Spectral characterization of novel LiZnVO$_4$ ceramic phosphor

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This paper reports on the spectral analysis of novel Lithium Zinc Vanadate (LiZnVO$_4$) ceramic phosphor prepared by a solid state reaction method. Emission spectrum of LiZnVO$_4$ has shown a bright *green* emission at 533 nm with λ_{exci} = 359 nm. A bright green colour emission has also been noticed directly from this phosphor under an UV source. For this luminescent phosphor, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS), Fourier-transform IR spectroscopy (FTIR), Raman Spectrum, Comprehensive Differential Thermo gravimetric Analysis (TG-DTA) have also been carried out.

1. Introduction

Production of more efficient luminescent materials has continually been carried out for different applications such as compact light sources, display screens and photonics devices etc [1]. Oxide phosphors have been investigated because of their higher chemical stability over the other phosphors such as sulfide phosphors [2]. During the past few years, vanadium oxides based materials have attracted a special attention due to their unique structures, optical, and magnetic properties. It has been known that vanadium oxide transforms into different complex vanadates, namely metavanadate, pyrovanadate and orthovanadates depending on the considered stiochiometry of the composition. Most of the crystal structures of the vanadates are formed to be in VO$_4$ or VO$_5$ polyhedra [3-6]. Once the vanadate center becomes excited, it can either display a broad luminescence in the visible region or it may transfers the energy to another luminescent center which subsequently reveals the expected characteristic emission [7]. Mixed-metal oxides play an important role in the development of several newer materials [8]. Several groups have investigated the effect of lithium and zinc on the luminescent properties [9-11]. Literature survey in this direction of work indicates that no systematic report has so far been made; hence we have undertaken the present work in order to develop and analyze the green luminescent Lithium Zinc Vanadate (LiZnVO$_4$) ceramic phosphor.

2. Experimental studies

LiZnVO$_4$ ceramic phosphor was prepared by a solid-state reaction method. High pure and reagent grade chemicals such as Li$_2$CO$_3$, ZnO and NH$_3$VO$_4$ were used as the starting materials. Chemicals were weighed on the basis of the composition and mixed in an agate mortar with acetone as a binder solvent for obtaining homogeneity. This chemicals mix was put into a silica crucible and sintered in an electrical furnace at 850ºC for 5h with an intermittent grinding.

The structure of the prepared ceramic phosphor was characterized on a XRD 3003 TT Seifert diffractometer with CuK$_\alpha$ radiation (λ=1.5406Å) at 40 kV and 20 mA and the 2θ range was varied between 10º and 70º. The morphology of the ceramic phosphor was observed on a Zeiss EVO MA 15 Scanning Electron Microscope and the elemental analysis of the synthesized products was carried out on an Oxford EDAX equipment (INCA-Penta Fet X3) attached to the SEM system. FTIR spectrum of the sample was recorded on a Nicolet IR-200 spectrometer using KBr pellet technique from 4000 cm^{-1} to 400 cm^{-1}. Raman spectrum was recorded by using a high resolution Jobin Yvon Model HR800UV system attached with a He-Ne laser (633 nm) as the excitation source having an output power of 15 mW with a laser beam spot size of 100 um from an appropriate lens system. Thermogravimetry (TG) and Differential thermal analysis (DTA) were simultaneously obtained for the precursor of the sample studied in N$_2$ atmosphere at a heating rate of 10°C/min on a Netzsch STA 409 Simultaneous Thermal Analyzer. The photoluminescence spectrum of this ceramic phosphor was measured on a Jobin Yvon Fluorolog-3 Fluorimeter with a Xe-arc lamp (450W) as an excitation source and the lifetime of the green emission (533 nm) was measured with a phosphorimeter attachment to the main system with a Xe-flash lamp (25 W).

3. Results and discussion

Prior to the measurement of photoluminescent spectrum of the sample, we have made a basic observation of *green* emission from LiZnVO$_4$ ceramic phosphor directly under an UV source, as shown in Fig. 1. XRD profile of LiZnVO$_4$ ceramic phosphor is shown in Fig. 2 and the measured peaks confirms its structure as rhombohedral, upon utilization of the JCPDS Card No.38-1332. The crystallite size of the prepared ceramic phosphor has been estimated using the Scherer's equation, D = [(0.9 λ) / (β cos θ)], where D is the crystallite size, λ is the X-ray wavelength (0.15406 nm), θ and β are the diffraction angle and full width at half maximum (FWHM) of an observed peak respectively. Intense diffraction peaks have been selected to compute the mean crystallite size and it is found to be in 96 nm.
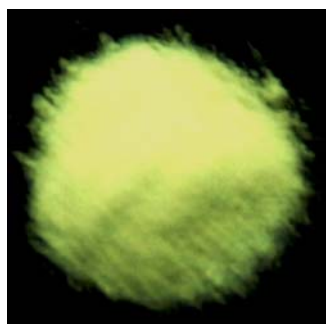

