at 750 °C. Some modes which are forbidden in a high-symmetry phase, which can be active in a phase with a distorted VO<sub>4</sub> tetrahedron. The degeneracy of these forbidden modes could be totally or partially removed in the distorted phase. CVO exhibiting a higher number of modes could be due to the greater distortion in the tetragonal zircon CVO lattice due to its larger size; the CeO<sub>8</sub> polyhedra could be generating more strain on the VO<sub>4</sub> tetrahedra as compared to the smaller SmO<sub>8</sub> polyhedra. Raman spectra of these SVO and CVO samples were in agreement both in the lower frequency range (100-480cm<sup>-1</sup>) and higher frequency range (750-900cm<sup>-1</sup>) with previously published data, the absence of good quality Raman scattering crosssection can be the reason why other peaks are missing [67]. The most prominent peak of SVO(Fig. 21) and CVO (Fig. 22) is assigned to the stretching mode Ag of vanadate, similar to the monazite phase. The peaks at 786 and 798 cm<sup>-1</sup> are attributed to  $E_g$  and  $B_{2g}$  antisymmetric stretching of VO<sub>4</sub> units [71]. Crystallinity is often linked with a shift in the Raman phonon modes and peak width. A redshift and lower peak width often imply a better crystallinity and vice versa [65, 66, 72]. Overall intensity also increases with better crystallinity [76, 77]. Redshift was observed with increasing sintering temperature in all samples; the stress will act on the position of the peaks [76], defects (non-stoichiometry, for instance) will widen them [73, 74, 75], and temperature will act on both position and width. From XRD and FESEM studies, it was already observed that grain size grows with sintering temperature. Hence, more crystallinity is expected with sintering, which is in agreement with the redshift and sharpness of the peaks. With an increase in temperature, the peak widths of the  $A_{1g}$  mode at (~850-860 cm-1) of all the samples were seen to decrease; this is attributed to the increase in crystallinity observed with increasing annealing temperature. In LVO and SVO, the  $A_{1g}$  mode displayed redshift, which again is evincing an increase in crystallinity and an increase in particle size. However, the CVO sample showed erratic behaviour, the red-shift was observed on annealing from 600 °C to 750 °C, but on further heating the  $A_{1g}$  mode shifted to higher energy levels, this could be attributed to the decrease in average particle size on sintering from 750 °C to 900 °C. It was also observed from the cell parameters the anomalous behaviour of CVO, where the lattice parameters increased on sintering to 750 °C, then decreases on further sintering to 900 °C. Hence, these two variations in CVO could be denoting a reduction in crystallinity on sintering from 750 to 900 °C.

