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Research Article

Bluish-White Emission from Lanthanide Free Self-Activator Vanadate Phosphors: Structural and Optical Characterization of LiCa3CdV3O12

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ABSTRACT

Significant emphasis has been placed on research concerning cost-effective and lanthanide free vanadate phosphors, which exhibit minimal optical absorption due to the luminescence colour being readily adjustable through their high compositional flexibility. Nevertheless, phosphors exhibiting bluish emission with high quantum efficiency have yet to be discovered. This study effectively identified bluish-white emitting, garnet structure-based LiCa3CdV3O12 phosphors exhibiting high quantum efficiency, with the crystal structure meticulously optimized using the Rietveld analysis approach. The material was synthesized by high temperature SSR method at 9500 C for 6 hours. These phosphors demonstrate a broad-band emission spectrum peak at 465 nm when excited by near UV light at 327 nm, revealing no significant distinction between the emission and excitation spectra. A highly compact tetrahedral [VO43-] unit is present in the LiCa3CdV3O12 phosphors, which is absent in other traditional garnet compounds, and produces a bluish-white emission. Furthermore, the sample demonstrate surface studies and EDX for determination of grain size and compositional studies respectively. The materials examined with CIE chromaticity to conform the emission region. The prepared materials are applicable in various blue coloured lighting devices.

Keywords: Bluish-white phosphor, lanthanide free phosphor, LiCa3CdV3O12, self-activated phosphor.

1. INTRODUCTION

The use of inorganic phosphor materials as a spectrum converter has been implemented in a broad variety of bluish-white emitting devices, ranging from the traditional fluorescent lights to white light emitting diodes (white LEDs). Approximately twelve years ago, lanthanide metals have been utilized in the production of phosphor materials for emitting devices. This is due to the numerous benefits that these metals possess, including a high luminescence efficiency and colour purity [1]. In addition, by the use of the lanthanide metals components as luminescent ions, it is possible to effortlessly get a pure white light [2]. White light has been produced in fluorescent lamps and white LEDs by employing solely these elements as luminescence centers in oxide, nitride, carbonate or sulphide [3]. This has been successful in producing white light [4]. The lanthanide ions, on the other hand, have narrow excitation spectra as a consequence of the 4f–4f forbidden transitions, which ultimately leads to low absorbances [5]. In addition, the cost of these metals is higher than that of transition metals, which restricts the

availability of materials of this kind. In order to find a solution to these problems, search efforts have been directed toward rare-earth-free phosphor materials.

Solid-state lighting can be focused on white light-emitting diodes (WLEDs) is considered a next-generation lighting source for general illumination due to its energy efficiency, long lifespan, eco-friendliness, small size, and fast response time [6,7]. The white light can be fabricated by using blue chip [8]. Coating phosphors on LED chips is a standard way to achieve pure white WLED emissions. Phosphor-converted WLEDs are made by combining a blue LED chip with a yellow phosphor (e.g., YAG: Ce3+) [9] or a blend of green and red phosphors, an ultraviolet (UV) LED chip with a tricolour (blue, green, and red) phosphor [10], or a UVLED chip with a single-phased white-emitting phosphor [11]. Here, we used $LiCa_3CdV_3O_{12}$ composition. There were $LiCa_3ZnV_3O_{12}$ [12], $LiCa_3MgV_3O_{12}$ [13].

The V–O bond spacing in $[VO_4]$ tetrahedra with T_d symmetry substantially affects the luminous behaviour of the ligand-to-metal CT transition between V^{5+} and O^{2-} in vanadate phosphors [14]. Vanadate emission energy is inversely related to V–O bond distance [15]. Thus, garnet structure-based vanadate materials with smaller ions may emit bluish light [16]. Our focus was on $LiCa_3CdV_3O_{12}$ compounds with tiny ions and compact crystal lattice volume, resulting in shorter V–O bond distances in $[VO_4^{3-}]$ tetrahedra and potential for bluish emission $LiCa_3CdV_3O_{12}$ compounds have been explored in dielectric fields [17]. Thus, the crystal structures and luminescence characterization of $LiCa_3CdV_3O_{12}$ compounds must be demonstrated. The fundamental luminescence behaviour of $LiCa_3CdV_3O_{12}$ phosphors synthesized using a conventional solid-state reaction method was fully investigated by analysing the crystal structure to find the first garnet-structured vanadate phosphor material with bluish emission.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis.