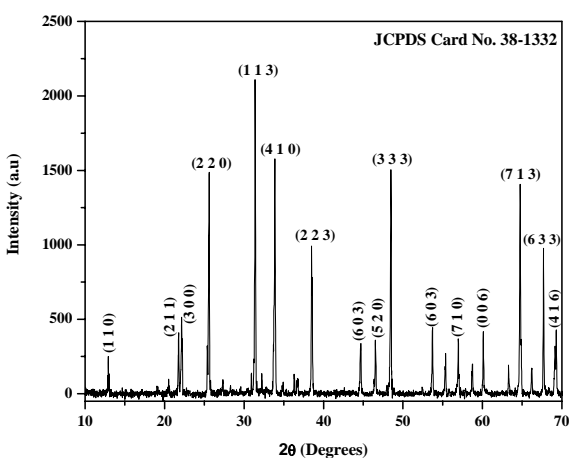*Fig. 1. Green emission from LiZnVO$_4$ ceramic phosphor under an UV source*

Fig. 2 XRD profile of LiZnVO$_4$ ceramic phosphor

The SEM image of the LiZnVO$_4$ ceramic phosphor is shown in Fig. 3 which reveals that the particles are densely agglomerated and the average diameter of the grain size is in the range of 1-2 µm. The narrow widths of the diffraction peaks also indicate that the prepared ceramic phosphors possess large sized grains and such sizes are found to be more encouraging for different applications [12, 13]. To verify the elements present in the optical material studied, an EDS profile has been recorded as shown in Fig.4. However, the EDS of the matrix could not show the presence of lithium because of instrument limitation [14]. The existence of the carbon peak at 0.2 keV in the EDS spectrum is due to the carbon tape that was employed in holding the specimen.
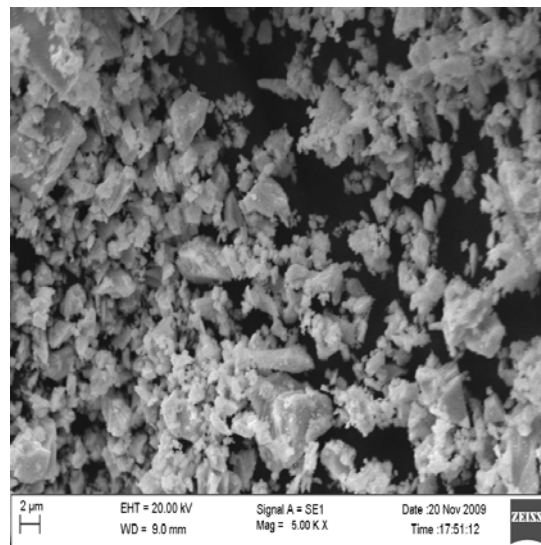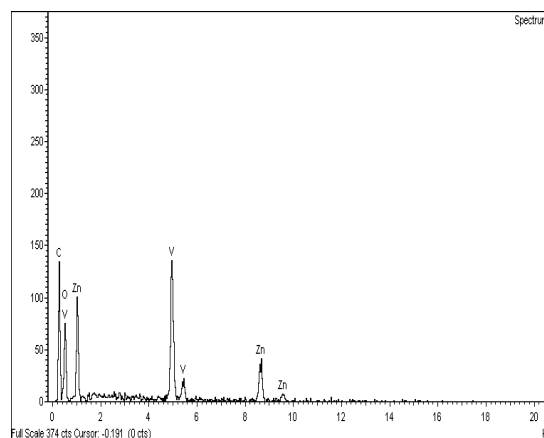

Fig. 3 SEM image of LiZnVO$_4$ ceramic phosphor.

Fig. 4. EDS profile of LiZnVO$_4$ ceramic phosphor

Fig. 5 shows the FTIR spectrum of LiZnVO$_4$ ceramic phosphor. Modes in the region of 1100 – 400 cm^{-1} are due to vanadium–oxygen stretching vibrations of VO$_4$ and the other metal-oxygen bonds present in the prepared material [15, 8]. A low intensity band at 414 cm^{-1} corresponds to the stretching vibration of Zn-O [3]. The peak at 490 cm^{-1} is due to the presence of γ-phase of Lithium Vanadate