#### **3.1.4 Photoluminescence Spectroscopy:**

Photoluminescence spectroscopy makes use of the principle of photo-excitation, which provides the energy necessary for the electrons in a material to be excited to a higher energy level, the most preferred energy level can be found from the bandgap perceived from the UV-Vis spectrum. The energy of the emission bands is lower than the energy source used to cause excitation. In absorption, wavelength  $\lambda_0$  corresponds to a transition from the ground vibrational level S<sub>0</sub> to the lowest vibrational level of S<sub>1</sub>. After absorption, the excited electron in the  $S_1$  state without emitting any radiation de-excites to the lowest energy state of  $S_1$ . The return to the  $S_0$ state from the excited S<sub>1</sub> state results in the recombination of the excited electron with the hole created during excitation. However, this recombination can comprise of both radiative and non-radiative processes; the recombination rates administer the emission intensity of the different bands. Generally, the non-radiative transitions are considered the dominant recombination process and are associated with impurities, the intensity of emission, and its dependence on the level of photo-excitation and temperature. The emission bands can be used to identify specific defects, and the emission intensity to approximate the concentration of these individual defects, in turn assisting in the study of the effects of impurities or dopants on the specific type of defect. Photoluminescence spectra observed in the SVO (Fig. 24) samples had four distinct peaks as a result of the transition from the  ${}^{4}G_{5/2}$  state to the  ${}^{6}H_{5/2}$ ,  ${}^{6}H_{7/2}$ ,  ${}^{6}H_{9/2}$ ,  ${}^{6}H_{11/2}$  states [78] consistent with previously reported data [79]. The most intense among these is the  ${}^{4}G_{5/2} \mathfrak{B}H_{7/2}$  (~600nm ~ orange emission) transition with  ${}^{4}G_{5/2} \mathfrak{B}H_{9/2}$ (645nm ~ red emission) being almost comparable. Other prominent peaks are found corresponding to the  ${}^{4}G_{5/2}$  (~562nm ~ green emission) and  ${}^{4}G_{5/2}$  (~104nm ~ red emission) transitions. These transitions have found application in high-density optical storage, color displays, undersea communication, and medical diagnostics. From previous studies, the molecular orbitals of the  $V^{5+}$  ion with the T<sub>d</sub> symmetry in the VO<sub>4</sub> group has a ground state  ${}^{1}A_{1}$ , and excited states  ${}^{1}T_{1}$ ,  ${}^{1}T_{2}$ ,  ${}^{3}T_{1}$  and  ${}^{3}T_{2}$  [80]. Hence, the emission spectra observed in LVO (Fig. 23) is the result of electronic transitions in the  $VO_4^{3-}$  groups. The charge-transfer transitions of the 3d orbital electrons of the  $V^{5+}$  to the 2p electron of the  $O^{2-}$  ion inside the  $VO_4^{3-}$  groups are the reason for these emissions [81]. According to the energy scheme of the vanadate tetrahedron, emission bands at 570 and 630 nm are associated with  ${}^{3}T_{2}$  ( ${}^{3}A_{1}$  and  ${}^{3}T_{1}$  ( ${}^{3}A_{1}$  electron transitions in the VO<sub>4</sub><sup>3-</sup> groups respectively [81, 82]. However, a different source suggests that the peaks associated with the aforementioned transitions are at 521 and 579 nm, respectively [80]. Another source claims that the peak shape is affected by the temperature and that the resulting broadband is a result of 3 bands, and the variation of intensity of the individual peaks guides the shape of the resultant peak, these emission bands at 500 and 570 nm corresponding to with  ${}^{3}T_{2}$  ( ${}^{3}A_{1}$  and  ${}^{3}T_{1}$  ( ${}^{3}A_{1}$  electron transitions respectively. This source also discusses a peak at 446nm, which has attributed to the  ${}^{1}T_{1}$  ( ${}^{3}A_{1}$  transition. They also suggest that the complicated behavior of the 500 and 570 nm bands with varying temperatures bring to light the complex energy schemes (probably three-level) [83]. These transitions are forbidden in the ideal T<sub>d</sub> symmetry of the VO<sub>4</sub><sup>3-</sup> group. Distortion of the VO<sub>4</sub> tetrahedrons from the ideal symmetry in the crystal lattice of LVO enhances the spin-orbit interaction and makes these transitions partially allowed [83]. Hence, the distortion in the VO<sub>4</sub> can be ascribed to the adjoining LaO<sub>9</sub> polyhedra.

