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CRYSTAL CHEMISTRY OF SYNTHETIC PYROMORPHITE-MIMETITE SOLID SOLUTIONS

Pyromorphite $Pb_5[PO_4]_3Cl$, mimetite $Pb_5[AsO_4]_3Cl$, and their solid solutions were synthesized from aqueous solutions. These minerals form a ternary system within apatite group of $P6_3/m$ symmetry (hexagonal bipyramid). Natural pyromorphite usually contains several percent of As. Also, natural mimetite often contains PO_4 substitutions. The objective of this study was determination of regularities in crystalline lattice parameters changes with anionic substitution of AsO_4^{-3} and PO_4^{-3}. The products were characterized using X-ray diffraction and scanning electron microscopy with microanalysis. The synthesis resulted in fine white precipitate. X-ray diffraction indicated crystalline character of the precipitate. Lattice parameters for end-members are in accordance with ICDD standards and equal for pyromorphite a = 10,009 Å and c = 7,338 Å and for mimetite a = 10,247 Å and c = 7,448 Å. Both lattice parameters increase proportionally to the increase of As substitution in pyromorphite in conformation with Vegard's law.

Пироморфит $Pb_5[PO_4]_3Cl$, миметезит $Pb_5[AsO_4]_3Cl$ и их твердые растворы были получены из водных растворов. Эти минералы образуют троичную систему в пределах группы апатитов симметрии $P6_3/m$ (гексагональная бипирамида). Природный пироморфит обычно содержит несколько процентов мышьяка. Природный миметезит часто содержит метасоматозы PO_4. Задачей настоящего исследования являлось определение закономерностей в изменениях параметров кристаллической решетки при анионном замещении AsO_4^{-3} и PO_4^{-3}. Продукты реакции были изучены с использованием методов рентгеновской дифракции и растровой электронной микроскопии с микроанализом. В результате синтеза выделилась мелкодисперсная фаза белого цвета. Рентгеновский анализ подтвердил кристаллическую структуру осадка. Параметры кристаллической решетки конечных членов соответствует стандартам ICDD, для пироморфита a = 10,009 Å и c = 7,338 Å, для миметезита a = 10,247 Å и c = 7,448 Å. Параметры обеих кристаллических решеток возрастают пропорционально увеличению метасоматоза мышьяка в пироморфите в соответствии с правилом Вегарда.

INTRODUCTION

Pyromorphite $Pb_5[PO_4]_3Cl$ and mimetite $Pb_5[AsO_4]_3Cl$ form continuous solid solutions [1, 3, 4, 6, 7]. These minerals form a ternary system with vanadynite $Pb_5[VO_4]_3Cl$ within apatite group of $P6_3/m$ symmetry (hexagonal bipyramid) and tend to crystallize as hexagonal rods elongated along c axis, often terminated with bipyramid. Natural pyromorphite usually contains several percent of As. Also, natural mimetite often contains PO_4 substitutions. The objective of this study was determination of regularities in crystalline lattice parameters changes with anionic substitution of AsO_4^{-3} and PO_4^{-3} in pyromorphite $Pb_5[PO_4]_3Cl$, mimetite $Pb_5[AsO_4]_3Cl$, and their solid solutions, that were synthesized from aqueous solutions (see [5]).

MATERIALS AND METHODS

Synthesis of pyromorphite, mimetite and their solid solutions was accomplished with $Na_2HAsO_4 \cdot 7H_2O$, K_2HPO_4, $Pb(NO_3)_2$, and KCl dissolved in 500 cm^3 redistilled water in separate beakers. With use of peristaltic pump, solutions were gradually mixed into large 5 dm^3 beaker filled with 1.5 dm^3 of continuously stirred redistilled water at 20 °C. After the solutions were exhausted, suspension was left still aging for two weeks, decanted, filtered, washed with redistilled water until no Cl^- was detected and washed two times with acetone. To synthesize solid solutions of the amount of P and As was varied in subsequent experiments, while the molar proportions of Pb:(P + As):Cl were kept constant at 5:3:1.