The standard solid-state reaction (SSR) was used to manufacture vanadate phosphor powder samples. Li_2CO_3 (Wako Chem., Japan, 99%), $CaCO_3$ (Wako Chem., Japan, 98%), CdO (99%), and V_2O_5 (98%) were employed as raw materials. Stoichiometrically weighed reagents were combined with an agate mortar and pestle in acetone. The dried sample was calcined in an alumina boat at 800 °C for 5h in air. After cooling to room temperature, calcined samples were crushed in an alumina mortar to obtain homogeneous samples. Finally, the samples were sintered at 950 °C for 6 hr [18].

2.2 Characterization Techniques

In order to investigate the structural properties, an X-ray diffractometer Rigaku Miniflex 600 was utilized. The wavelength of the X-ray diffractometer was set at 1.54059 Å, and the source of radiation was a Cu Kα. The scanning rate was set at 4°/min. The spectrophotometer (F-7000 FL, 1914-024, Version-5J14000-03) was used to investigate the luminescence properties in order to get a better understanding of photoluminescence. An Xe lamp with 135 watts of power is used to recoat the emission and the excitation at a step of 0.2 inches. By using a FE-SEM JEOL, JSM-6500F with an 80W Xe light source and a 25 kV high tension voltage between the anode and the cathode electron accelerating voltage, the morphological and compositional characterizations were optimized.

3. RESULTS AND DISCUSSION

3.1 Phase-Identification and Structural Studies

The features of the crystalline XRD of the $LiCa_3CdV_3O_{12}$ vanadate phosphors are depicted in Figure 1. The standard file of number 000630654 is for $LiCa_3ZnV_3O_{12}$. This demonstrates that more phase instability would not be caused by the replacement of Cd. Ia-3d is the space group with simple cubic structure for the materials.

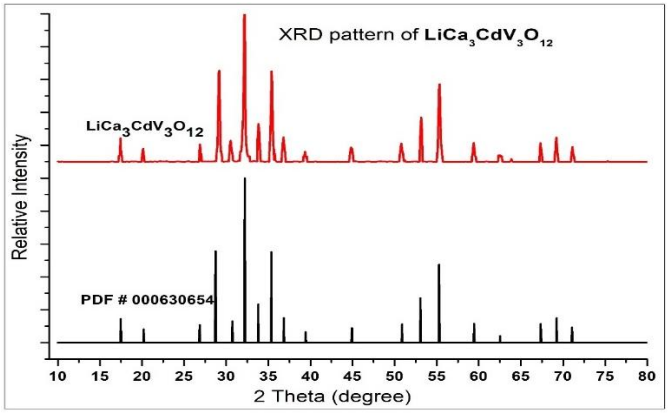

Figure 1: The XRD pattern of $LiCa_3CdV_3O_{12}$ is compared using PDF #000630654.

It is possible to index the diffraction data of the $LiCa_3CdV_3O_{12}$ samples by using the dimensional group of the cubic structure. It is not possible to observe any diffraction peaks of raw material. In order to investigate the crystal structure of $LiCa_3CdV_3O_{12}$, the almost similar garnet compound (PDF #000630654) that was included in the first model was utilized [19]. As illustrated in Figure 2, the difference profile for the $LiCa_3CdV_3O_{12}$ host is depicted as blue lines of Rietveld refinement. Additionally, a comparison of the predicted and actual diffraction patterns is presented as black triangles as measured (observed) intensity, red lines as calculated intensity, blue as difference, and vertical green as Bragg's locations. R_w = 8.895%, R_p = 11.123%, and projected R_{we} 5.315% are all examples of low residual parameters, which indicates that the refinement is reasonably consistent. The complete information on the crystallographic data is shown in Table 1. After careful analysis, it was discovered that the cell characteristics are a = b = c = 11.23721 Å. The coordinates of the crystallographic site, the parameters that determine the occupation of the site, and analogous dislocation values that are isotropic across nature are listed in Table 1.

