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Synthesis, crystal structure and luminescent properties of pyrovanadates $A_2CaV_2O_7$ ($A = Rb, Cs$)

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ABSTRACT

The novel vanadium oxides $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$ have been prepared by solid-state reaction and their crystal structures determined and refined using X-ray, neutron powder and electron diffraction data. $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$ are isostructural, crystallizing in space group $P2_1/n$ with unit cell parameters: $a = 13.8780(1)$, $b = 5.96394(5)$, $c = 10.3376(1)$ Å, $\beta = 104.960(1)^\circ$ and $a = 14.0713(2)$, $b = 6.0934(1)$, $c = 10.5944(1)$ Å, $\beta = 104.608(1)^\circ$, respectively. Their crystal structures can be described as a framework of CaO_6 octahedra and V_2O_7 pyrogro groups with alkaline metals found in the tunnels formed. Photoluminescence (PL) and PL excitation spectra of the considered pyrovanadates have been studied in the vacuum ultraviolet (VUV) to visible light (Vis) range as well as their pulse cathode luminescence (PCL) spectra and the kinetic parameters of PCL. In the PL and the PCL spectra of both pyrovanadates recorded at $T = 300$ K a broad band with maxima at 2.2, 2.4 eV and two shoulders (bands) at 2.0 and 2.58 eV have been observed. At $T = 10$ K the band at 2.0 eV becomes the main band in the spectra. Two types of luminescence centers for each pyrovanadate, with very similar excitation bands at 3.75, 4.84, 6.2, 7.3 and 9.1 eV, have been found. The nature of the luminescence centers connected with the bands at 2.0, 2.2, 2.4 and 2.58 eV is discussed.

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1. Introduction

Complex vanadium oxide compounds have drawn the attention of researchers and developers as promising luminescent materials [1–12]. The technical applications of vanadium oxides compounds have been proved by dozens of patents [5,6]. On the basis of complex vanadium oxides different luminescence materials have been developed and suggested, such as phosphors for plasma display panels and field-emission displays ($YVO_4:Eu$) [2,3,5,6] or active laser media ($YVO_4:Ln$ ($Ln = Nd, Er, Tm, Ho$)) [7–10], $Ca_3(V-O_4)_2:Nd^{3+}$ [4]. Effective and advanced crystals for diode pumped lasers can be made from $YVO_4:Nd^{3+}$ [9,10] while luminescent screens with various luminescence spectra [3,5–12] can be made from (Y, Gd, Lu) VO_4 , dark blue, $\lambda = 470$ – 480 nm [3], $ScVO_4$, green, $\lambda = 510$ – 520 nm [3] and $LuVO_4$, red, $\lambda = 600$ – 610 nm [3].

The vanadate based luminescent materials listed above contain discrete $[VO_4]^{3-}$ groups in their structures. Properties of compounds containing pyro- $[V_2O_7]^{4-}$ group have been studied to a lesser extent,

and then mainly from a synthetic and structural point of view [3,13–15]. There are rather few reports concerning pyrovanadates of composition $A_2B^{2+}V_2O_7$ ($A =$ alkaline metal, $B =$ bivalent metal). Only the crystal structures of $Na_2ZnV_2O_7$ [14], $K_2MgV_2O_7$ [15] and $A_2MnV_2O_7$ ($A = Rb, K$) [16] have been studied in detail. $Na_2ZnV_2O_7$ and $K_2MnV_2O_7$ crystallize in a melilite (åkermanite)-type structure (space group $P-42_1m$, $Z = 2$; $a = 8.2711(4)$, $c = 5.1132(2)$ Å and $a = 8.609(3)$, $c = 5.538(4)$ Å, respectively) and consist of infinite $B^{2+}V_2O_7$ layers of corner-sharing tetrahedra stacked along the c axis. The alkaline metals are positioned between the layers, with a distorted anti-prismatic coordination of oxygen atoms. $K_2MgV_2O_7$, as well as $Rb_2MnV_2O_7$, has a melilite (åkermanite) related structure (space group $P4_2/mnm$, $Z = 4$) [15] with the c axis length being twice that of melilite (åkermanite). The doubling of the c axis appears due to a mirror plane between the MgV_2O_7 layers. As a result the local coordination sphere around the potassium atoms changes into a distorted tetragonal prism keeping the motif of intralayer network unchanged.

