Dyes and Pigments 148 (2018) 219–223

Contents lists available at ScienceDirect

Dyes and Pigments

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

# Eu and Cu co-substituted calcium vanadate — The crystal structure, luminescence and color

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ARTICLE INFO

*Article history:*
Received 7 April 2017
Received in revised form
6 September 2017
Accepted 8 September 2017
Available online 8 September 2017

ABSTRACT

Europium- and copper-doped calcium vanadates with the general formula $Ca_{3-1.5x-y}Eu_xCu_y(VO_4)_2$ (x = 0, 0.075; y = 0, 0.06 and 0.18) were synthesized by the solid state reaction. Synthesized materials were analyzed by the powder X-ray diffraction (PXRD), UV–Vis, Raman, luminescence spectroscopy, and colorimetry. Unit cell dimensions of the obtained samples were analyzed by the Rietveld refinement of the PXRD data. The crystal symmetry corresponds to the *R*3*c* group. Europium-doped samples exhibited luminescent properties, typical for the majority of europium-containing inorganic compounds. Additional copper-doping partially suppressed the europium luminescence. The europium-and-copper-doped samples possess bright yellow colors. Thus, obtained materials are perspective for the application as inorganic yellow pigments.

## 1. Introduction

The whitlockite-type calcium vanadate $Ca_3(VO_4)_2$ structure belongs to the *R*3*c* space group [1,2]. This material is known as a high-temperature ferroelectrics with $Tc = 1113$ °C [2–4]. The ferroelectric properties were observed in the range between room temperature and *Tc* [2–4]. Above *Tc* the transition from the non-centrosymmetric *R*3c to the centrosymmetric *R*-3m space group was revealed by Raman spectroscopy [4] and a second harmonic generation [2,4]. The calcium vanadate has the absorption band in the UV range (~310 nm) with the low-intensity shoulder within the visible region [5].

Rare-earth-doped vanadates with the general formula $Ca_{3-x}M_{2x}(VO_4)_2$, where M — rare earth element, were studied as luminophores [2,4,6,7] and materials for a second harmonic generation in a laser technique [2,4].

Moreover, some vanadates could be illustrated with a bright color. As an example, bismuth vanadate, $BiVO_4$ is presented with an intense yellow color and, hence, can be used as the inorganic pigment [8,9] substituting the toxic cadmium- and lead-based elements. To compare the toxicity of the chemical elements, which were mentioned in this work, the GN 2.1.5.1315–03 standard which regulates the maximum permissible concentrations (MPC) of chemicals in water, was used. This standard is approximately equivalent to the World Health Organization (WHO) standard. But it is worth to mention, that the WHO standard doesn't cover the broad range of the chemical elements, which were used in this study. Thus, according to the GN 2.1.5.1315–03 standard, the MPCs of the mentioned chemical elements are as followings: $MPC_{Cd} = 0.001$ mg/L, $MPC_{Pb} = 0.01$ mg/L, $MPC_{Bi} = 0.1$ mg/L, and $MPC_V = 0.1$ mg/L.

Nowadays, scientists are looking for the modern materials with multifunctional characteristics. Contemporary inorganic pigments illustrate some luminescent properties in addition to their main characteristics, that widens their potential application area. The color, luminescence and structural features of the europium- and copper-doped calcium vanadate with the general formula $Ca_{3-1.5x-y}Eu_xCu_y(VO_4)_2$ ($x = 0$, 0.075; $y = 0$, 0.06 and 0.18) were experimented in the present work. Europium ions are well-known as the orange-red luminescent agent, with the ionic radius, which was close to the calcium-ion values ($R_{Eu3+} = 0.89$ Å; $R_{Ca2+} = 1.00$ Å, for coordination number 6 [10]). In contrary to europium, copper ions are much smaller, than calcium ions ($R_{Cu2+} = 0.73$ Å, for

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http://dx.doi.org/10.1016/j.dyepig.2017.09.017
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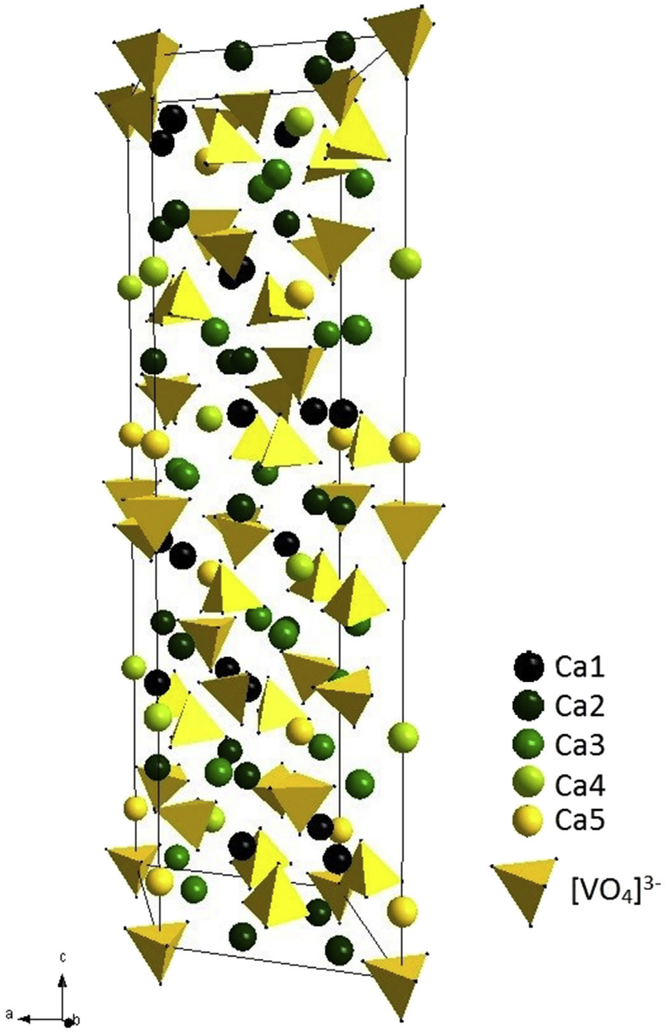