#### **3.1.5 Fourier Transform Infrared spectroscopy:**

The Fourier Transform Infrared spectroscopy spectra are consistent with the spectra of orthovanadates in previously reported data [84]. Two modes were observed in all samples, corresponding to the bending ( $v_2$  and  $v_4$ ) and the stretching ( $v_1$  and  $v_3$ ) vibrations of the O—V—O bond in the VO<sub>4</sub><sup>3-</sup> tetrahedron. The bending modes ( $v_2$  and  $v_4$ ) appear at 424nm (LVO) and ~450 nm (SVO and CVO). The stretching modes ( $v_1$  and  $v_3$ ) modes exist over a range of around 720 nm to 860 nm in all samples. Comparing the absorbance of the two particular modes of vibration in the VO<sub>4</sub><sup>3-</sup> tetrahedron, tetragonal zircon samples, SVO (Fig. 26) and CVO (Fig. 27) seem to have more intense ( $v_1$  and  $v_3$ ) stretching modes as compared to the ( $v_2$  and  $v_4$ ) bending modes, whereas monoclinic monazite LVO (Fig. 25) has equal absorbance at both modes. This could be attributed to the structural differences in both the phases, O—V—O bonds in SVO and CVO in their Tetragonal zircon phase is found to be more constrained than the O—V—O bonds in the case of LVO in its monoclinic monazite phase. This may be attributed to the lower bulk modulus (B<sub>0</sub>) of monazite being 2% smaller than low-pressure zircon [85]. The absorbance of the samples are seen to be dependent on the crystallinity. The absorbance of the all the modes were seen to decrease with increasing annealing temperature. But, in the case of CVO, the absorbance of CVO750 was the least, contradicting the trend displayed by the SVO and LVO. Since, higher annealing temperature results in an increase in crystallinity, it can be assumed that absorbance reduces with increasing crystallinity. The fact that CVO900 has higher absorbance could further bolster our previous claim that CVO900 is less crystalline than CVO750.



Figure. 7: Schematic of photoluminescence experiment setup.



Figure 8:- The graph v/s intensity and angle of diffraction obtained [2 $\theta$ ], data obtained by performing XRD for LVO with temperature variation (at temperatures 600 °C, 750°C and 900°C).



Figure 9:- The graph v/s intensity and angle of diffraction obtained [2θ] , data obtained by performing XRD for CVO with temperature variation (at temperatures 600 °C , 750°C and 900°C).



Figure 10:- The graph v/s intensity and angle of diffraction obtained  $[2\theta]$ , data obtained by performing XRD for SVO with temperature variation (at temperatures 600 °C , 750°C and 900°C).



Figure 11:- Above figures depict the variation in cell parameters of LVO, SVO, and CVO respectively; where a,b and c are cell parameters.



Figure 12:- FESEM images for LVO and grain size variation with temperature variation [at temperatures 600 °C , 750 °C and 900°C].



Figure 13:- FESEM images for SVO and grain size variation with temperature variation [at temperatures 600 °C , 750 °C and 900 °C ].

750 °C



Figure 14:- FESEM images for CVO and grain size variation with temperature variation [at temperatures 600 °C , 750 °C and 900 °C ].



10µm





Figure 16:- EDX images for CVO at 900°C

Electron Image 20









Figure 19:- EDX images for SVO at 900°C



Figure 20:- Data obtained from Raman for LVO with temperature variation.



Figure 21:- Data obtained from Raman for SVO with temperature variation.



Figure 22:- Data obtained from Raman for CVO with temperature variation.



Figure23:- Graph of Photoluminescence of LVO obtained at different sintering temperatures.



Figure 24:- Graph of photoluminescence of SVO obtained at different sintering temperatures.



Figure 25:- FT-IR spectra comparing the absorbance of the two modes displayed by LVO.



Figure 26:- FT-IR spectra comparing the absorbance of the two modes displayed by SVO.



Figure 27:- FT-IR spectra comparing the absorbance of the two modes displayed by CVO.

Sample	a	b	с	α	β	γ	$\chi^2$	R <sub>p</sub>	$R_{wp}$	Rexp
LVO600	7.04421	7.2817	6.7227	90	104.86	90	2.28	11.9	10.8	7.17
LVO750	7.04423	7.2819	6.7223	90	104.86	90	1.92	15.8	13.6	9.8
LVO900	7.04891	7.2870	6.7273	90	104.86	90	2.16	15.2	13.6	9.25
CVO600	7.4009	7.4009	6.4983	90	90	90	2.34	18.2	15.2	9.95
CVO750	7.4015	7.4015	6.4986	90	90	90	3.41	17.5	14.3	7.73
CVO900	7.3986	7.3986	6.4967	90	90	90	3.33	18.5	15.2	8.31
SVO600	7.2631	7.2631	6.3874	90	90	90	2.22	14.6	10.5	7.05
SVO750	7.2629	7.2629	6.3865	90	90	90	2.07	21.3	12.9	8.98
SVO900	7.2627	7.2627	6.3852	90	90	90	2.75	27	15.9	9.61

Table 1: Lattice parameters and refinement parameters obtained from Rietveld refinement of the samples.