The same structures were found for the phosphates $Na_2B^{2+}P_2O_7$ ($B = Zn, Co$); $K_2B^{2+}P_2O_7$ ($B = Zn, Co, Cu$) [17,18]. But in addition to the melilite(åkermanite) and åkermanite-related phosphates

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Table 1Crystal data for $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$.

	$\text{Rb}_2\text{CaV}_2\text{O}_7$	$\text{Cs}_2\text{CaV}_2\text{O}_7$
Unit cell parameters	$a = 13.8780(1) \text{ \AA}$ $b = 5.96394(5) \text{ \AA}$ $c = 10.3376(1) \text{ \AA}$ $\beta = 104.960(1)^\circ$	$a = 14.0713(2) \text{ \AA}$ $b = 6.0934(1) \text{ \AA}$ $c = 10.5944(1) \text{ \AA}$ $\beta = 104.608(1)^\circ$
Unit cell volume ($\text{\AA}^3$)	826.62(1)	880.08(1)
Space group	$P2_1/n$	
Formula units, Z	4	
R_p, R_{wp} (%)	1.95(2.44) ^a , 2.61(3.09) ^a	1.92(1.74) ^a , 2.48(2.19) ^a
$R(F^2)$ (%)	3.47(3.82) ^a	3.39(3.40) ^a
χ^2	3.761	1.686

^a Neutron powder diffraction data.

with layered structures, there exist other phosphates with the general composition $A_2^+B^{2+}P_2O_7$, A = alkaline metal, B = bivalent metal, e.g. ($K_2MnP_2O_7$, $K_2CdP_2O_7$, $K_2SrP_2O_7$, $Cs_2SrP_2O_7$, etc.) having framework structures [19–22]. The crystal structures of these compounds can be described as a framework of BO_6 - octahedra and $[P_2O_7]^{4-}$ pyrogroups with alkaline metals in the tunnels formed. However, variations in the connection patterns make it possible to separate them in two groups: $K_2CdP_2O_7$ and $Cs_2SrP_2O_7$ having C-centered structures and $K_2MnP_2O_7$ and $K_2SrP_2O_7$ having primitive structures, although the structures are not completely identical within the groups.

There have been no reports of the existence of pyrovanadates with framework structure and the ideal composition $A^{+2}B^{2+}V_2O_7$ (A = alkaline metal, B = bivalent metal) so far. Here we present the synthesis, crystal structure and luminescence properties of the novel framework pyrovanadates $A_2\text{CaV}_2\text{O}_7$ (A = Rb, Cs).

2. Experimental

$\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ were prepared by solid-state reaction in air from stoichiometric mixtures of AVO_3 (99.9%) (A = Rb, Cs) and CaCO_3 (99.9%) according to the reaction:

The mixtures were placed in platinum crucibles and annealed at $T = 500\text{--}550^\circ\text{C}$ and $400\text{--}580^\circ\text{C}$ during 120 h, to obtain $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$, respectively. This procedure was repeated several times with intermediate cooling and regrinding in an agate mortar.

The XRD patterns were collected at room temperature on a transmission STADI-P (STOE, Germany) diffractometer equipped

with a linear mini-PSD detector, using $\text{Cu K}\alpha_1$ radiation in the 2θ range $2^\circ\text{--}120^\circ$ with a step of 0.02° . Polycrystalline silicon ($a = 5.43075(5) \text{ \AA}$) was used as external standard. The phase purity of the samples was checked by comparing their X-ray powder diffraction (XRD) patterns with those in the PDF2 database (Powder diffraction file, ICDD, USA), release 2007. The neutron powder diffraction data were collected at room temperature using the 7A diffractometer at the IWW 2M reactor (Zarechny) in the 2θ range $2^\circ\text{--}120^\circ$ with a step of 0.02° , $\lambda = 1.5323 \text{ \AA}$. The crystal structure of $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ was refined with the GSAS program suite [23] using X-ray and neutron powder diffraction data simultaneously. Combining XRD and neutron data in a refinement is not straightforward, since the photons are scattered by electrons while the neutrons by the nucleus of the atoms. The results of individual refinements based on only X-ray or neutron diffraction data would therefore not completely coincide. However, the use of only XRD or only neutron diffraction data has its weakness. For light elements like oxygen the low scattering power compared to rubidium, cesium and vanadium can be a problem in XRD while for neutron diffraction the close to zero cross-section for vanadium is a limitation. We therefore decided to use one model for both data sets. The unit cell parameters were refined using the XRD data. These values were then used for the neutron data and the wavelength was refined instead. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = x \times L(2\theta) + (1 - x) \times G(2\theta)$ (where L and G are the Lorentzian and Gaussian parts, respectively). The angular dependence of the peak width was described by the relation $(\text{FWHM})^2 = U \tan^2\theta + V \tan\theta + W$, where FWHM is the full line width at half maximum. The background level was described as a combination of fifteen Chebyshev polynomials.

