

## Monoclinic structure of hydroxylpyromorphite $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ – hydroxylmimetite $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ solid solution series

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Seven samples of hydroxyl analogues of pyromorphite-mimetite solid solutions series were synthesized from aqueous solutions at 80°C in a computer-controlled chemistate: 200 mL aqueous solutions of 0.05M  $\text{Pb}(\text{NO}_3)_2$  and 0.03M  $\text{KH}_2\text{AsO}_4$  and/or  $\text{KH}_2\text{PO}_4$  were dosed with a 0.25 mL/min rate to a glass beaker, which initially contained 100 mL of distilled water. Constant pH of 8 was maintained using 2M KOH. The syntheses yielded homogeneous fine-grained white precipitates composition of which was close to theoretical  $\text{Pb}_{10}[(\text{PO}_4)_{6-x}(\text{AsO}_4)_x](\text{OH})_2$ , where  $x = 0, 1, 2, 3, 4, 5, 6$ . High-resolution powder X-ray diffraction data were obtained in transmission geometry at the beamline 11-BM at the Advanced Photon Source (Argonne National Laboratory in Illinois, USA). The structure Rietveld refinements based on starting parameters of either hexagonal hydroxylpyromorphite or monoclinic mimetite-*M* were performed using GSAS+EXPGUI software.

Apatite usually crystallizes in the hexagonal crystal system with the space group  $\text{P6}_3/\text{m}$ . For the first time, however, the lowering of the hexagonal to monoclinic crystal symmetry was observed in the hydroxyl variety of pyromorphite-mimetite solid solution series. This is indicated by better fitting of the modeled monoclinic structure to the experimental data. The same is not the case for analogous calcium hydroxylapatite series  $\text{Ca}_5(\text{PO}_4)_3\text{OH} - \text{Ca}_5(\text{AsO}_4)_3\text{OH}$  (Lee et al. 2009). Systematical linear increase of unit cell parameters is observed with As substitution from  $a=9.88$ ,  $b=19.75$ , and  $c=7.43$  for  $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$  to  $a=10.23$ ,  $b=20.32$ , and  $c=7.51$  for  $\text{Pb}_{10}(\text{AsO}_4)_6(\text{OH})_2$ . A strong pseudo-hexagonal character ( $\gamma \approx 120^\circ$  and  $b \approx 2a$ ) of the analyzed monoclinic phases was established.

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Lee Y.J., Stephens P.W., Tang Y., Li W., Philips B.L., Parise J.B., Reeder R.J., 2009. Arsenate substitution in hydroxylapatite: Structural characterization of the  $\text{Ca}_5(\text{P}_x\text{As}_{1-x}\text{O}_4)_3\text{OH}$  solid solution. *American Mineralogist*, 94, 666-675.