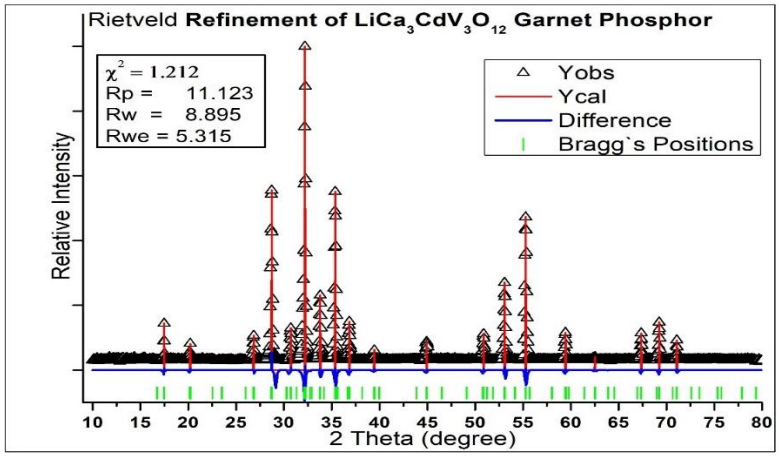

Figure 2: The Rietveld XRD pattern of $LiCa_3CdV_3O_{12}$ shows black triangles as measured (observed) intensity, red lines as calculated intensity, blue as difference, and vertical green as Bragg's locations.

Table 1: The refine structural parameters of $LiCa_3CdV_3O_{12}$ are presented, which also includes the structural parameters.

Composition	$LiCa_3CdV_3O_{12}$	**Refinement Parameters**	$LiCa_3CdV_3O_{12}$
Crystal lattices	Cubic	Chi^2	1.212
Space group	Ia-3d	R_p	11.123%
(hkl)	(311) at 2θ = 32.28°	R_{wp}	8.895%

Translational lattice parameters (a = b = c) in nm	1.123721 nm	Expected R_w	5.315%
Error in a	1.87 % (compare with Standard PDF)	**Wyckoff symbols**	
Volume of unit cell $(nm)^3$	1.41897 nm^3	Ca^{2+}	24c
Z	8	Cd^{2+} + Li^{+}	16a
Average Size $\mathbf{D_{obs}}$	23.4746 nm	V^{5+}	24d
Average Size $\mathbf{D_{cal}}$	23.8252 nm	O^{2-} (for **Ia-3d**)	96h

3.2. Topographical and Compositional Characterizations

Figure 3 displays scanning electron microscope (SEM) of the garnet phosphors that were manufactured $LiCa_3CdV_3O_{12}$ for the purpose of analysing their morphology. Both the size and the morphology of the $LiCa_3CdV_3O_{12}$ particles have been shown to be comparable, which is in line with the average size of the crystallites found in these materials. On the other hand, the morphology of each and every sample that is being investigated is a distinguishing characteristic of garnet phosphor that was initially recorded [20]. The chemical composition of $LiCa_3CdV_3O_{12}$ garnet phosphor, as shown in Figure 4. It is possible to assert that all samples demonstrate a satisfactory conformity to the theoretical and defined composition. In EDX, there is lithium was not due to comparable lower atomic mass.

