Radioluminescent Properties and Crystal Structure of New Materials on the Base of Tetra and Hexametavanadates of Alkali-Alkaline-Earth Elements

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Abstract – In the paper the crystal structure parameters and luminescent properties of new materials on the base of hexametavanadates of alkali-alkaline-earth elements are presented in comparison with similar parameters and properties of tetrametavanadates.

1. Introduction

Alkali-alkaline-earth element vanadates are key technological materials family widely used in applications such as optical switches and phosphors, chemical sensors, catalysts and solid-state batteries and have attracted considerable attention to physics and material science. Many interesting physical properties are known for these systems, and their origins are closely related to the structure type. The structural variation is caused by different electron configurations of the vanadium leading to a preference for certain geometric from e.g. low dimensional (chains, sheets) to more complex tree-dimensional blocks formed by vanadium-oxygen polyhedra – the main building unit of the crystal structures of various vanadates [1–7].

First the main attention was devoted to orthovanadates, which are widely known as effective crystallophosphors [1, 2, 5]. They are used as active media for lasers [1, 6], as antistocks luminophors [5], as thermoluminescent detectors [1], as luminescent detectors [1], as luminescent screen (for example on the base of YVO_4:Eu [1]. Ca_2VO_4Cl compound is known as scintillation media: wavelength – 440 nm, decay ~ 1 μs, output ~ 1% in comparison with CsI:Tl [1].

Recently the new scintillation materials was developed on the base of $M_2Sr(VO_3)_4$ compounds, where M = Na, K, Rb, Cs. The parameters of their luminescence (maxima of luminescent bands, the half width of the bands, the decay time of the luminescence and the relative intensity bands under photo-, X-ray and pulse electron beam excitation) have been firstly published in [4, 7]. The nature of luminescence centers in $M_2Sr(VO_3)_4$ compounds corresponds to the centers connected with the vanadate VO_4 units, probably in the form of tetra-cyclic $[V_4O_{12}]$ units. For $M_2Sr(VO_3)_4$ compounds it was found some differences between luminescence spectra under photon (X-rays) and pulse cathode excitation [4, 7]. This effect makes these compounds interesting candidates in the development of detectors with the selective sensitivity for the corpuscular and photon radiation.

In present paper the radioluminescent properties of the new hexametavanadates of alkali-alkaline-earth elements in comparison with properties of the known tetrametavanadates are presented.

2. Samples and their structure

The new family of cyclic compounds: $A_4M(VO_3)_6$ hexavanadates (where A = K, M = Sr and A = K, Cs, M = Ba) and $M_2Sr(VO_3)_4$ tetravanadates (where M = Na, K, Rb, Cs) were successfully prepared by solid state route [3].

The crystal structure of $A_4M(VO_3)_6$ and $M_2Sr(VO_3)_4$ compounds was obtained due to results of X-ray and neutron structure analysis in the frame of Rietveld method. It was found that $A_4M(VO_3)_6$ compounds have *R3c* (Z = 6) space group structure with the parameters presented in Table I. $M_2Sr(VO_3)_4$ compounds have *P4/nbm* or *P4/mmm* space group structures with the parameters presented in Table II.

3. Luminescence experimental equipments

The X-ray luminescence spectra were measured by using URS-55 setup on the base of MDR-23 monochromator (300–800 nm). The X-ray luminescence was excited by X-ray BSV-2 tube (Cr anode, 30 kV, 10 mA).

The pulsed cathodoluminescent (PCL) spectra were measured by using KLAVI-type setup with polychromator (200–830 nm) and the CCD-camera. The PCL was excited by the electron beam (current density 1000 A/cm^2, pulse duration 2 ns, energy 250 keV). All measurements have been made at room temperature.