For the transmission electron microscopy studies, (ED - electron diffraction and EDS - energy-dispersed X-ray microanalysis), the samples were crushed in butanol. A drop of this dispersion was put on a copper grid covered with a holey carbon film. The microscope used was a JEOL 2000FX, operated at 200 kV, equipped with a LINK AN10000 EDX system.

The PL spectra in UV-vis region (1.38–4.13 eV) and PL excitation spectra in the VUV-UV region (3.64–10.33 eV) under synchrotron radiation (SR) excitation have been measured at 10 K and 300 K. Measurements on the synchrotron excitation set-up were performed using the Beam-Line I facility of the SUPERLUMI station (HASYLAB, DESY, Hamburg). The ARC SpectraPro-308i monochromator (0.3 m) equipped with the R6358P (Hamamatsu) photomultiplier was used to analyse the luminescence excitation spectra and photoluminescence under SR excitation. The excitation spectra were corrected for the equal number of exciting photons

Fig. 1. Selected area electron diffraction patterns of $\text{Rb}_2\text{CaV}_2\text{O}_7$ recorded along $[001]^*$ and $[010]^*$.

Table 2
Atomic coordinates and isotropic thermal parameters for $A_2CaV_2O_7$ ($A = Rb, Cs$).

Atom	Wyckoff	x/a	y/b	z/c	$U_{iso} \times 100 (\text{\AA}^2)$
Ca	4e	0.0203(2)	0.0151(4)	0.2357(9)	0.243(2)
A(1)	4e	0.3249(1)	0.3229(1)	0.2717(5)	0.2744(9)
A(2)	4e	0.8592(1)	0.8451(1)	0.7252(5)	0.732(1)
V(1)	4e	0.1228(2)	0.1215(4)	0.2739(8)	0.273(2)
V(2)	4e	0.3625(2)	0.3688(4)	0.2625(8)	0.261(3)
O(1)	4e	0.0373(4)	0.0495(8)	0.077(1)	0.078(2)
O(2)	4e	0.0979(5)	0.1000(9)	0.520(1)	0.518(2)
O(3)	4e	0.1273(5)	0.1155(8)	0.280(2)	0.279(2)
O(4)	4e	0.2430(5)	0.242(1)	0.179(1)	0.192(2)
O(5)	4e	0.3594(5)	0.3700(9)	0.508(1)	0.498(2)
O(6)	4e	0.4319(5)	0.431(1)	0.304(1)	0.291(3)
O(7)	4e	0.3993(5)	0.4102(8)	0.054(1)	0.049(2)

Note. Data for $Cs_2CaV_2O_7$ are given in *italic*; All atomic positions were found to be fully occupied.

using a standard method with sodium salicylate, whereas the emission spectra are presented without any corrections. In addition the PL spectra in the range 1.55–4.13 eV and the luminescence excitation spectra in the range 3.14–6.2 eV under soft UV-light (deuterium lamp) excitation at room temperature were measured at Stockholm University and at Ural State Technical University – UPI in parallel. The results obtained at both universities coincide. There is only a small divergence in the excitation spectra obtained by using of synchrotron radiation excitation and deuterium lamp excitation. It can be explained due to the different spectral sensitivities of the optical channels.

The PCL spectra of pyrovanadates have been measured under electron beam excitation (electron gun KLAVI-R) with parameters: $E = 150$ keV, $\tau = 2$ ns, pulse current 1000 A. The kinetic parameters of PCL have been measured at Ural State Technical University – UPI. The electron gun MIRA-2D was used as a source of the exciting radiation (electron beam $E = 160$ keV, $\tau = 15$ –20 ns, pulse current 150 A). The decay curves of PCL have been measured by using a PMT-7 photomultiplier tube, a MDR-2 monochromator and a Tektronix TDS-2024B oscilloscope. The parameters of the luminescent bands were extracted from the spectra by peak fitting by using a Gaussian–Lorentzian cross-product distribution form,

$$A(E) = \frac{A_0}{1 + f \left(\frac{E-W}{\sigma} \right)^2 \exp \left[\frac{1-f}{2} \left(\frac{E-W}{\sigma} \right)^2 \right]} \quad (1)$$

where A_0 is the maximal amplitude of the band, W is center of the band, σ is the width of the band, and f defines the shape of the band (from Gaussian for $f \sim 0.5$ to Lorentzian for $f = 1$).

