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Raman and Fourier transform infrared spectroscopic study of pyromorphite-vanadinite solid solutions

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ABSTRACT

Due to the great range of the application fields for apatites, there is a strong need to complete the data set determining the properties of these minerals. In this study, Raman and Infrared spectra of the phases from pyromorphite $Pb_5(PO_4)_3Cl$ - vanadinite $Pb_5(VO_4)_3Cl$ series were investigated. Totally, 9 samples (2 end-members and 7 solid solutions of the series) were synthesized at 25 °C and pH = 3.5, and analyzed. In the Raman and Infrared spectra of the studied Pb-apatites, the bands typical for the vibrations in the PO_4 and the VO_4 tetrahedra appeared. The bands attributed to the stretching vibrations (ν_1, ν_3) occurred in the 1050–910 cm^{-1} and 830–720 cm^{-1} regions, whereas the bending vibrations (ν_2, ν_4) were visible at the 580–540 cm^{-1}, 430–380 cm^{-1} and 370–290 cm^{-1} range. The position of the bands depended on the P/(P + V) ratio in the analyzed solid, since there are differences in the ionic radii and the atomic mass of P^{5+} and V^{5+}, which affect the bong lengths, bond forces and the banding energies of the substituting tetrahedra. The analysis allowed observing gradual shifts of the bands caused by the replacement of phosphorous with vanadium in the studied phases. The positions and the intensities of selected bands are proposed to serve as a semi-quantitative estimation of the chemical composition of the phases from the pyromorphite - vanadinite series.

1. Introduction

Pyromorphite $Pb_5(PO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$ are minerals which belong to the apatite supergroup with a general chemical formula $\mathbf{M}_5(TO_4)_3X$, where **M** is a bivalent cation distributed on two distinct crystallographic sites, TO_4 is a trivalent oxyanion and X is a monovalent anion [1–3]. The crystal structure of apatites allows for a wide range of substitutions within the metal cations and the anionic sites; the phases with Pb occupying the metal site are of constantly increasing scientific interest [4–14]. The most common anionic substitution within the Pb-apatites is a partial replacement of phosphorous with vanadium and/or arsenic; pyromorphite and vanadinite form a ternary system with mimetite $Pb_5(AsO_4)_3Cl$. The minerals crystallize in hexagonal system in the $P6_3/m$ symmetry class [15–16], though the mimetite is also found in the $P2_1/b$ symmetry group [17]. The complete solid solution series between pyromorphite and mimetite was reported [18–20]. The structures and the properties of the phases, likewise of their hydroxyl counterparts, were investigated in detail [11–12,19–20]. The systematic changes of peak positions and intensities in the Raman and the IR spectra of the minerals were also demonstrated [11–12,19]. However, the knowledge about the effect of the vanadate substitutions on the properties of the Pb-apatites group is rather superficial, sparse or outdated [21]. Single publications about admixture of vanadates in pyromorphite and phosphates in vanadinite are available [6,22]. A continuous solid solution series for pyromorphite - vanadinite system can successfully be precipitated under laboratory conditions in a form of small crystals [21,23,this study], however, it seems that only some of the phases are found in nature [6,22,24]. It might be due to the fact, that the differences of the ionic radii between the $^{IV}P^{5+}$ (0.17) and $^{IV}V^{5+}$ (0.355) are significant, more than 50%, which is well in excess of the accepted boundary of tolerance 25–30% for possible isomorphic substitution in continuous solid solutions. On the other hand, the concept of polymorph within the series has recently been proposed by Baikie et al. [25]; the data need to be confirmed, however.

Apatite is a ubiquitous accessory mineral in igneous rocks. It is also commonly found in metamorphic rocks [1,26], low-temperature sedimentary environments [1,27] and precipitates in hydrothermal solutions [1,28]. The crystallographic properties of apatite which allow for numerous substitutions and its high thermodynamic stability decide on its widespread application, for example as the environmentally-innocuous catalyst [29] or as the metal sequestration agent in water treatment and contaminated soil remediation [30–33]. Hence, there is a strong need to supplement and to arrange systematically the

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knowledge on properties of the Pb-apatites, taking into account all possible anionic substitutions. Relatively fast and cost-effective method for identification of chemical composition of the phases is essential.

