Journal of Luminescence 195 (2018) 234–239

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

# Spectroscopy evaluation of crystalline and amorphous $Cd_2V_2O_7$ as blue phosphors

E. Cervantes-Juárez[a], A.N. Meza-Rocha[b], R. Licona-Ibarra[c], U. Caldiño[a,1], E. Alvarez-Ramos[d], J.G. Quiñones-Galván[e], R. Lozada-Morales[a,*]

[a] Benemérita Universidad Autónoma de Puebla. Postgrado en Física Aplicada. Facultad de Ciencias Físico-Matemáticas, Av. San Claudio y Av. 18 sur, Col. San Manuel Ciudad Universitaria, Puebla Pue. C. P. 72570, Mexico

[b] CONACYT-Benemérita Universidad Autónoma de Puebla. Postgrado en Física Aplicada. Facultad de Ciencias Físico-Matemáticas, Av. San Claudio y Av. 18 sur, Col. San Manuel Ciudad Universitaria, Puebla Pue. C. P. 72570, Mexico

[c] Benemérita Universidad Autónoma de Puebla. Facultad de Ciencias Químicas, Av. San Claudio y Av. 18 sur, Col. San Manuel Ciudad Universitaria, Puebla Pue. C. P. 72570, Mexico

[d] Departamento en Física, Universidad de Sonora, Hermosillo, Sonora 83000, Mexico

[e] Departamento de Física, Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Boulevard Marcelino García Barragán 1421, Guadalajara, Jalisco C.P. 44430, Mexico

ARTICLE INFO

*Keywords:*
Cadmium pyrovanadate
Blue emission
Charge transference
Partial density of state (DOS)

ABSTRACT

$Cd_2V_2O_7$ compounds in crystalline and amorphous phases were fabricated by the melt-quenching process. Characterizations such as X-ray diffraction, Raman spectroscopy and photoluminescence were performed. X-ray diffraction patterns of the crystalline sample showed peaks associated with a pure $Cd_2V_2O_7$ monoclinic structure, in agreement with the Raman vibrational spectrum. In the case of the amorphous sample, X-ray diffraction patterns only exhibited a broad band, typical of a glassy structure, whereas its Raman spectrum displayed two broad vibrational modes centered at 350 and 850 $cm^{-1}$, attributed to stretching vibrations of $VO_3$ groups. In spite of the structural differences, both samples presented similar photoluminescence features, consisting of a wide band in the 375–525 nm range with two peaks at 411 and 432 nm, associated respectively with the $^3T_2 \rightarrow {}^1A_1$ and $^3T_1 \rightarrow {}^1A_1$ electronic transitions in the $VO_4$ tetrahedron, under 340 nm excitation. Thus, blue light emission with CIE1931 chromaticity coordinates $x\sim 0.200$ and $y\sim 0.145$, and color purity of 62–63%, is achieved from the crystalline and amorphous $Cd_2V_2O_7$ compounds. The emission decay time profiles were well fitted to a bi-exponential function from which the calculated average lifetime values resulted to be 112 ± 13 and 99 ± 4 ns for the crystalline and amorphous $Cd_2V_2O_7$ samples, respectively. Theoretical calculations based on the density of electronic states revealed that the photoluminescence arises through charge transference processes from 3d orbitals of four-fold coordinated vanadiums to 2p orbitals of three-fold coordinated oxygens in the $VO_4$ tetrahedron, being the basic unit of $Cd_2V_2O_7$ in crystalline and amorphous phases.

## 1. Introduction

The wide variety of physical properties of vanadate compounds allows a great variety of potential technological applications such as chemical sensor, cathode materials, optical and memory switching among others [1–3]. Particularly, their potential optical applications have been mainly focused on studying the photoluminescence features when they are doped with trivalent lanthanide ions [4–6]. However, their intrinsic photoluminescence covering completely the visible region offers a rare earth free phosphor solution [7,8], attracting attention in lighting technology. In these systems, the intrinsic photoluminescence is originated by charge transference (CT) from 3d-vanadium (3d-V) to 2p-oxygen (2p-O) orbitals in the $VO_4$ tetrahedron, which is the basic unit of vanadate compounds. Depending on the type of metallic ions contained between the $VO_4$ units, the emission can be tuned from the UV to visible region [9–14]. Among the vanadate systems, the $Cd_2V_2O_7$ semiconductor compound has been mainly considered for photocatalytic applications in the visible region [15,16]. In this direction as a contribution in potential optical applications, photoluminescence studies on $Er^{3+}$ doped crystalline and amorphous $Cd_2V_2O_7$ were previously performed as function of the $CdO/V_2O_5$ relative starting content, which allowed to analyze the structural effect