Table I. Structure parameters of $A_4Ba(VO_3)_6$, A = K, Rb, Cs

Parameter		K	Rb	Cs
Space group		*R3c*	*R3c*	*R3c*
Z		6	6	6
a = b, Å		13.5402(1)	13.7361(1)	13.9575(1)
c, Å		18.8558(2)	19.2460(2)	19.8205(2)
V, Å^3		2993.8	3144.8	3343.9
A1	*x*/*a*	0	0	0
	y/*b*	0	0	0
	z/*c*	0.0007(8)	0.0006(3)	0.0000(2)
	*U**100	3.1(2)	3.9(1)	4.35(9)
A2	*x*/*a*	0.4148(6)	0.4136(3)	0.4132(2)
	y/*b*	-0.001(1)	0.0015(6)	0.0076(2)
	z/*c*	0.0062(4)	0.0002(3)	-0.0054(2)
	*U**100	3.1(1)	3.39(5)	3.86(5)
Ba	*x*/*a*	0	0	0
	y/*b*	0	0	0
	z/*c*	0.7571(3)	0.7629(2)	0.7668(2)
	U *100	3.32(7)	3.22(7)	2.97(9)
V1	*x*/*a*	0.2681(5)	0.2737(6)	0.2773(5)
	y/*b*	0.4134(6)	0.4174(6)	0.4227(5)
	z/*c*	0.0202(3)	0.0245(3)	0.0250(3)
	U *100	2.2(2)	2.5(2)	2.2(2)
V2	*x*/*a*	0.0589(6)	0.0602(6)	0.0579(5)
	y/*b*	0.2469(6)	0.2511(6)	0.2599(5)
	z/*c*	0.1392(3)	0.1424(3)	0.1345(3)
	U *100	4.3(3)	3.7(2)	3.5(2)
O(1)	*x*/*a*	0.330(1)	0.332(2)	0.3314(9)
	y/*b*	0.0101(6)	0.012(1)	0.0078(7)
	z/*c*	0.1529(5)	0.1693(8)	0.1735(8)
	U *100	5.8(2)	3.5(2)	4.1(2)
O(2)	*x*/*a*	0.554(1)	0.551(1)	0.547(1)
	y/*b*	0.0938(7)	0.0964(8)	0.093(1)
	z/*c*	0.1158(5)	0.1213(4)	0.1225(5)
	U *100	3.1(3)	2.9(3)	4.1(2)
O(3)	*x*/*a*	0.1924(9)	0.186(1)	0.179(1)
	y/*b*	0.3558(9)	0.3587(9)	0.360(1)
	z/*c*	0.0951(5)	0.0961(5)	0.0906(7)
	U *100	9.2(4)	5.4(3)	4.1(2)
O(4)	*x*/*a*	0.355(1)	0.3644(9)	0.371(1)
	y/*b*	0.536(1)	0.5526(8)	0.5535(9)
	z/*c*	0.0557(5)	0.0427(4)	0.0429(7)
	U *100	9.6(5)	2.8(3)	4.1(2)
O(5)	*x*/*a*	0.4369(8)	0.4463(9)	0.479(1)
	y/*b*	0.213(1)	0.222(1)	0.247(1)
	z/*c*	0.0422(5)	0.0379(5)	0.0227(6)
	U *100	4.8(3)	3.8(4)	4.1(2)
O(6)	*x*/*a*	-0.0360(8)	-0.025(1)	-0.031(1)
	y/*b*	0.1139(9)	0.140(1)	0.166(1)
	z/*c*	0.1187(4)	0.1002(6)	0.0804(6)
	U *100	5.3(4)	9.3(5)	4.1(2)
wRp	X*	1.59	2.03	1.63
	N*	1.77	2.32	
Rp	X*	1.18	1.55	1.27
	N*	1.40	1.84	
$R(F^2)$	X*	5.50	5.66	4.48
	N*	4.28	4.47	

* X and N symbols means X-ray and neutron data respectively

Table II. Structure parameters of $M_2Sr(VO_3)_4$, M = Na, K, Rb, Cs

Parameters		Na	K	Rb	Cs	Cs*
Space group		*P4/nbm*	*P4/nbm*	*P4/nbm*	*P4/nbm*	*P4/mmm*
Z		2	2	2	2	1
a = *b*, Å		10.63449(4)	10.94106(6)	11.08889(8)	11.19525(10)	7.9183(3)
c, Å		4.96205(4)	5.31600(4)	5.46682(8)	5.57998(6)	5.5778(3)
V, Å^3		561.17	635.37	672.22	699.37	349.7
A	*x*/*a*	0	0	0	0	1/2
	y/*b*	0	0	0	0	0
	z/*c*	1/2	1/2	1/2	1/2	1/2
	*U**100	1.61(2)	2.77(2)	2.88(2)	2.90(2)	2.47(2)
M	*x*/*a*	1/4	1/4	1/4	1/4	0
	y/*b*	1/4	1/4	1/4	1/4	0
	z/*c*	1/2	1/2	1/2	1/2	1/2
	U *100	1.60(2)	0.84(2)	1.81(2)	1.37(2)	1.22(2)
V	*x*/*a*	0.5353(2)	0.5328(2)	0.5295(2)	0.5309(3)	0.2805(2)
	y/*b*	1/4	1/4	1/4	1/4	0.2805(2)
	z/*c*	0	0	0	0	0
	U *100	1.52(2)	1.19(2)	1.99(2)	1.66(2)	1.31(2)
O(1)	*x*/*a*	0.6305(2)	0.6251(2)	0.6202(2)	0.6182(2)	0.2360(3)
	y/*b*	0.3695(2)	0.3749(2)	0.3798(2)	0.3818(2)	1/2
	z/*c*	0.1553(4)	0.1000(5)	-0.0520(6)	0.0005(47)	0
	U *100	1.29(3)	2.13(3)	2.82(3)	2.44(3)	2.43(3)
O(2)	*x*/*a*	0.1839(1)	0.2062(1)	0.2733(2)	0.2502(20)	0.1937(1)
	y/*b*	0.0529(1)	0.0542(1)	0.0558(2)	0.0564(1)	0.1937(1)
	z/*c*	0.2352(3)	0.2375(3)	0.2402(3)	0.2407(3)	0.2405(3)
	U *100	1.13(3)	2.11(3)	2.77(3)	2.26(3)	2.20(3)
wRp	X*	3.16	3.33	3.90	3.44	3.35
	N*	4.30	3.29	3.52	3.58	3.60
Rp	X*	2.23	2.30	2.36	2.41	2.33
	N*	3.18	2.54	2.63	2.70	2.71
$R(F^2)$	X*	6.60	5.68	3.19	3.64	3.36
	N*	4.73	4.13	2.85	2.72	2.60