**Fig. 1.** Crystal structure of the calcium vanadate ($R3c$ space group).

coordination number 6 [10]). Therefore, it was expected that introduction of copper ions will reduce the unit cell parameters and modify the local crystal field within the structure, which may lead to the initial color modification. It was additionally expected that all these compounds were much less toxic compared to the lead-, cadmium-, and bismuth-based pigments: according to the GN 2.1.5.1315–03, $MPC_{Eu}$ = 0.3 mg/L; $MPC_{Cu}$ = 1 mg/L; $MPC_{Ca}$ = 3.5 mg/L.

## 2. Experimental procedure

$CaCO_3$, $NH_4VO_3$, $Eu_2O_3$, and CuO were used as starting compounds for the synthesis of the next samples:

**E0C0** — Calcium vanadate with the nominal formula $Ca_3(VO_4)_2$;
**E7.5C0** — Eu-for-Ca-substituted vanadate with nominal formula $Ca_{2.8875}Eu_{0.0750}(VO_4)_2$;
**E7.5C6** — Eu&Cu-for-Ca-substituted vanadate with nominal formula $Ca_{2.8275}Eu_{0.0750}Cu_{0.06}(VO_4)_2$;
**E7.5C18** — Eu&Cu-for-Ca-substituted vanadate with nominal formula $Ca_{2.7075}Eu_{0.0750}Cu_{0.18}(VO_4)_2$;

All samples were obtained through the solid state synthesis according to the following procedure: reagents were mixed in stoichiometric proportions in quantities to obtain ca. 2 g of the final compound and ground in an agate mortar. The obtained powders were annealed in a muffle furnace at 650 °C (heating for 1 h, holding for 2 h), then at 750 °C (heating for 1 h, holding for 2 h), and then at 900 °C (heating for 1 h, holding for 2 h) with intermediate grinding in an agate mortar. This procedure provided decomposition of calcium carbonate and ammonium vanadate without the vanadium loss. Then, the obtained powders were annealed at 1150 °C (heating for 1.5 h, holding for 5 h, and air quenching) with subsequent regrinding in an agate mortar. This annealing procedure was repeated two times for each sample.

PXRD patterns for all target samples were registered using the Bruker D8 Advance with $CuK\alpha_{1,2}$ radiation and $2\theta$ range from 5 to 120°, step = 0.015°. Crystal structures of obtained compounds were refined by the Rietveld method in the space group $R3c$ using the JANA 2006 software [11]. Raman spectra were registered on a RENISHAW in Via Reflex (scanning range = 200–1500 $cm^{-1}$, $\lambda = 514.5$ nm). The color of the target samples was characterized using diffuse reflectance spectroscopy recorded on the Perkin Elmer Lambda 950 spectrometer (13 cm integrating sphere with SPECTRALON top coating, scanning range = 200–1000 nm, scanning step = 1 nm). Luminescent spectra were measured on the Perkin Elmer LS 55 spectrometer (650 V, emission and excitation slit = 5.0 nm). Colorimetric measurements in the CIE L*a*b* color space were provided using the reflex camera Olympus e-420 (5400K illuminant; ISO = 200; lightroom with length-width-depth = 35 cm–25 cm–32 cm) and the PhotoImpact 12 software.

## 3. Results and discussion

### 3.1. Crystal structure features

The experimental, refined and differential PXRD patterns of all samples were presented in the supplementary information, Figs. A1-A4. The crystal structure of the calcium vanadate was presented in Fig. 1. Selected data, including unit cell parameters *a* and *c*, unit cell volume *V*, *R*-factors were given in the Table 1. It was found that **E0C0**, **E7.5C0**, **E7.5C6** samples were pure and weren't contain any admixture phases. The **E7.5C18** sample contained traces of $Ca_7V_4O_{17}$ and CuO.

It was also observed that despite the smaller size of $Eu^{3+}$ in comparison with $Ca^{2+}$ ion, partial Ca-by-Eu substitution caused the

**Table 1**
Characteristics of the samples $Ca_{3-x-y}Eu_{2x}Cu_y(VO_4)_2$: color, *R*-factors, selected refined parameters of crystal structure (cell parameters *a* and *c*, cell volume *V*).

| Sample | Color | $R_p$, % | GOF | *a*, Å | *c*, Å | *V*, $Å^3$ | By-phases, mass. % |
|---|---|---|---|---|---|---|---|
| **$Ca_3(VO_4)_2$** | | | | | | | |
| E0C0 | Light yellow | 1.62 | 1.33 | 10.82(1) | 38.04(1) | 3858.14(3) | – |
| E7.5C0 | Light yellow | 0.91 | 2.89 | 10.84(1) | 38.04(1) | 3869.31(2) | – |
| E7.5C6 | Yellow | 0.90 | 1.84 | 10.83(1) | 38.02(1) | 3861.38(2) | – |
| E7.5C18 | Khaki | 0.96 | 1.74 | 10.81(1) | 38.00(1) | 3849.39(2) | $Ca_7V_4O_{17}$ (traces)<br>CuO (traces) |