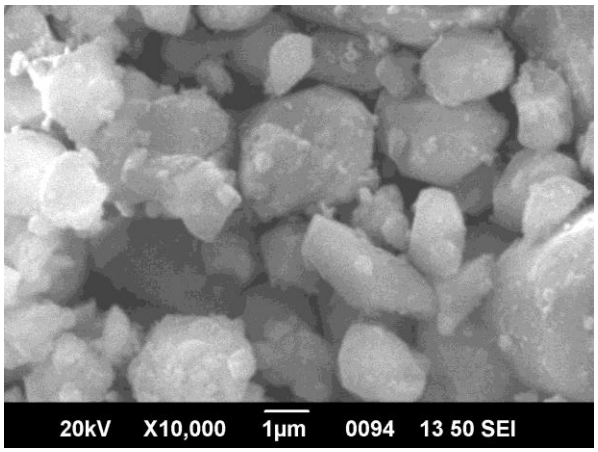

Figure 3: SEM images of $LiCa_3CdV_3O_{12}$ garnet phosphor at different magnifications.

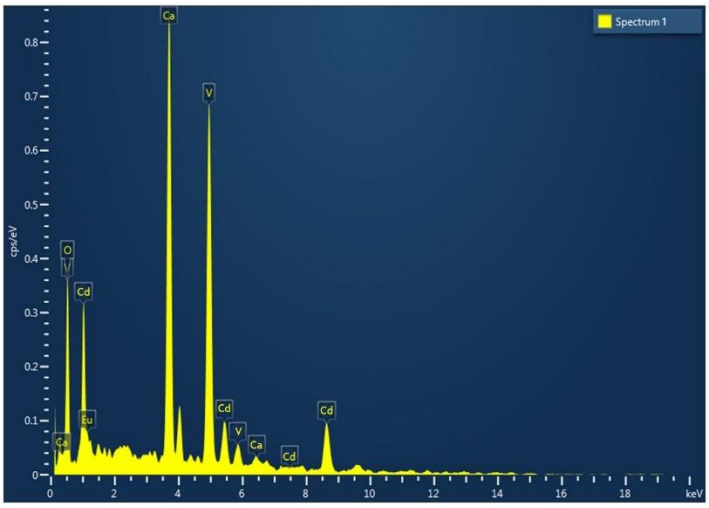

Figure 4: EDS of $LiCa_3CdV_3O_{12}$ for chemical composition.

3.3. Photoluminescence

Figure 5 depicts the emission spectrum of $LiCa_3CdV_3O_{12}$ lanthanide free vanadate phosphors. The emission spectrum is stimulated by 327 nm of radiation. The emission peak is obtained at wavelengths 465 nm for VO_4^{3-} in the transition from $^3T_1$, $^3T_2$ to $^1A_1$ [21]. The emission peak is shown in the energy level diagram Figure 7 (b). Figure 6 depicts the excitation spectrum of $LiCa_3CdV_3O_{12}$ vanadate phosphor. The excitation spectrum is stimulated by 465 nm for VO_4^{3-}. The dark blue line depicts that the electronic transition is taken place from $^1A_1$ to $^1T_1$, $^1T_2$ for the lanthanide-free vanadate phosphor.