3. Results

3.1. Crystal structure

The XRD diffraction patterns could be indexed with monoclinic unit cells, Table 1. An analysis of systematically absent reflections in XRD and electron diffraction patterns ($h0l$: $h + l = 2$, $0k0$: $k = 2n$) indicates a $P2_1/n$ space group for both compounds. Selected area diffraction patterns of $Rb_2CaV_2O_7$, viewed along the $[010]$ and $[001]$ zone axes are shown in Fig. 1. The EDS analyses of pyrovanadates were made to check the purity of the samples. The obtained compositions were in good agreement with the nominal composition. $K_2MnP_2O_7$ [19] was used as a starting model for the crystal structure refinement of both pyrovanadates. The details of the refinement, refined atomic coordinates and temperature factors, selected interatomic distances are found in Tables 1–3. The calculated, observed and difference patterns are shown in Figs. 2 and 3.

The crystal structure of $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$, isostructural to $K_2MnP_2O_7$ [19], can be described as a polyhedral framework of the corner-sharing CaO_6 octahedra and V_2O_7 pyrogro-

tunnels are formed parallel to the b axis in the crystal, where alkali metals are located, see Fig. 4. The CaO_6 octahedra connect each other through the V_2O_7 pyrogrogroups, forming layers parallel to the ab and bc planes in the structure. Each Ca^{2+} atom is surrounded by oxygen from six different $V_2O_7^{4-}$ groups. The average Ca–O interatomic distances in the octahedra are 2.337 and 2.354 Å for $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$, respectively, which are very close to the sum of the ionic radii for O^{2-} and Ca^{2+} , 2.35 Å [24]. However, it should be mentioned that according to the refinement the CaO_6 octahedra in $Rb_2CaV_2O_7$ are slightly distorted. The pyrogrogroups have a trans-conformation and settle down along the c direction. The average V–O interatomic distances in the tetrahedra are 1.713 and 1.718 Å for $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$, respectively, in agreement with the sum of the ionic radii for V^{5+} and O^{2-} , which is 1.705 Å. The longest V–O distance in the tetrahedra is from vanadium to a bridging oxygen atom. The alkaline metals located inside tunnels are displaced towards the oxygen atoms and occupy two types of positions with coordination number 8 and 9. The substitution of Cs^+ for Rb^+ atoms results in a slight elongation of the $V_2O_7^{4-}$ pyrogrogroups, accompanied with an increase of $V(1)$ – $O(4)$ – $V(2)$ bond angles from $122.6(4)^\circ$ in $Rb_2CaV_2O_7$ to $135.9(6)^\circ$ in $Cs_2CaV_2O_7$.

3.2. Luminescence properties

3.2.1. Luminescence and luminescence excitation spectra under VUV and UV excitations

The photoluminescence and luminescence excitation spectra of $Rb_2CaV_2O_7$ and $Cs_2CaV_2O_7$ were measured under VUV SR

Table 3
Selected interatomic distances (Å) for $A_2CaV_2O_7$ ($A = Rb, Cs$).