[15]. The bands observed at 647 cm^{-1}, 712 cm^{-1}, 790 cm^{-1} and 930 cm^{-1} are attributed to V-O vibration modes of LiZnVO$_4$ ceramic phosphor [16, 17]. The bands at 3432 cm^{-1} and 1642 cm^{-1} are assigned to O–H stretching and H–O–H bending vibrations respectively. These two bands are the characteristic vibrations of moisture presence on the sample surface [18]. Fig. 6 shows the Raman spectrum of LiZnVO$_4$ ceramic phosphor. Intense Raman peaks imply the stronger interactions between the atoms, which mainly arise from the stretching and bending of the shorter metal–oxygen bonds [19]. The Raman bands located at 186 cm^{-1}, 250 cm^{-1} and 476 cm^{-1}are ascribed to the Li-O vibrations [16]. The peaks noticed at 122 cm^{-1}, 296 cm^{-1}, 795 cm^{-1} and 906 cm^{-1} are attributed to V-O vibrations and an intense peak found at 840 cm^{-1} is due to the asymmetric stretching υ_{as} (VO$_4$) and symmetric stretching υ_s (VO$_4$) vibration modes of the VO$_4$ groups [16, 20 and 21]. The Raman band at 228 cm^{-1} is attributed to the Zn-O vibration [3].
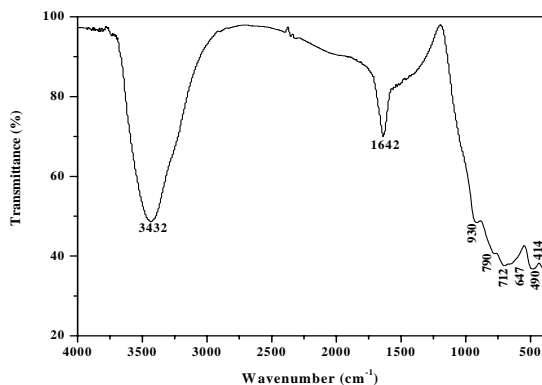

Fig. 5   FTIR spectrum of LiZnVO$_4$ceramic phosphor

Fig.7 shows the TG and DTA results of the LiZnVO$_4$ precursor containing the chemicals mixture of raw materials (Li$_2$CO$_3$, ZnO and NH$_3$VO$_4$) in stoichiometric ratio from the room temperature to 1100°C. In the temperature range from 35°C to 300°C, the sample shows both exothermic and endothermic peaks in the DTA curve, which is in accordance with the first weight loss. These observations can be attributed to the decomposition of the organic species which are used during the grinding of raw materials for homogeneity [22]. The second weight loss in the range of 300°C and 700°C is due to the degradation of organic material from the as synthesized material which could possible due to the removal of CO$_2$ and H$_2$O. The exothermic peak observed at around 650 ^{o}C is due to the elimination of CO$_2$ and also because of the formation of constituent oxides [23]. Upon increasing the temperature a solid state reaction occurs amongst the chemicals of Li$_2$CO$_3$, ZnO and NH$_3$VO$_4$ and peaks observed in the DTA curve confirm such a reaction. An exothermic peak at 840°C is attributed to the heat loss during the crystallization of LiZnVO$_4$ ceramic phosphor. The well phosphored mixture of Li$_2$CO$_3$, ZnO and NH$_3$VO$_4$, upon its sintering at 850°C for 5h, show an XRD pattern corresponding to LiZnVO$_4$ (JCPDS Card No. 38-1332) validating the assignment of the exothermic peak at 840°C in the DTA curve as due to crystallization of LiZnVO$_4$. TG curve indicates a weight loss of nearly 25% when the temperature is raised from 35°C to 700°C because of the degradation of the material by loosing the existing moisture, organic species and other gases. No significant weight loss has been observed in the TG curve beyond 700°C.
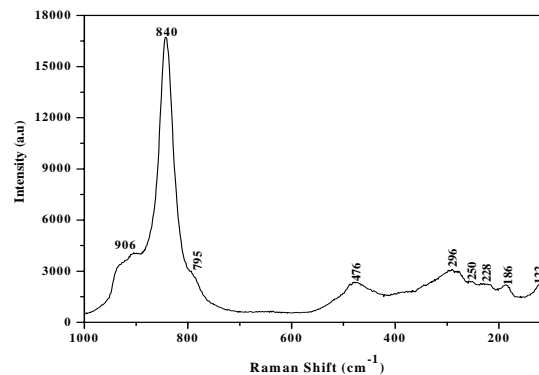

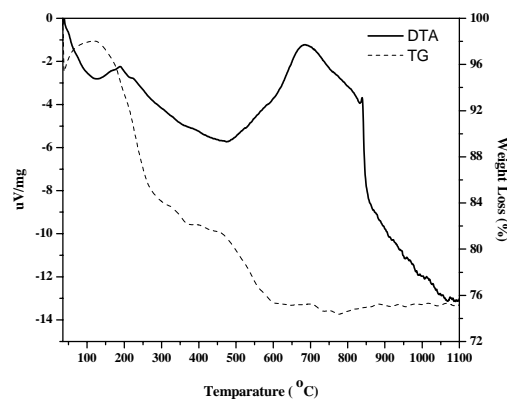*Fig. 6   Raman spectrum of LiZnVO$_4$ ceramic phosphor*