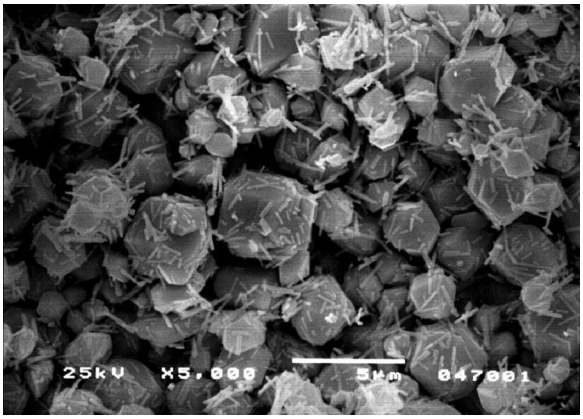


Fig.1a. SEM microphotograph of synthetic $Pb_5[PO_4]_3Cl$

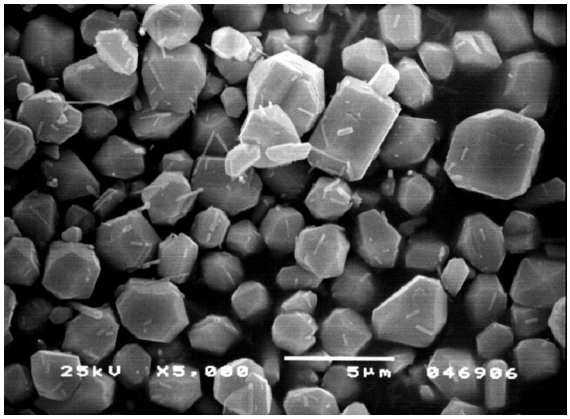


Fig.1b. SEM microphotograph of synthetic $Pb_5[(P_{0.7}As_{0.3})O_4]_3Cl$

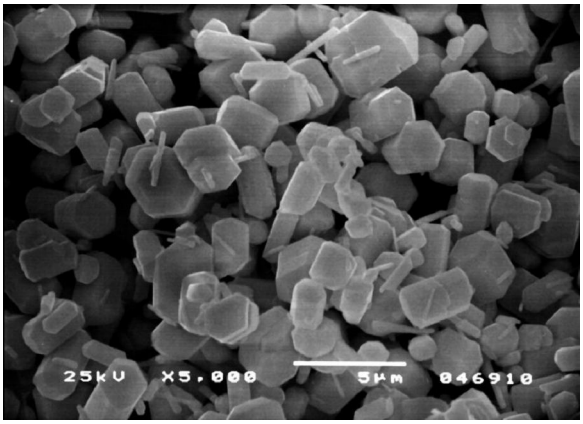


Fig.1c. SEM microphotograph of synthetic $Pb_5[(P_{0.3}As_{0.7})O_4]_3Cl$

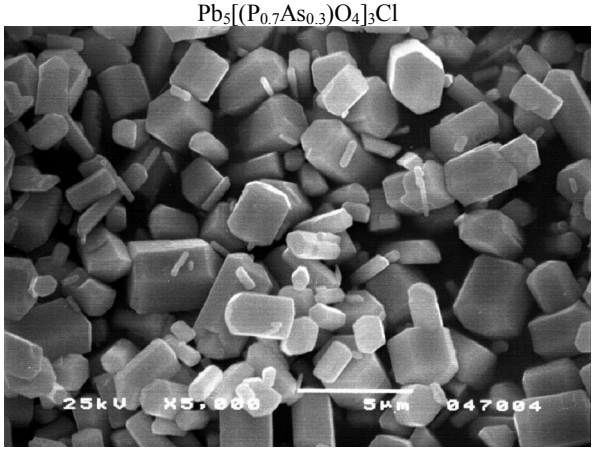


Fig.1d. SEM microphotograph of synthetic $Pb_5[AsO_4]_3Cl$

The dissolution experiments were carried out at 20±1 °C and constant pH value ~2.5.

Powder XRD patterns of synthetic pyromorphite, mimetite and their solid solutions were obtained by Philips PW 3020 X'Pert-APD Diffractometer system (with Cu anode and graphite monochromator) using a step scan mode at a step size of 0.02° 2Θ and a rate of 1s per step, with quartz (samples from P10As0 to P5As5) and silicon powder (samples from P4As6 to P0As10) as internal standard. Unit cell parameters were calculated using DHN/PDS (DHN Powder Diffraction System) software package and refined by least squares method. SEM was performed with JEOL 5200 microscope on gold-coated samples.

RESULTS AND DISCUSSION

The precipitates were homogeneous in size and comprised euhedral hexagonal crystals 1-5 µm in size as=measured on SEM microphotographs (Fig.1).

During the synthesis it was expected that when a given composition fell outside the solid solution field, two or three components would crystallize and show clearly in the x-ray diffraction records. None of the 11 compounds, however, yielded any sign of the presence of more then one component. The synthesis resulted in fine white precipitate. X-ray diffraction results indicated crystalline character of the precipitate. Pyromorphite, mimetite, and their solid solutions were the only identified phases.

Lattice parameters for end-members are in accordance with ICDD standards and equal for pyromorphite a = 9.995 Å and c = 7.331 Å, and for mimetite a = 10.251 Å and c = 7.445 Å. Both lattice parameters increase according to Vegard's law [2] proportionally to the increase of As substitution in pyromorphite (Fig.2).

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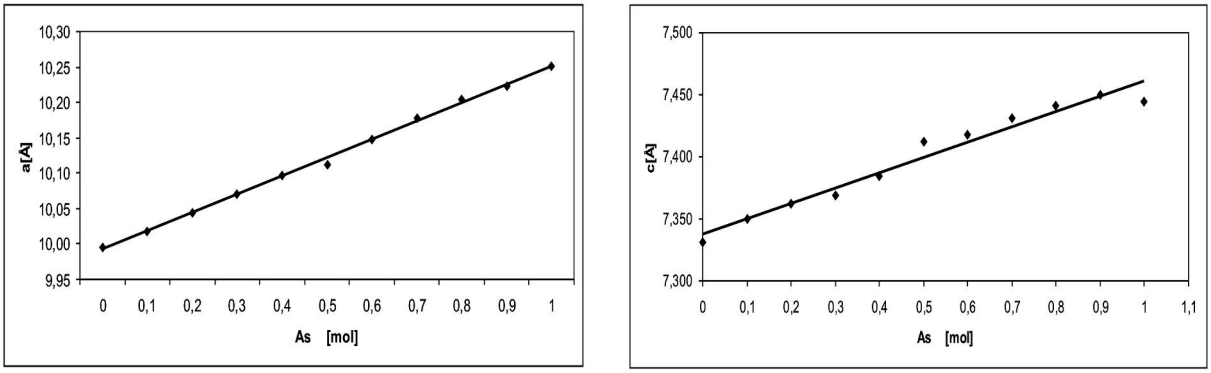


Fig.2. Correlation of lattice parameter a (upper graph) and parameter c (lower graph) with anionic substitution of AsO_4^{-3} for PO_4^{-3} in pyromorphite-mimetite solid solutions

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