Sample	Temperature (°C)	Particle size (µm)
	600	~1.6
LaVO₄	750	~2.7
	900	~9.22
	600	0.3
CeVO <sub>4</sub>	750	3.3
	900	2.9
	600	~0.9087 (length) ~0.204(diameter)
SmVO <sub>4</sub>	750	~0.80
	900	~2.9

Table 2: Grain size of LVO , CVO and SVO sintered at 600, 750 and 900°C.

Raman Mode Symmetry	Theoretical Peak Position ωT (cm-1)	Observed Peak Position (LVO600) ωE (cm-1)	Observed Peak Position (LVO750) ωE (cm-1)	Observed Peak Position (LVO900) ωE (cm-1)
Ag	102	103.02	102.955	102.548
Bg	115	114.609	114.336	114.023
Bg	127	127.611	127.349	126.889
Ag	134	138.313	137.957	137.904
Ag	143	146.855	146.044	145.635
Ag	154	159.672	159.544	159.352
Bg	183	189.539	190.103	190.174
Ag	188	196.953	-	-
Bg	204	208.817	208.673	208.182
Ag	230	236.893	236.013	235.221
Ag	252	252.895	251.72	251.2
Bg	297	308.236	308.033	307.699
Bg	316	330.6187	330.486	329.7785

Ag	317	326.596	326.566	326.0698
Ag	336	348.807	348.558	348.282
Ag	355	374.329	374.101	373.699
Ag	380	398.067	397.636	397.248
Bg	410	425.720	424.76	425.093
Bg	427	440.470	439.965	439.519
Ag	784	769.26	769.029	768.751
Bg	799	789.115	788.766	788.521
Ag	806	794.848	794.642	794.300
Ag	836	82 0.859	820.577	820.207
Bg	850	842.918	842.68	842.242
Ag	870	859.271	859.017	858.682
Bg	892	881.171	880.679	880.192

Table 3: Peak positions of the Raman spectra of LVO sintered at 600, 750 and 900°C.

Raman Mode Symmetry	Approximate theoretical Peak Position $\omega T (cm^{-1})$	Observed Peak Position (SVO600) $\omega E (cm^{-1})$	Observed Peak Position (SVO600) $\omega E (cm^{-1})$	Observed Peak Position (SVO600) ωE (cm <sup>-1</sup> )
$T(B_{1g})$	128.36	122.935	122.662	122.382
T(E <sub>s</sub> )	151.1	151.666	152.117	151.858
$T(B_{1g})$	243.1	240.271	240.735	239.872
$\nu_2(\mathbf{B}_{2g})$	260.9	260.58	260.285	260.016
$v_2(A_{1g})$	381.9	380.433	380.111	379.606
$\nu_4(B_{1g})$	472.2	476.699	476.426	476.090
$\nu_{3}(B_{1g})$	794.6	797.384	797.152	796.834
$\nu_{3}(E_{e})$	808.1	815.509	815.217	814.84
$\nu_{i}(A_{ig})$	871.1	876.796	876.573	876.131

Table 4: Peak positions of the Raman spectra of SVO sintered at 600, 750 and 900°C.

Raman Mode Symmetry	Theoretical Peak Position ωT (cm-1)	Observed Peak Position (CVO600) ωE (cm-1)	Observed Peak Position (CVO750) ωE (cm-1)	Observed Peak Position (CVO900) ωE (cm-1)
T(E <sub>s</sub> )	112.1	-	109.136	-
$T(B_{1g})$	122.3	122.565	121.544	121.508
T(E <sub>g</sub> )	149.7	145.437	145.761	-
R(E <sub>s</sub> )	224.6	225.849	226.163	225.203
$T(B_{1g})$	233.9	232.653	233.1911	232.1932
$\nu_2(B_{2g})$	258.2	260.6919	260.489	259.865
$\nu_2(A_{1g})$	365.5	379.324	377.111	376.8753
$\nu_4(B_{1g})$	453.0	467.075	465.511	466.2669
$\nu_3(\mathbf{B}_{1g})$	797.0	787.1085	785.034	786.1216
$\nu_{3}(E_{g})$	801.9	799.3214	796.8067	798.656
$\nu_{i}(A_{ig})$	859	862.2152	859.8122	861.2587

Table 5: Peak positions of the Raman spectra of CVO sintered at 600, 750 and 900°C.