Bond	$Rb_2CaV_2O_7$	$Cs_2CaV_2O_7$	Bond	$Rb_2CaV_2O_7$	$Cs_2CaV_2O_7$
Ca–O(1)	2.256(7)	2.38(2)	A(1)–O(1)	3.061(6)	3.30(1)
Ca–O(2)	2.372(8)	2.34(2)	A(1)–O(2)	3.023(8)	3.15(2)
Ca–O(3)	2.339(7)	2.35(2)	A(1)–O(3)	3.005(10)	3.43(1)
Ca–O(5)	2.343(7)	2.37(2)	A(1)–O(3)	3.102(10)	3.14(2)
Ca–O(6)	2.350(7)	2.37(2)	A(1)–O(3)	3.205(7)	3.19(2)
Ca–O(7)	2.365(8)	2.32(2)	A(1)–O(5)	3.078(8)	3.12(2)
	2.337	2.354	A(1)–O(5)	3.110(7)	3.25(1)
			A(1)–O(7)	3.063(8)	3.24(2)
				3.081	3.229
V(1)–O(1)	1.747(6)	1.67(2)			
V(1)–O(2)	1.623(7)	1.68(2)	A(2)–O(1)	3.308(8)	3.36(2)
V(1)–O(3)	1.651(7)	1.67(1)	A(2)–O(2)	3.161(8)	3.21(1)
V(1)–O(4)	1.870(6)	1.78(1)	A(2)–O(4)	2.991(6)	3.20(2)
	1.723	1.705	A(2)–O(4)	3.030(7)	3.19(1)
			A(2)–O(5)	2.952(8)	3.10(2)
V(2)–O(4)	1.797(6)	1.85(1)	A(2)–O(6)	2.983(9)	3.44(1)
V(2)–O(5)	1.701(7)	1.70(2)	A(2)–O(6)	3.206(6)	3.41(2)
V(2)–O(6)	1.661(6)	1.68(2)	A(2)–O(6)	3.314(9)	3.14(2)
V(2)–O(7)	1.656(7)	1.69(2)	A(2)–O(7)	3.130(8)	3.29(2)
	1.703	1.731		3.119	3.259

Note. Average values are given in boldface.

Fig. 2. Observed (crosses), calculated (solid line), difference (bottom) neutron (a) and X-ray (b) powder diffraction patterns of $\text{Rb}_2\text{CaV}_2\text{O}_7$.

excitation at 300 and 10 K (Figs. 5–7). The emission spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ (Fig. 5a and b) at 300 K (curves 2 and 4) exhibit very similar broad bands (1.6–3.1 eV, FWHM = 0.73 eV) which can be considered as the superposition of two peaks at 2.2 and 2.4 eV with two shoulders connected with bands at 2.0 and 2.58 eV as proved by profile fitting (Fig. 6). At 10 K the peak with maximum at 2.0 eV (FWHM = 0.5 eV) starts to dominate in the spectrum (Fig. 5c). The intensity of its emission increases approximately more than two times. At first sight it could seem that the investigated vanadates $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ exhibit an unusual red-shift with decreasing measurement temperature, however, this is not the case. In fact it can be seen in Fig. 5a and b that the intensity of the bands is redistributed leading to an increase in intensity for the peak at 2.0 eV causing what appears to be a red-shift. It is noteworthy that the positions of maxima and shapes of the PL spectra at $T = 10$ K are very similar for $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$. However, in the former case a fine structure in the energy range 2.03–3 eV of the PL spectra (bands with the average frequency interval equals to $h\nu = 862 \text{ cm}^{-1}$) was found. This fine structure can be attributed to the electron-phonon interactions.

The PL excitation spectra of the $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ were measured for the band 2.38–2.4 eV at 300 K and for the band 2.07–2.08 eV at 10 K. The results are presented in Fig. 7 (normalized to 1). The main peaks in the excitation spectra are located (in order of decreasing excitation energy) at 9.1, 7.3 shoulder, 6.2 eV, 4.84 and 3.75 eV (Table 4).

Fig. 3. Observed (crosses), calculated (solid line), difference (bottom) neutron (a) and X-ray (b) powder diffraction patterns of $\text{Cs}_2\text{CaV}_2\text{O}_7$.

The photoluminescence and luminescence excitation spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ under UV excitation at 300 K are presented in Fig. 8. The luminescence spectra obtained under UV excitation have the same shape as the luminescence spectra obtained under VUV SR excitation. Closer examination of the PL band at 2.38–2.4 eV obtained under UV excitation showed that the lowest-energy excitation peak for this band is at 3.75 eV (Fig. 8, (5)). The position

Fig. 4. Crystal structure of $\text{A}_2\text{CaV}_2\text{O}_7$ (A = Rb, Cs) viewed along the b axis.

Fig. 5. Photoluminescence spectra of (a) $\text{Rb}_2\text{CaV}_2\text{O}_7$ measured at $T = 10\text{ K}$ (1), $T = 300\text{ K}$ (2) and (b) $\text{Cs}_2\text{CaV}_2\text{O}_7$; $T = 10\text{ K}$ (3), $T = 300\text{ K}$ (4). $E_{\text{exc}} = 6.52\text{ eV}$. (c) Pulse cathode luminescence spectra for $\text{Rb}_2\text{CaV}_2\text{O}_7$ (5) and $\text{Cs}_2\text{CaV}_2\text{O}_7$ (6) at 300 K .