The presented study concerns anionic substitutions at the T-position in chlorapatites. The aim of the research was to complete the missing spectroscopic data for pyromorphite-vanadinite solid solution series. The results presented in this study along with their detailed analysis not only fill the evident gap in the systematic knowledge, but also provide a tool to estimate a range of the anionic substitutions among the natural or synthetic samples of the pyromorphite - vanadinite system.

2. Experimental

2.1. Synthesis

Pyromorphite $Pb_5(PO_4)_3Cl$, vanadinite $Pb_5(VO_4)_3Cl$ and seven of their solid solutions $Pb_5(XO_4)_3Cl$, where X = P + V, were synthesized from the aqueous solutions of $Pb(NO_3)_2$, $(NH_4)_2HPO_4$, Na_3VO_4 and NaCl. With the use of a computer-controlled chemistate, 250 mL solutions containing Pb^{2+}, PO_4^{3-}, VO_4^{3-} or Cl^- ions in appropriately set molar proportions were gradually mixed together into a large 3-L beaker filled with 1.25 L of continuously stirred redistilled water. The syntheses were carried out at room temperature (25 °C) and pH = 3.5 and the suspensions were left for two weeks for aging [13,19–20,34]. After this time, the precipitates were separated from the solutions by decantation and filtration, washed several times with redistilled water and acetone, and dried at 110 °C for 12 h.

2.2. Methods

The preliminary characterization of the synthetic solids was performed by X-ray powder diffraction (XRD). The XRD patterns of synthetic phases were obtained with a RIGAKU Miniflex X-ray diffractometer using CuKα radiation, a step scan mode at a step size of 0.05°2θ and a rate of 1 s per step. Lattice parameters were calculated for hexagonal crystal system (space group $P6_3/m$) using the Expo 2014 computer program. To determine the chemical composition of the synthesized solids, 100 mg of each sample was dissolved in 0.02 M EDTA at room temperature and analyzed for Pb, P, V and Cl. The total Pb and V(V) concentrations were measured using atomic absorption spectroscopy AAS (SavantAA GBC Scientific Equipment, Australia). The PO_4 concentrations were determined by the colorimetric molybdenum blue method [34–35] and the Cl with a use of the turbidimetric method with silver nitrate [36]. To determine morphology of the precipitates, scanning electron microscopy (SEM) was performed with a FEI QUANTA 200 FEG microscope with energy dispersive spectrometer (EDS) on the carbon-coated samples. Fourier-transform infrared (FTIR) spectra were recorded with a Nicolet 7600 spectrometer in the mid infrared region (4000 to 400 cm^{-1}). Samples were prepared by the standard KBr method. The Raman spectra were recorded at room temperature by the Thermo Scientific DXR Raman Microscope using a laser with a wavelength of 532 nm. Approximately 0.5 g of dry crystalline powder sample was analyzed in the range between 100 and 3428.2 cm^{-1} (laser power of 5 mW, slit aperture of 25 μm). The analysis of each sample was repeated 3 times on various grains. Interpretation of the Raman and the IR spectra was carried out using the Thermo Scientific OMNIC Series Software. Deconvolution was performed in the range of 200–1100 cm^{-1} for the Raman spectra and at 400–1200 cm^{-1} for the IR spectra. The band fitting was performed using a Gaussian function.