#### Chapter - 4

#### 4.1. Conclusion:-

From our experiments we were able to confirm the data we obtained were in agreement with previously reported data, we saw that the compounds can exist in both monoclinic monazite (space group:  $P2_1/n$ , Z=4) and tetragonal zircon (I4 $_1/amd$ , Z=4), depending on the size of the A-site cation. We were able to confirm this with the help of the XRD we obtained. In these samples, it was observed that  $La^{3+}$  with the larger size cation in its compound exists in the monazite phase and the smaller Ce<sup>3+</sup> and Sm<sup>3+</sup> in their compounds, exist in the zircon phase. Ce being on the border of both phases might be able to display a prospective phase transition under less extreme conditions compared to the rest of the rare earth elements. We could surmise a possible phase transition would be possibly on doping CeVO<sub>4</sub> with La<sup>3+</sup>. FESEM and EDX were performed to calculate particle size and to throw light on the morphology exhibited by the grains, we saw that particle size increased with increasing temperature, but also saw that CeVO<sub>4</sub> didn't adhere to the generic trend, crystallinity increased with temperature which was evident from the shape and structure of the grains, it also assisted in making valuable outlook on the nature of the Raman spectra we obtained for the samples. EDX analysis was performed to ascertain the phase purity and the stoichiometry of the compounds. Much of the behavioural aspects of the compounds were characterized using Raman spectroscopy. It was found that various parameters affected the position of the Raman peaks from particle size to size of the non-degenerate and doubly degenerate modes found. The Raman spectra we obtained were as well in line with previously reported data. LaVO<sub>4</sub> exhibited Raman spectra concurrent with the Raman spectra of Monoclinic Monazite compounds and displayed around 26 modes, although a total of 36 modes exist as known through theoretical calculations. CeVO<sub>4</sub> and SmVO<sub>4</sub> both showed the characteristic spectrum of the Tetragonal Zircon phase both displaying 11 and 10 respectively out of the total 12 modes calculated theoretically. Photoluminescence spectra observed in the SVO samples had four distinct peaks. These transitions have found application in high-density optical storage, colour displays, undersea communication, and medical diagnostics. Lanthanum (3+) ion doesn't show the photoluminescence spectra but LVO shows the emission spectra which is the result of electronic transitions in the VO<sub>4</sub><sup>3-</sup> groups. FTIR displayed different levels of absorbance in monoclinic and tetragonal phases for the stretching and bending modes, evincing that the pattern is characteristic of the particular phase, possibly due to the structural restriction observed in the two phases.

#### 4.2. Future Scope:

Orthovanadates being an important class of compounds, the properties which we found in our experiments performed made it quite inevitable that the materials can be easily used for WLED's and many other optoelectronic devices. This host material has known use in many applications: some of these are even used in everyday life, as host for  $Eu^{3+}$  ions in cathode ray tubes (CRT's) in colour television (2), while others are used in modern, more high-end equipment (as a host material for lasers when doped with Nd<sup>3+</sup>) (3). YVO4 is a crystalline zircon-type material, which means that it has a tetragonal crystal structure. This material can either be synthesized in an acidic or basic environment. As we had come across the research paper "Tuning oxygen vacancy photoluminescence in monoclinic Y<sub>2</sub>WO<sub>6</sub> by selectively occupying yttrium sites using lanthanum" [86]. We hope to find an application for doping SVO with La<sup>3+</sup>, to observe possible changes in the luminescence spectra displayed by La-doped SVO.

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