Fig. 6. Photoluminescence spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ measured at $T = 10\text{ K}$, $T = 300\text{ K}$, with the curve of profile fitting.

Fig. 7. Luminescence excitation spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ measured at 300 K for $E_{\text{em}} = 2.38\text{ eV}$ (1) and at 10 K for $E_{\text{em}} = 2.07\text{ eV}$ (2); luminescence excitation spectra of $\text{Cs}_2\text{CaV}_2\text{O}_7$ measured at 300 K for $E_{\text{em}} = 2.38\text{ eV}$ (3) and at 10 K for $E_{\text{em}} = 2.07\text{ eV}$ (4).

of the main peak in the PL spectra measured under soft UV excitation (3.35–5.16 eV) remains constant at 2.4 eV (Fig. 8, (1–4)).

3.2.2. Luminescence spectra and kinetic parameters under pulse electron beam excitation

The PCL spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ have been measured in the range 1.5–3.25 eV at 300 K (Fig. 5c). The shapes of the PCL spectra for both vanadates are similar to the shape of the PL spectra obtained under VUV- and UV-excitations at 300 K (Fig. 5a and b). The PCL spectra are situated at 1.6–3.1 eV for both pyrovanadates. The broad band in the PCL spectra has two main peaks with maxima at $\sim 2.2\text{ eV}$ and $\sim 2.4\text{ eV}$, and two shoulders at 2.06–2.08 and 2.52–2.58 eV according to profile fitting. The intensity of the shoulders is higher for pulse electron beam excitation than for SR excitation. This can be explained by the differences in the excitation density.

The kinetic luminescence parameters under pulse electron beam excitation for pyrovanadates have been measured at 300 K . It was found that the luminescence decay curves for the main bands at 2.0, 2.2 and 2.4 eV for $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ have an exponential form. For example, the decay curve for band at 2.38 eV for $\text{Rb}_2\text{CaV}_2\text{O}_7$ is shown in Fig. 9. The PCL emission band at 2.0 and 2.2 eV for both vanadates has the same decay time $\sim 46\text{ }\mu\text{s}$. Thus there is only one exponential component in the PCL decay curve.

4. Discussion

Despite the large number of publications about luminescence properties of vanadates [1–12], the available experimental and theoretical data are not sufficient to give a unifying explanation of the nature of the luminescence centers in these compounds. There have been attempts to explain the nature of the bands in the optical spectra of vanadates by the presence of vanadium–oxygen clusters such as $[\text{VO}_4]^{3-}$, $[\text{V}_2\text{O}_7]^{4-}$, $[\text{VO}_6]^{9-}$ or cyclic $[\text{V}_4\text{O}_{12}]^{4-}$ [1–3,11,12] ($[\text{VO}_4]^{3-}$ clusters in $\text{Ca}_2\text{VO}_4\text{Cl}$ and NaCaVO_4 [11] and $[\text{VO}_6]^{9-}$ clusters in LaVO_3 and YVO_3 [12] (Table 4)). There have been some recent attempts [10,11] to explain the nature of luminescence in vanadates

Table 4
Positions of emission and excitation bands for vanadates.

Compound	Emission bands (eV)	PL excitation bands (eV)
$\text{Rb}_2\text{CaV}_2\text{O}_7$	2.38, 2.21, 2.07	3.75, 4.84, 6.2, 7.3, 9.1
$\text{Cs}_2\text{CaV}_2\text{O}_7$	2.38, 2.21, 2.07	3.75, 4.84, 6.2, 7.3, 9.1
KSrVO_4 [26]	2.48	4.2, 5.0, 7.43, 8.2, 10
NaCaVO_4 [11]	2.51	3.3, 3.75, 4.75, 5.55, 6.5, 9.4
LaVO_3 [12]	No data	2–4, 4.75–5.5, 6.3, 7.3, 8–9

Fig. 8. Photoluminescence spectra of $\text{Rb}_2\text{CaV}_2\text{O}_7$ at 300 K for: $E_{\text{exc}} = 3.64$ eV (1), $E_{\text{exc}} = 4$ eV (2), $E_{\text{exc}} = 5.16$ eV (3), $E_{\text{exc}} = 3.35$ eV (4); luminescence excitation spectra $\text{Rb}_2\text{CaV}_2\text{O}_7$ at 300 K for $E_{\text{em}} = 2.38$ eV (5).

