Thermochemical and Luminescent Properties of RbVO₃, CsVO₃, and Rb_{0.5}Cs_{0.5}VO₃

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Abstract—RbVO₃, CsVO₃, and Rb_{0.5}Cs_{0.5}VO₃ have been synthesized by the Pechini process. The vanadates have an orthorhombic structure (sp. gr. *Pbcm*), melt congruently in the range 650–530°C, and undergo a reversible phase transition in the range 520–340°C. We have determined the onset temperatures and end points of the transformations at a temperature scan rate of 3°C/min and their enthalpies, and measured the photo-, roentgeno-, and cathodoluminescence and diffuse reflectance spectra of the vanadates. The luminescence spectra each are well fitted with three pseudo-Voigt functions. CsVO₃ has the highest integrated emission intensity. The emission intensity of the Rb_{0.5}Cs_{0.5}VO₃ solid solution is lower than that of the simple vanadates because of the optical absorption around its intrinsic luminescence band. This may be due to the presence of stable vacancy-type structural defects in Rb_{0.5}Cs_{0.5}VO₃.

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INTRODUCTION

Vanadate (V^{5+}) based phosphors have been known for a long time [1–3]. Vanadates have been used to develop phosphors, active media for lasers, and luminescence screens emitting in different spectral regions.

Recent work has shown that the AVO₃ (A = Rb, Cs) vanadates can be used as materials for energy-saving light emitting diode lighting devices, that is, for the next generation of daylight bulbs [4, 5].

According to the $V_2O_5-Rb_2O$ and $V_2O_5-Cs_2O$ phase diagrams [6, 7], rubidium and cesium vanadates melt congruently at 565 and 640°C and undergo a polymorphic transformation at 520 and 403°C, respectively. These temperatures should, however, be considered only approximate because the procedures used to determine them were not described in detail [6, 7]. At room temperature, the two vanadates have an orthorhombic structure. Their high-temperature structures have not yet been determined.

Fotiev et al. [6, 8] found unlimited solid solubility in the $RbVO_3$ -CsVO_3 system. $Rb_{0.5}Cs_{0.5}VO_3$ was reported to melt at ~635°C and undergo a polymorphic transformation at ~420°C. There is no more information about the thermochemical or luminescent properties of this compound.

The purpose of this work was to study and compare the thermal and luminescent properties of $RbVO_3$, $CsVO_3$, and $Rb_{0.5}Cs_{0.5}VO_3$.

EXPERIMENTAL

The vanadates were synthesized by the Pechini process. To a nitric acid solution of V_2O_5 and rubidium and/or cesium carbonate were added citric acid and ethylene glycol in the molar ratio 1 : 3. The solution was boiled down to give first a dark resinlike substance and then a polymeric precursor. After compaction, the precursor was heat-treated in air at ~500°C for 60 h with several intermediate grindings. The resultant powders were single-phase and white (RbVO₃ and CsVO₃) or light yellow (Rb_{0.5}Cs_{0.5}VO₃) in color.

The phase composition of the powders was determined by room-temperature X-ray diffraction (MAXima-X XRD-7000 diffractometer, Shimadzu, Japan) using ICDD Powder Diffraction File data, Sets 1–47 [9]. Thermal analysis was performed using a differential scanning calorimeter (DSC Q10, TA Instruments, USA) in the range 20–725°C at a temperature scan rate of 3°C/min.

Luminescence and diffuse reflectance spectra were measured at room temperature (diffuse reflectance is an important optical characteristic of materials and is related to light reflection in a particular spectral range). Recall that only the luminescence spectra of RbVO₃ and CsVO₃ have been measured earlier [1, 4, 5].

The following facilities and instruments were used in the measurements: a DDS-400 deuterium lamp, FEU-106 photomultiplier (photoluminescence (PL) and photoluminescence excitation (PLE) spectra), MDR-23 monochromator, URS-55A X-ray generator

RESULTS AND DISCUSSION

According to our results, the vanadates are isostructural at room temperature (Fig. 1). The orthorhombic cell parameters (sp. gr. *Pbcm*) of RbVO₃, Rb_{0.5}Cs_{0.5}VO₃, and CsVO₃ were refined by the Rietveld profile analysis method: a = 5.272, 5.353; 5.409; b =11.452, 11.877, 12.279; c = 5.731, 5.766, 5.800 Å, respectively.

