



High-temperature thermal and X-ray diffraction studies, and room-temperature spectroscopic investigation of some inorganic pigments

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ABSTRACT

Inorganic Cr- and Mn-containing pigments of different structural types were investigated by high-temperature and spectroscopic methods. The differential scanning calorimetry in the temperature interval 298–1723 K was applied to measure temperatures of phase transition and melting of the studied compounds. High-temperature X-ray diffraction in the range 298–1713 K was used for the determination of the thermal expansion coefficients for the first time. Factor group analysis was used to predict general vibration modes of pigments and determine the activity of these vibrations in Raman and IR spectra, the Assignment of bands in Raman, IR and diffuse reflectance spectra was undertaken.

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1. Introduction

Compounds with the general formula $M^{II}_5(A^V O_4)_3 L$ ($M^{II} = Ca, Sr, Ba, Cd, Pb$; $A^V = P, As, V, Mn, Cr$; $L = OH, F, Cl, Br, I$) are subjects of interest to both geo- and bio-chemistry and each of them may be characterized as apatites. All of them can be referred to apatite class. These compounds are prospective materials for many technological applications. In particular, they can be used as a matrix for waste forms due to their isomorphous capacity, as inorganic pigments or they can be the building block of biocompatible and luminescent materials [1–4]. Apatite-type lanthanum silicates and germanates have also received a lot of interest as materials for solid oxide fuel cells [5–7]. Most of the individual compounds of the aforementioned general formula and solid solutions are based on them known as natural minerals, such as apatite $Ca_5(PO_4)_3F$, hydroxyapatite $Ca_5(PO_4)_3OH$, pyromorphite $Pb_5(PO_4)_3Cl$, endlicheite $Pb_5(PO_4)_3F_xCl_{1-x}$ [8]. The science and technology community are interested in the exploration and application of such complexes.

Apatite compounds are structurally built of discrete AO_4 tetrahedra linked to one another by M^{II} -polyhedra, which form joint layers (Fig. 1). Apatite-type structures typically offer two crystallographic

positions for cations differing in coordination number and local symmetry. The atoms occupying the first positions 4f form polyhedra shaped as three-capped trigonal prisms MO_9 having symmetry C_3 whose columns run along the threefold axis. The coordination number (CN) of lead atoms occupying the second position depends on the type of ligand L: CN = 7 when $L = F$ (distorted pentagonal bipyramids MO_6F), whereas CN = 8 when $L = Cl$ (distorted two-capped trigonal prisms MO_6Cl_2). In consequence of differences of halogen positions, chlorine atoms occupy positions between layers formed by AO_4 tetrahedra, whereas fluorine atoms occupies positions within the layers (Fig. 1a) [9,10].

$CoCr_2O_4$ has a spinel structure and it crystallizes in a cubic space group $Fd\bar{3}m$. Co atoms are located in tetrahedral positions 8a, while Cr atoms are located in octahedral positions 16d. O atoms of 32e position form a compact layer (Fig. 1b) [11].

The structure of Pb_2CrO_5 is built by distorted monocapped trigonal prisms connected to each other by edges to form endless hexahedral “rods” which are parallel to crystallographic axis b . These “rods” are joined by edges and tops of CrO_4 tetrahedra (Fig. 1) [12].

The structure of $K_2Ba(CrO_4)_2$ has yet to be solved: there are only space group and unit-cell parameters in XRD databases [13].

Compounds with the apatite structure, which are the subject of this study, i.e. $Ca_5(CrO_4)_3Cl$, $Sr_5(CrO_4)_3F$, $Ba_5(MnO_4)_3F$ and $Ba_5(MnO_4)_3Cl$, contain manganese (V) and chromium (V) in their composition. There