by the presence of structural defects such as nonequivalent tetracycle $[\text{V}_4\text{O}_{12}]^{4-}$ units [25], F-type centers [8] or oxygen vacancies around V^{4+} ions [9] or oxygen O^- defects (as for SrWO_4 [26]). However, these attempts have not been entirely successful due to incompleteness of the models. There are numerous cases where the same peaks have been observed in PL spectra of vanadates containing different structural groups. For example, the lines at 2.38–2.4 eV (515–520 nm) and 2.25–2.34 eV (530–550 nm) are present in spectra of different compounds with dissimilar structural groups, e.g. tetracycle $[\text{V}_4\text{O}_{12}]^{4-}$ units in $\text{Na}_2\text{Ca}(\text{VO}_3)_4$ [25], $[\text{VO}_4]^{3-}$ units in $\text{Rb}(\text{Ca},\text{Sr})\text{VO}_4$ and KSrVO_4 [27] and $[\text{V}_2\text{O}_7]^{4-}$ units in $\text{Cs}_2\text{CaV}_2\text{O}_7$ [27]. On the basis of similarity of luminescence spectra of different vanadate compounds with different structural groups one can assume that the most likely explanation of luminescence in these compounds is the existence of luminescence centers with oxygen O^- defects in different vanadium–oxygen clusters. This model is discussed assuming an L-like center for the investigated pyrovanadates. In their spectra were found two different centers of luminescence depending on temperature. The intensity redistribution of the bands in the luminescence spectra of pyrovanadates when reducing the temperature from 300 to 10 K (Fig. 5) can be an evidence of the existence of two centers: the band at 2.0 eV (center I) and the bands 2.2, 2.4 and probably 2.58 eV (center II). The nature of center I and center II of the pyrovanadates can be related (due to the crystal structure) to vanadium–oxygen pyrogroups V_2O_7 with some oxygen defects (O^- defects in $[\text{V}_2\text{O}_7]^{4-}$) like L-center in SiO_2 (the L-center for SiO_2 is the structure fragment with an O^- defect $[\text{O} \equiv \text{Si} - \text{O}^- \cdots \text{Me}^+]$) [28,29]. In analogy with the L-centers in SiO_2 [27], the model of L-centers can be related to quasimolecular complexes $[\text{O} \equiv \text{V} - \text{O} - \text{V} = \text{O}^- \cdots \text{Me}^+]$ (disturbed V_2O_7 fragment) for our compounds. In the frame of further development of the model for luminescence L-type center in pyrovanadates [27] it is possible to suggest that the excitation bands of pyrovanadates can be related to the complex set of singlet–singlet transitions in disturbed

Fig. 9. The luminescence decay curve at 300 K for $\text{Rb}_2\text{CaV}_2\text{O}_7$ for the band 2.38 eV.

$[\text{V}_2\text{O}_7]^{4-}$ fragments. The electronic excitations of $[\text{V}_2\text{O}_7]^{4-}$ groups decay with charge transfer to the $[\text{O}^- \cdots \text{Me}^+]$ part of the center. The luminescence bands can be attributed to triplet–singlet transition ($T_1 \rightarrow S_0$) in disturbed $[\text{V}_2\text{O}_7]^{4-}$ centers with a decay time of 46 μs . The expected fast (nano- and subnanosecond range) singlet–singlet $S_1 \rightarrow S_0$ transitions in these centers were not observed maybe due to the limitations of the equipment used.

5. Concluding remarks

Novel pyrovanadates $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ isostructural to alkaline phosphates of bivalent metals $A_2^{2+}\text{M}^{2+}\text{P}^{5+}_2\text{O}_7^{2-}$, such as $\text{K}_2\text{MnP}_2\text{O}_7$ [19] have been studied. The crystal structure of the considered vanadates can be described as a framework of CaO_6 octahedra and V_2O_7 pyrogroups with alkaline metals placed in the tunnels formed. Luminescence properties of $\text{Rb}_2\text{CaV}_2\text{O}_7$ and $\text{Cs}_2\text{CaV}_2\text{O}_7$ in VUV under SR excitation, UV and visible ranges, pulse cathode luminescence and the kinetic parameters under pulse electron beam excitation have been studied. Two different luminescence centers' band 2.0 eV (center I) and bands 2.2, 2.4 and probably 2.58 eV (center II) were found. The nature of the luminescence band at 2.58 eV needs more study.

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