3. Results and Discussion

3.1. Solid Characterization

As a result of syntheses, the white to cream, homogeneous precipitates in the form of very fine, crystalline powders were obtained. Precipitates were identified by XRD as pyromorphite $Pb_5(PO_4)_3Cl$, vanadinite $Pb_5(VO_4)_3Cl$ and their solid solutions. The analysis did not yield any impurities within the detection limit of the method. The end members were identified by comparing peak positions of the experimental powder XRD patterns with the Inorganic Crystal Structure Database (ICSD), standards' number: 19-0701 and 43-1461 for pyromorphite and vanadinite, respectively. A number of diffraction peaks for the pyromorphite - vanadinite solid solution series were systematically shifted due to replacement of PO_4 by VO_4 as presented in Fig. 1. The diffraction peaks shifted towards higher diffraction angles with an increasing P content in the phase, indicating a decrease in d-spacing in this direction. Calculation of the unit cell parameters reviled the values of: a = 9.9775 Å and c = 7.3318 Å for pyromorphite and a = 10.3043 Å and c = 7.353 Å for vanadinite. The values agreed well with those reported in the pyromorphite and the vanadinite ICSD cards. The differences within the unit cell parameters as well as the shift of the peaks result from a change in the size of the anion in the structure from 49.5 pm for $(VO_4)^{3-}$ to 31 pm for $(PO_4)^{3-}$. The detailed crystallographic studies of the solid solutions will be subjected to a separate paper. The results of the wet chemical analysis of the synthetic

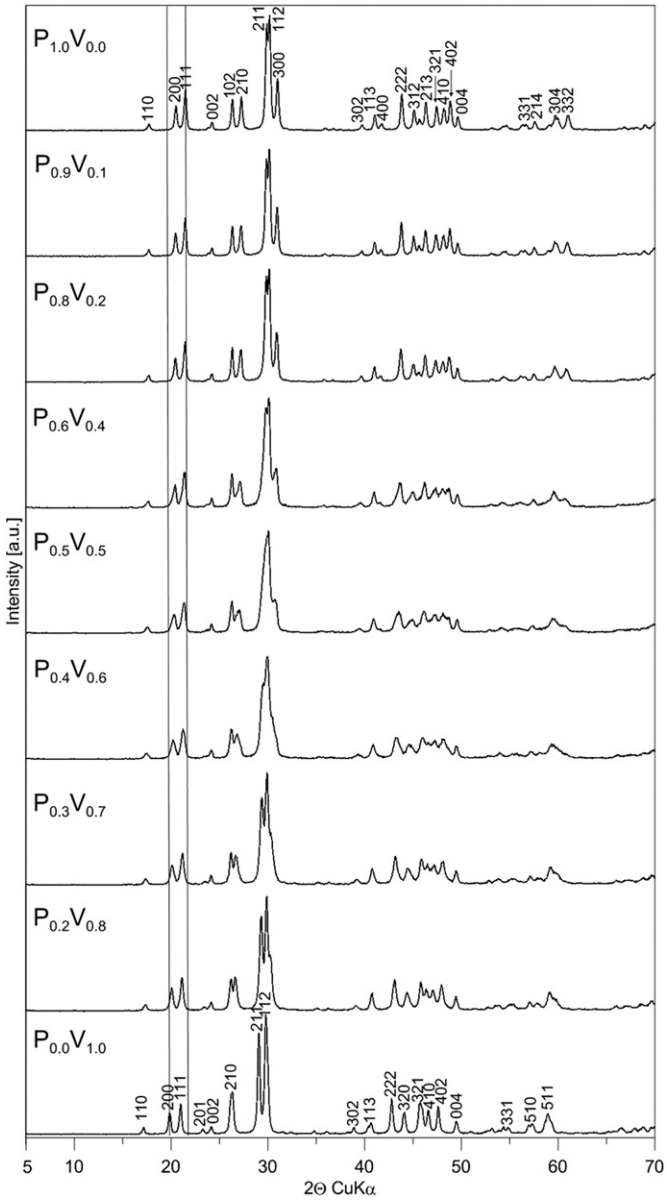

Fig. 1. X-ray diffraction pattern of pyromorphite-vanadinite solid solution series.