* Corresponding author.
*E-mail address:* rlozada@fcfm.buap.mx (R. Lozada-Morales).
[1] On sabbatical leave from Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, P.O. Box 55–534, 09340 México D.F., Mexico.

https://doi.org/10.1016/j.jlumin.2017.11.030
Received 13 July 2017; Received in revised form 23 October 2017; Accepted 19 November 2017
Available online 21 November 2017

changes of the $Er^{3+}$ related emissions, under 488 nm laser excitations [17]. In regard to the $Cd_2V_2O_7$ host, to our best knowledge there are no reports on their intrinsic photoluminescence in crystalline and amorphous phases based on theoretical analysis, that clarify among which V and O pairs within the $VO_4$ tetrahedron the luminescence is originated. So that, motivated by the scarce reports on the photoluminescence of $Cd_2V_2O_7$ in amorphous and crystalline phases and their potential applications in rare earth free phosphors, in this work a comparative study of the experimental photoluminescence with theoretical calculations of density of electronic states (DOS), complemented by X-ray diffraction patterns and Raman spectroscopy, is performed. The studied samples were prepared using the melt-quenching technique in amorphous and crystalline phases by varying the CdO and $V_2O_5$ starting proportions [18].

## 2. Experimental and calculation details

The samples were synthetized by using the melt-quenching method. The amorphous and crystalline phases were obtained by mixing 85/15 and 67/33 of $CdO/V_2O_5$%mol, respectively [18]. The mixtures were melted in a high-alumina crucible at 1200 °C for 30 min and poured onto a copper mold at room temperature. Hereafter, the $Cd_2V_2O_7$ amorphous and crystalline samples will be referred as $Cd_2V_2O_7$-A and $Cd_2V_2O_7$-C, respectively.

The crystalline structure was determined by X-ray diffraction in a Siemens D500 diffractometer with the Cu $k_\alpha$ line (1.54 Å). Raman spectra were recorded in a LabRAM HR spectrometer by using a Helio-Neon laser emitting at 632.8 nm. Excitation and emission spectra were recorded in a Horiba Jobin-Yvon Fluorolog 3–22 spectrofluorometer operating with a 450 W ozone-free Xe lamp in steady mode. Lifetime data were obtained through an Opolette HE 355 LD + UVDM, with pulses of 10 ns in duration. The resulting transient fluorescence signal was analyzed with a Jobin–Yvon monochromator Triax 550 and detected with a HORIBA-Jobin–Yvon i-Spectrum Two ICCD. All measurements were performed at room temperature.

Theoretical calculations of geometry and electronic structure of $Cd_2V_2O_7$-C were performed using the CASTEP software package by the Density Functional Theory (DFT) scheme, with a plane-wave basis set to expand the Khon-Sham wavefunctions [19]. The exchange and correlation effects of valence electrons were processed by the generalized gradient approximation (GGA), within the Perdew–Burke–Ernzerhof (PBE) formulation [20]. This functional has been employed for solid-state calculations in systems with "d" valence electrons [21–23]. It was used a plane-wave cutoff energy of 380 eV to obtain the crystal structure and electronic properties precisely. To approximate the core electrons, ultrasoft pseudopotentials were used [24], taking into account that the configuration of the valence electrons of each atom is: Cd $\rightarrow 4d^{10}\ 5s^2$; O $\rightarrow 2s^2\ 2p^4$ and V $\rightarrow 3s^2\ 3p^6\ 4s^2\ 3d^3$. The structure was stabilized by the Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimization method with a total energy convergence tolerance of $5 \times 10^{-7}$ eV, maximum ionic displacement of $5 \times 10^{-4}$ Å and force per atom of 0.01 eV/Å.