The compounds were found to be very similar in their behavior during heating and subsequent cooling (after melting). As an example, Fig. 2 shows DSC heating and cooling curves of the double metavanadate $Rb_{0.5}Cs_{0.5}VO_3$. The endothermic peaks correspond to the onset temperatures for transformations during heating: the transition from the low-temperature to the high-temperature phase (425°C) and melting (581°C). The exothermic peaks correspond to the onset temperatures for transformations during cooling: solidification (524°C) and the transition from the high-temperature to the low-temperature phase (396°C).

The markedly lower solidification and polymorphic transformation temperatures observed during cooling are related to a thermal hysteresis (supercooling of the crystal lattice). Such behavior was observed in all three compounds studied (Fig. 3). It is worth pointing out that both the enthalpies and temperatures of transformations are not always identical in powders and melted materials.

The facts that, for each compound, the enthalpies of the transformations under consideration (melting \leftrightarrow solidification and structural transition (Figs. 2, 3)) differ little and that only the parent vanadates were present in samples cooled to room temperature after melting suggest that these transformations are reversible and reach completion.

The luminescence spectra of the vanadates are presented in Figs. 4–6. The shape of the spectra is seen to be independent of the type of excitation. They have the form of a broad, composite emission band across the entire visible range, from 400 to 800 nm.

The PL spectra of the vanadates (Figs. 4–6, spectra 3) were measured under excitation at 280 nm. The shape of the PL spectra is seen to be independent of the excitation wavelength. The PL band of the three compounds peaks at 535 nm, in good agreement with earlier results [1, 4, 10]. The full width at half maximum (FWHM) of the band is 144, 117, and 143 nm for CsVO₃, RbVO₃, and Rb_{0.5}Cs_{0.5}VO₃, respectively. The highest emission brightness is offered by CsVO₃. The emission intensity in RbVO₃ is 43% relative to cesium vanadate, and that in Rb_{0.5}Cs_{0.5}VO₃ is at a level of 20%.



Fig. 1. Portions of X-ray diffraction patterns from (a) $RbVO_3$, (b) $Rb_{0.5}Cs_{0.5}VO_3$, and (c) $CsVO_3$.

The PCL spectra of the vanadates (Figs. 4–6, spectra *I*) are similar in shape and peak position to their PL spectra, but there are distinctions related to the dependence of the output intensity on the type of excitation. The PCL intensity in RbVO₃ and Rb_{0.5}Cs_{0.5}VO₃ is 19 and 18% of that in CsVO₃.

The RL spectra of the vanadates (Figs. 4–6, spectra 2) are slightly shifted to shorter wavelengths relative to their PL and PCL spectra and have a peak at 500 nm for CsVO₃ and RbVO₃ and at 525 nm for Rb_{0.5}Cs_{0.5}VO₃. The FWHM of the emission band is 133, 140, and 120 nm, respectively. The RL spectra have an additional, prominent emission band, centered at ~635 nm, which was also reported for other vanadates, in particular for double tetra- and hexavanadates [3].

This band and the shape of the PL, RL, and PCL spectra suggest that they have a rather complex structure. The luminescence spectra consist of several emission subbands. The shift of the RL spectra to shorter wavelengths relative to the PL and PCL spectra



Fig. 2. Heating and cooling curves of the double vanadate $Rb_{0.5}Cs_{0.5}VO_3$.



Fig. 3. (1) Exo- and (2) endothermic peaks of reversible polymorphic transformations in DSC heating and cooling scans, respectively, for (a) $RbVO_3$, (b) $Rb_{0.5}Cs_{0.5}VO_3$, and (c) $CsVO_3$.



Fig. 4. (1) PCL, (2) RL, (3) PL, (4) PLE, and (5) DR spectra of CsVO₃.

can be interpreted in terms of the effect of the type of excitation on the emission intensity of their elementary components. To this end, the RL and PCL spectra were decomposed into elementary components (Fig. 7). We jointly decomposed all six spectra, with identical peak positions of the components, using a pseudo-Voigt function, an approximate representation of the convolution of a Gaussian and Lorentzian. A detailed analysis indicates that the spectra each comprise three components (subbands), whose relative intensities

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Fig. 5. (1) PCL, (2) RL, (3) PL, (4) PLE, and (5) DR spectra of RbVO₃.