Fig. 7.   TG–DTA curve of LiZnVO$_4$ ceramic phosphor

Fig. 8 (a) shows an excitation spectrum of LiZnVO$_4$ ceramic phosphor with an emission at λ_{emis} = 533 nm and it has revealed a broad band having its maximum intensity at 359 nm ($^1A_1 \rightarrow {}^1T_1$) [6]. This absorption band (excitation peak) of VO$_4^{3-}$ group is because of a charge transfer from the oxygen ligands (O^{2-}) to the central vanadium atom (V^{5+}) [24]. This result is encouraging because of the fact that this material possesses an excitation wavelength in the UV region. Fig. 8 (b) shows an emission spectrum of LiZnVO$_4$ ceramic phosphor with an excitation at 359 nm. Vanadates, like tungstates, can exhibit luminescence phenomenon without any addition of an activator; but only upon heating it to a certain temperature. Generally, defects such as oxygen vacancies

are known to be the most common defects in oxides and usually act as radiative centers in luminescence processes. Local defects such as atom vacancies or interstitials may induce new energy levels in the band gap and these vacancies became possible for the observance bright green emission from the prepared LiZnVO₄ ceramic phosphor. The V^{5+} ion has a closed-shell electronic structure with no d electron. Considering the electronic structure of the VO_4^{3-} ion in Td symmetry, a one electron charge transfer process from the oxygen 2p orbital to the 3d orbital of the V^{5+} ion is involved in the excitation and luminescence phenomenon. From molecular orbital calculations reported are the excited states of $^3T_1$, $^3T_2$, $^1T_1$, $^1T_2$ in order of increasing energies and the ground $^1A_1$ state. The bright greenish luminescence of the LiZnVO₄ at 533 nm is due to the ($^3T_2 \rightarrow {}^1T_1$) transitions that are made allowed by spin-orbit interatction [25 and 6]. Fig. 9 presents the decay curve of the green emission band at 533 nm with an excitation at 359 nm and the emission lifetime is found to be 105 µs.
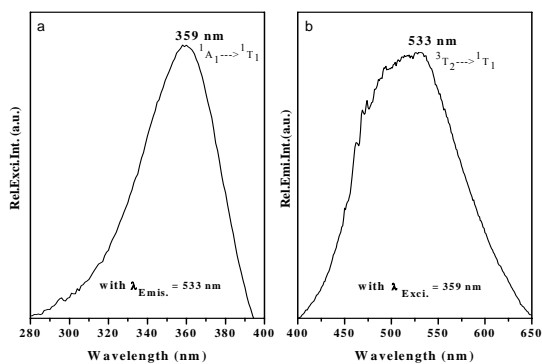

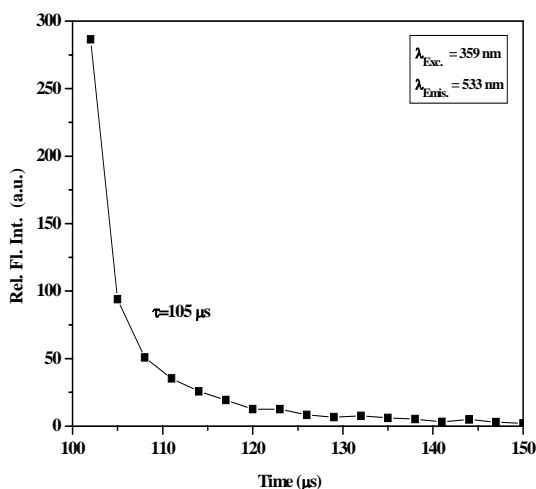*Fig. 8 (a) Excitation and (b) emission spectra of LiZnVO₄ ceramic phosphor*

Fig. 9 Decay curve of the green emission (533 nm) of LiZnVO₄ ceramic phosphor with λ_{exci} =359 nm

4. Conclusions

Brightly green luminescent LiZnVO₄ ceramic phosphor has been prepared by a solid-state reaction method. Photoluminescent spectral analysis has successfully been carried out. A Broad excitation band was measured due to the absorption of VO_4^{3-} group in the LiZnVO₄. Existence of luminescence centers with oxygen O^- defects in the vanadium-oxygen clusters could be a possible reason for the observance of bright green emission from the LiZnVO₄ ceramic phosphor. Besides, we have further analyzed this luminescent material by using XRD, SEM, EDS, FTIR and Raman spectral profiles to understand its structure, morphology and functional groups. Our preliminary study on LiZnVO₄ has explored its potentiality as an efficient phosphor host for its use in luminescent display systems.

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