## 3. Results and discussion

X-Ray diffraction patterns portrayed in Fig. 1 were recorded to evaluate the crystalline structure of the samples analyzed. In the case of the $Cd_2V_2O_7$-C sample, all diffraction peaks correspond to a pure monoclinic structure with spatial group C12/m (12). The diffraction peak position variation is less than 0.2%, which reveals that the melt-quenching method and starting proportion of $CdO/V_2O_5$ chosen, enables to synthetize excellent polycrystalline phase purity [18]. The broad band at around $2\theta = 30^\circ$ observed in the $Cd_2V_2O_7$-A sample indicates short range order typical of a glassy structure. It should be pointed out that the transition from crystalline to amorphous $Cd_2V_2O_7$ takes place for CdO content higher than 67%mol, whereas for CdO

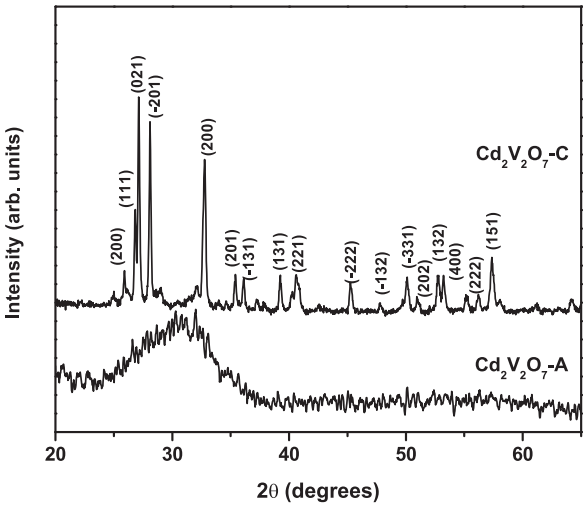


**Fig. 1.** Typical X-ray diffractograms for the $Cd_2V_2O_7$-C and $Cd_2V_2O_7$-A samples.

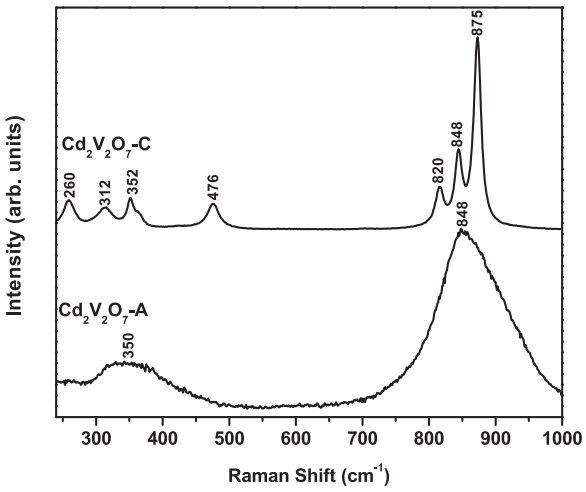


**Fig. 2.** Raman spectra of the $Cd_2V_2O_7$-C and $Cd_2V_2O_7$-A samples.

contents of 67%, 50% and 0%mol, pure $Cd_2V_2O_7$, $CdV_2O_6$ and $V_2O_5$ crystalline phases are obtained [18].

The Raman spectra of the $Cd_2V_2O_7$-C and $Cd_2V_2O_7$-A samples are illustrated in Fig. 2. The $Cd_2V_2O_7$-C sample displays vibrational modes located at 260, 312, 352, 476, 820, 848 and 875 $cm^{-1}$ associated with a crystalline structure, while the $Cd_2V_2O_7$-A one shows two broad bands at around 350 and 848 $cm^{-1}$, related to an amorphous phase due to deconvolutions of the vibrational modes located at 820, 848 and 875 $cm^{-1}$, and 312 and 352 $cm^{-1}$, observed in the crystalline sample, respectively. The broadening of such bands have been previously attributed to ruptures of the V-O-V bridges, which are promoted by the incorporation of high $Cd^{2+}$ contents (CdO higher than 67%mol) [18].

Fig. 3(a) and (b) display respectively the typical excitation spectra of the $Cd_2V_2O_7$-C and $Cd_2V_2O_7$-A samples by monitoring their emissions at 440 nm. The spectra consist of wide bands in the range of 250–420 nm, with similar line-shapes. Gaussian deconvolutions (illustrated by the solid line) reveal that both excitations are mainly composed by three Gaussian bands centered at around 300, 376 and 400 nm. In both cases, the contribution of the Gaussian peak centered at 400 nm is negligible (less than 10%). The emission spectra of $Cd_2V_2O_7$-C and $Cd_2V_2O_7$-A upon 340 nm excitation, showed in Fig. 3(c), cover the 375–525 nm range and exhibit two peaks at 411 and 432 nm. These bands originated by charge transfer between oxygen 2p and vanadium 3d orbitals in the $VO_4$ tetrahedron, with $T_d$ symmetry [25], have been attributed to the following transitions illustrated in