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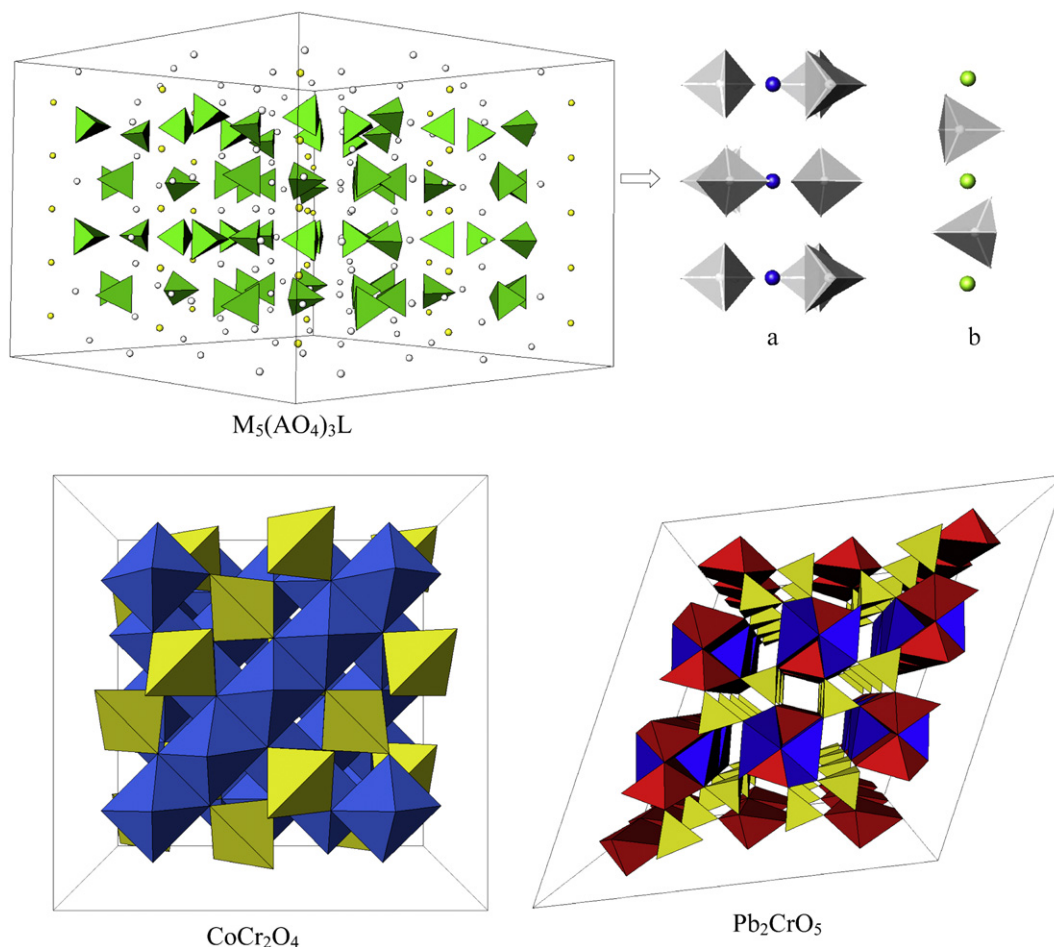


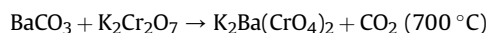
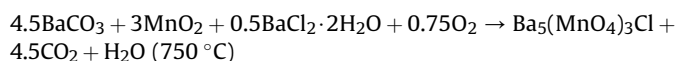
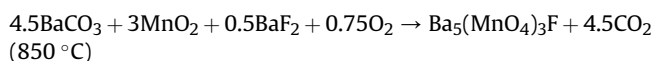
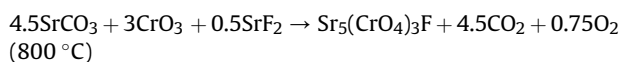
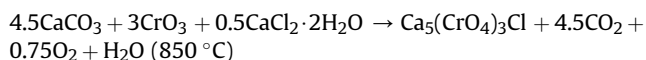
Fig. 1. Structure fragments of the studied compounds. For apatite structure different positions of halogen (L) are shown: $Sr_5(CrO_4)_3F$ (a) and $Ba_5(MnO_4)_3Cl$ (b) (blue spheres are F atoms, green spheres – Cl atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are only a few publications dedicated to phases containing d-elements with uncommon oxidation state [9,14,15]. This dearth of information encouraged us to study such representatives of apatite class. Compounds of chromium (III) and chromium (VI) can also be used as pigments. In particular, we report in this work results for Pb_2CrO_5 , $K_2Ba(CrO_4)_2$, and $CoCr_2O_4$ as potential pigments. The physicochemical properties of the aforementioned above Cr- and Mn-containing pigments were studied by X-ray diffraction method, including high-temperature experiments, IR, Raman and optical spectroscopy, and differential thermal analysis.

2. Experimental

2.1. Preparation of samples

Samples of the studied compounds were prepared by the solid-state reaction in accordance with the following equations. Final synthesis temperature is presented in brackets:



A reaction mixture of a set stoichiometry was placed in a porcelain crucible and calcined for 10 h with dispersion in an agate mortar every 2 h.

For all studied phases synthesis temperatures were reduced. Synthesis schemes were simplified in comparison with literature data by using one-step process [9–14].

2.2. Apparatus and measurement procedure

An atomic ratio of compounds under study was analyzed on a Shimadzu energy-dispersive roentgen fluorescent spectrometer EDX-900HS (from $_{11}Na$ to $_{92}U$) with sensitive detector without liquid nitrogen.

The phase individuality of the synthesized compounds was monitored by X-ray diffraction. X-ray diffraction patterns were recorded on an XRD-6000 Shimadzu diffractometer (CuK_2 radiation, geometry $\theta-2\theta$) in the 2θ range from 10° to 120° with scan increment of 0.02° .

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