* X and N symbols means X-ray and neutron data respectively

4. Results and discussion

The X-ray and PCL luminescence spectra for some $A_4M(VO_3)_6$ and $M_2Sr(VO_3)_4$ compounds are presented in Fig. 1–6. The parameters of luminescence spectra for $A_4M(VO_3)_6$ and $M_2Sr(VO_3)_4$ compounds are given in Table III.

The positions of the PCL band maxima for $A_4M(VO_3)_6$ compounds are 550–570 nm, the half width of the bands equal to 130–150 nm. These parameters are close to the parameters of $M_2Sr(VO_3)_4$. It means that the nature of the luminescence centers of hexavanadates is similar to nature of those for tetravanadates (typical intrinsic exciton luminescence). But there are some differences. For $A_4M(VO_3)_6$ there are small shifting PCL spectra to red region and small broadening of their half width in comparison with the parameters of $M_2Sr(VO_3)_4$ compounds. It can be connected with different crystal structure of these compounds (Table I and II). The main difference of hexavanadates from tetravanadates is absence of photo- and X-ray luminescence for $A_4M(VO_3)_6$.

Table III. Parameters of luminescence spectra for $A_4M(VO_3)_6$ and $M_2Sr(VO_3)_4$ compounds

Compounds	PL		X-ray		PCL	
	λ_0, nm	$\Delta\lambda$, nm	λ_0, nm	$\Delta\lambda$, nm	λ_0, nm	$\Delta\lambda$, nm
$A_4M(VO_3)_6$						
$Cs_4Ba(VO_3)_6$	—	—	—	—	550	130
$K_4Ba(VO_3)_6$	—	—	—	—	555	140
$K_4Sr(VO_3)_6$	—	—	—	—	570	150
$M_2Sr(VO_3)_4$						
$Na_2Sr(VO_3)_4$	520	125	520	125	550	160
$K_2Sr(VO_3)_4$	525	135	525	125	550	155
$Rb_2Sr(VO_3)_4$	550	145	540	130	580	227
$Cs_2Sr(VO_3)_4$	530	130	530	115	550	215

5. Conclusion

We have synthesized a new family of compounds: hexametavanadates of alkali-alkaline-earth elements ($A_4M(VO_3)_6$, where A = K, M = Sr and A = K, Cs, M = Ba) and carried out their structural and luminescent properties. Based on the Rietveld technique the structure space groups were showed to be *R3c* (Z = 6). Some parameters of the luminescence spectra (intrinsic exciton luminescence) of $A_4M(VO_3)_6$ in comparison with the parameters of $M_2Sr(VO_3)_4$ compounds have been measured and discussed. The nature of the luminescence centers corresponds to the centers connected with vanadate units, probably in the form of chain of VO_4 units. These new compounds can be used for development of scintillation detectors for corpuscular radiation.