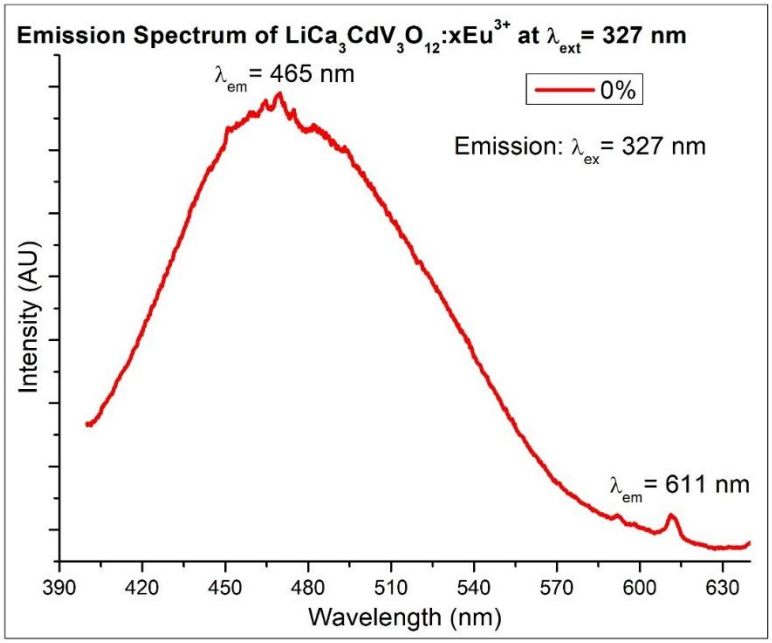

Figure 5: The emission spectrum of $LiCa_3CdV_3O_{12}$ was monitored at 327 nm and emission wavelengths were 465 nm for lanthanide free vanadate phosphor.

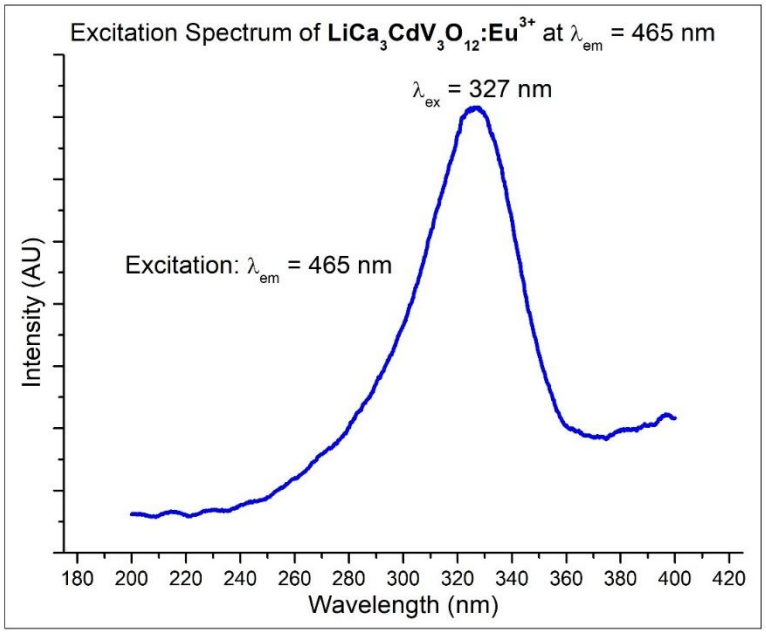

Figure 6: The excitation spectra of $LiCa_3CdV_3O_{12}$ for vanadate were simulated at 465 nm excited at 327 nm.

3.4. Colour Chromaticity

An illustration of the CIE chromaticity diagram of lanthanide free phosphor can be found in Figure 7 (a). The sample has an emission spectrum that appears to be in blue areas. The chromaticity studies provide information

about the colour and the colour coefficient that is dependent on temperature (CCT). The raster image of the CIE diagram of phosphor that has been prepared draws its power from 6W and is illuminated by light with a wavelength of 356 nm. The colour coordinates (x, y) of the $LiCa_3CdV_3O_{12}$ are (C_x, C_y) = (x, y) = (0.224, 0.316). This is true across the entire wavelength range, which extends from 400 nm to 720 nm. It has been discovered that the colour-dependent temperature for the obtained coordinates (CCT) is 14818 K. Table 2 contains additional parameters, such as the dominant colour coordinates (x_d, y_d), the percentage of colour purity, and the average lifetime (in ns).