Fig. 6. (1) PCL, (2) RL, (3) PL, (4) PLE (550-nm emission), and (5) DR spectra of Rb_{0.5}Cs_{0.5}VO₃.

depend on the type of excitation, which leads to changes in the shape of the spectra and peak positions.

It follows from the fitting results (Fig. 7) that the relative intensity of component 3 under X-ray excitation is substantially higher than that under optical or pulsed electron beam excitation. At the same time, the relative intensity of the other subbands varies insignificantly. The intensity of component 1 in the vanadates systematically increases in the order $C_S \rightarrow Rb \rightarrow C_SRb$ in both the RL and PCL spectra. The intensity of subband 3 decreases in this order, and that of component 2 is roughly constant in the three compounds studied. Comparison of the RL spectra indicates that the decrease in the integrated luminescence output in the order $Cs \rightarrow Rb \rightarrow CsRb$ is caused by the marked decrease in the emission intensity of component 3 and only slight decrease in the emission intensity of component 2.

To obtain an integral characteristic of the emission in CsVO₃, RbVO₃, and Rb_{0.5}Cs_{0.5}VO₃, we determined their chromaticity coordinates: 0.36, 0.47; 0.32, 0.45; and 0.37, 0.45, respectively. This is characteristic of white emission with a greenish yellow tinge.

The PLE and DR spectra of the vanadates (Figs. 4-6, spectra 4, 5) are similar in many respects. A distinctive feature of the DR spectra, measured with the abovementioned equipment, is that the emission from the sample cannot be separated from the reflected light, so the DR spectra at wavelengths shorter than 410 nm are in fact a PLE spectrum.

Cesium and rubidium vanadates (Figs. 4, 5, spectra 5) absorb little or no light in the range 400 to 1100 nm. At the same time, the spectrum of the solid solution between cesium and rubidium vanadates (Fig. 6, spectrum 5) has an optical absorption region in the visible

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Fig. 7. Decomposition of the (a–c) RL and (d–f) PCL spectra of (a, d) $CsVO_3$, (b, e) $RbVO_3$, and (c, f) $Rb_{0.5}Cs_{0.5}VO_3$ into elementary components: (1–3) components (subbands).

range, between 400 and 650 nm, with two peaks at 415 and 580 nm.

Comparison of the DR spectra and the fitting results for the luminescence spectra leads us to conclude that the reduction in the emission intensity of component 3 in $Rb_{0.5}Cs_{0.5}VO_3$ is caused by the optical absorption in the range 400–640 nm (Fig. 6, inset), which is responsible for the light yellow color of the material. The optical absorption in the 415- and 580-nm bands of $Rb_{0.5}Cs_{0.5}VO_3$ may be interpreted as evidence for the presence of vacancy-type structural defects [3].

In the range 200–410 nm, the PLE and DR spectra of the three vanadates have three excitation (absorption) bands, centered at 215, 270, and 370 nm (in the spectra of $Rb_{0.5}Cs_{0.5}VO_3$, the latter band peaks at 375 nm). These bands, their positions, and the particular character of the spectra obtained with different types of excitation corroborate the reliability of the present experimental results. The observed excitation (absorption) bands in the PLE and DR spectra are attributable to band–band transitions with O $2p \rightarrow V 3d$ charge transfer in the vanadates [1, 3, 10].

CONCLUSIONS

We studied the thermochemical properties and PL, RL, PCL, and DR spectra of CsVO₃, RbVO₃, and

 $Rb_{0.5}Cs_{0.5}VO_3$. The double vanadate was synthesized for the first time.

A comparative analysis of the luminescent and optical properties of the vanadates indicates that their spectra contain three emission components (subbands). $CsVO_3$ has the highest integrated emission intensity. The emission intensity of the $Rb_{0.5}Cs_{0.5}VO_3$ solid solution is lower than that of $CsVO_3$ and $RbVO_3$ because of the optical absorption around its luminescence band. This may be due to the presence of stable structural defects, typical of a wide range of oxides [11]. We assume that $Rb_{0.5}Cs_{0.5}VO_3$ contains vacancy-type structural defects, which suggests that its crystal structure has a nonoptimal configuration.

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