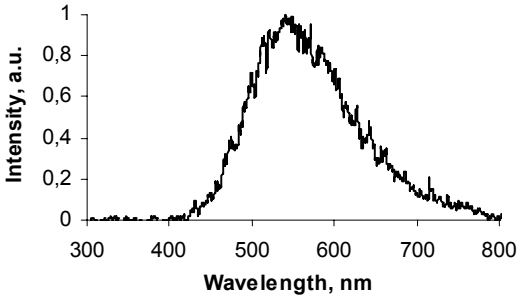

Fig. 1. PCL spectra of $Cs_4Ba(VO_3)_6$

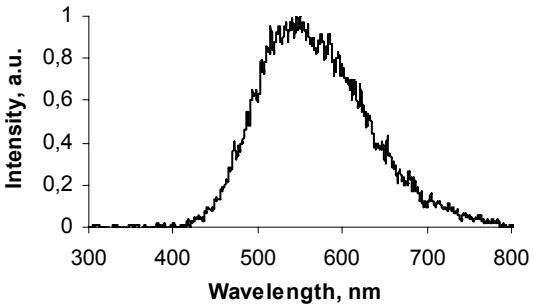

Fig. 2. PCL spectra of $K_4Ba(VO_3)_6$

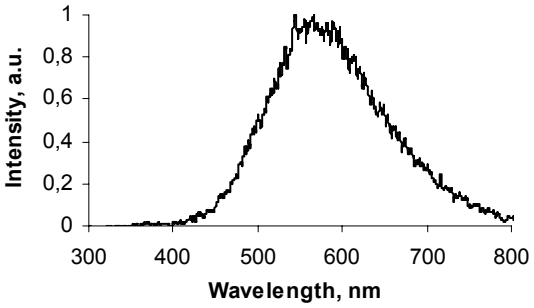

Fig. 3. PCL spectra of $K_4Sr(VO_3)_6$

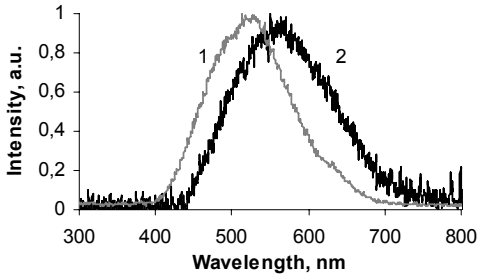

Fig. 4. X-ray (1) and PCL (2) spectra of $K_2Sr(VO_3)_4$

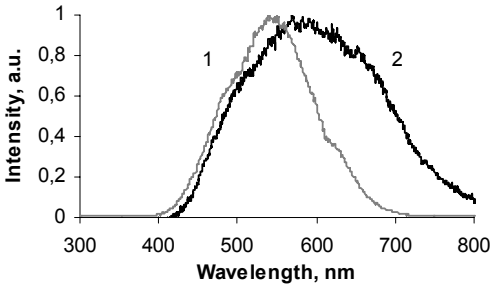

Fig. 5. X-ray (1) and PCL (2) spectra of $Rb_2Sr(VO_3)_4$

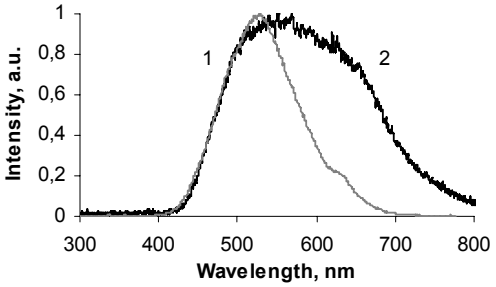

Fig. 6. X-ray (1) and PCL (2) spectra of $Cs_2Sr(VO_3)_4$

References

[1] A. Fotiev, B. Shulgin, A.S. Moskvin, F.F. Gavrilov. *Vanadates crystallophosphors.* Moscow, Nauka, 1976. 206 p.

[2] A.A. Fotiev, B.V. Slobodin, and M.Ya. Khodos. *Vanadates: Composition, Synthesis, Structure, Properties,* Nauka, Moskow, 1988.

[3] I. Tordjman, C. Martin, and A. Durif, Bull. Soc. Fr. Mineral. Cristallogr. **90**, 293 (1967).

[4] B.V. Slobodin, L.L. Surat, V.G.Zubkov, A.P. Tyu-tyunnik, I.F.Berger, M.V.Kuznetsov, L.A.Perelyaeva, I.R.Shein, A.L.Ivanovskii, B.V. Shulgin, V.I. Solomonov, G. Svensson, B. Forslund, M.J. Sayagues, Phys. Rev. B., **72**, 155205 (2005).

[5] G.Blasse, J. Chem. Phys, **45**, 2356 (1966).

[6] J.R.O'Connor, Appl. Phys. Lett, **5**, 118 (1964).

[7] B.V. Slobodin, L.L. Surat, V.G. Zubkov, A.P. Tyutyunnik, B.V.Shulgin, A.V.Kruzhalov, V.S. Cheremnykh, A.N.Tcherepanov, G.Svensson, B.Forslund, V.I.Solomonov, O.A.Snigireva, *in Proc. of the 8 Int. Conf. SCINT-2006, Alushta, Ukraine, 2005. pp. 53–55.*