a b

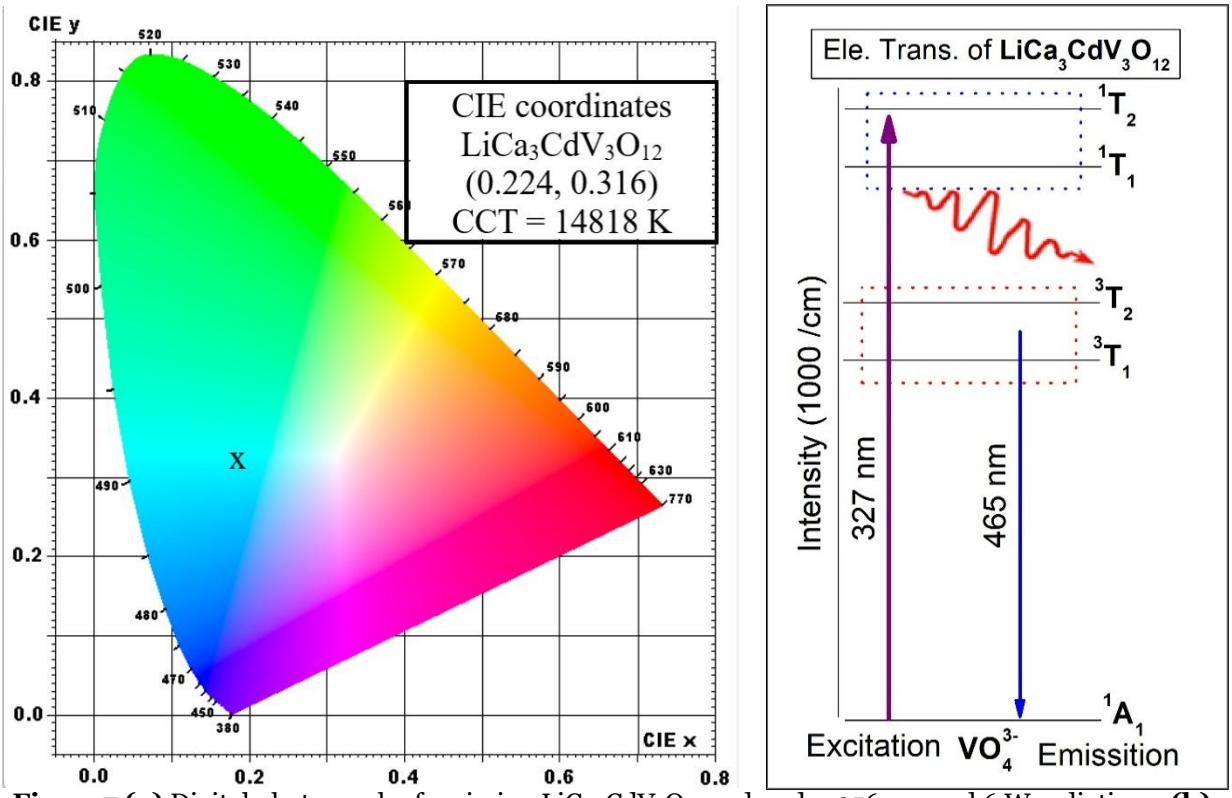

Figure7 (a) Digital photograph of emission $LiCa_3CdV_3O_{12}$ and under 356 nm and 6 W radiations. **(b)** Energy transition diagram of $LiCa_3CdV_3O_{12}$.

Table 2: CIE parameters: dominant colour coordinates (x_d, y_d), colour purity, and the average lifetime.

Dominant Wavelength (nm)	x	y	x_d	y_d	x_s	y_s	Colour Purity	Life Time	CCT
465 nm	0.224	0.316	0.124	0.058	0.31006	0.31616	41.58%	569.4155 ns	14818 K

4. CONCLUSION

A lanthanide-free vanadate garnet-type phosphor self-triggered was prepared with preheated 800° C and then calcined at 950° C. XRD characterisation methods confirmed the garnet phosphor's desired use. The phase identifications were examined by an X-ray diffractometer and the materials had a cubic crystal structure with lattice constant 11.23721 A°. The XRD data was refined by Rietveld refinement software to chi square 1.212. SEM and EDX measured morphology and compositions. EDX examined present of elements in the material. The phosphors were excited at 327 nm to study their photoluminescence. The excitation spectra were monitored at 465 nm for VO_4. Emission peaks for vanadate were 465 nm CIE digital diagram revealed colour chromaticity coordination (0.224, 0.316) for VO_4. These results show that garnet phosphor is optimal for blue-white.

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