

Single crystal analysis of La-doped pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$)

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INTRODUCTION:

The presence of rare earth elements (REE) has been reported in natural pyromorphite (Markl et al. 2014). However, the mechanisms of incorporation of REE, their structural position in Pb-apatite, and charge compensation mechanisms are poorly understood, as compared to widely described calcium apatite (e.g. Fleet and Pan 1995, 1997a, 1997b). Nevertheless, the presence of REE in Pb-apatite is of interest because of its potential use in industrial processes. Exchange of REE^{3+} for Ca^{2+} requires a coupled substitution. The two most common mechanisms of REE substitution in Ca, P-bearing apatite supergroup members are (Rønso 1989; Pan and Fleet 2002):

- $\text{REE}^{3+} + \text{Me}^+ \leftrightarrow 2\text{Ca}^{2+}$
- $\text{REE}^{3+} + \text{ZrO}_4^{4-} \leftrightarrow \text{Ca}^{2+} + \text{PO}_4^{3-}$

In natural Ca-apatite, Me⁺ is most frequently Na, and ZrO_4^{4-} is most often SiO_4 . In this study, pyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$ was chosen as the model Pb-apatite, and La was chosen as the model REE, as its chemical and physical properties well represent the entire group of light rare earth elements. Na⁺ and K⁺ were used as model charge-compensating ions. It was hypothesized that the substitution occurs through the following reactions:

- $\text{La}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Pb}^{2+}$
- $\text{La}^{3+} + \text{K}^+ \leftrightarrow 2\text{Pb}^{2+}$

We aimed to provide an explanation of the site occupancy and substitution mechanism, to determine the effect of Na⁺ and K⁺ substitution on the magnitude of La³⁺ substitution, and to capture similarities and differences with the better-studied Ca-apatite. Our findings contribute to a better understanding of light REE substitution in Pb-apatite, which is particularly important because REE are considered critical metals and REE-rich Pb-apatite may prove to be useful in future industrial applications.

METHODOLOGY:

The research methodology involved the synthesis of pyromorphite crystals from aqueous solutions (Figure 1), which is most relevant to natural environmental conditions and to natural REE-enriched pyromorphite found in the oxidation zones of deposits. Therefore, in the present study, we report a single-crystal X-ray diffraction study of four synthetic pyromorphite analogs $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$ containing La and Na (sample ID: La-Na-Pym) or La and K (sample ID: La-K-Pym) substitutions and control samples (samples ID: Na-Pym and K-Pym) synthesized from aqueous solutions under the same conditions in the absence of La. The synthesized samples were characterized using scanning electron microscopy (SEM), microprobe analysis, Raman spectroscopy, and single-crystal X-ray diffraction.

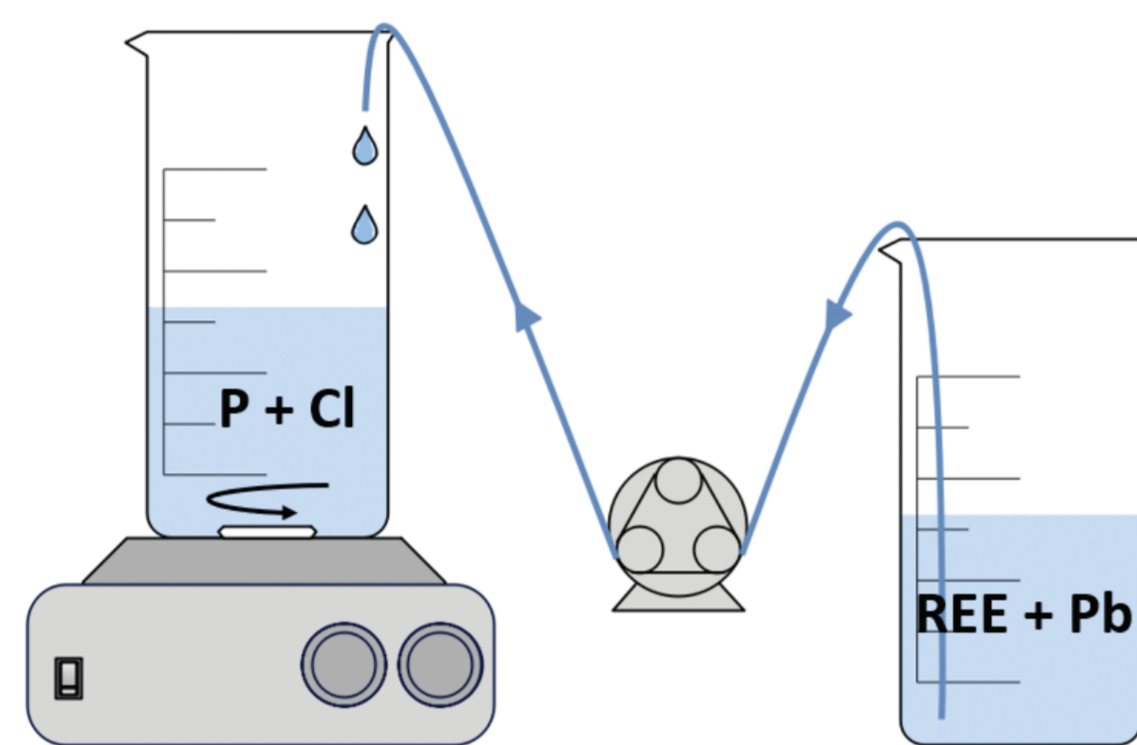


Figure 1. Simplified scheme of synthesis procedure.

RESULTS:

The empirical chemical compositions calculated based on microprobe results for La-doped samples were as follows:

- $\text{Pb}_{4.77(9)}\text{La}_{0.10(6)}\text{Na}_{0.02(2)}(\text{PO}_4)_{3.03(1)}\text{Cl}_{0.89(6)}$
- $\text{Pb}_{4.88(7)}\text{La}_{0.05(2)}\text{K}_{0.01(3)}(\text{PO}_4)_{3.01(2)}\text{Cl}_{1.15(10)}$

And for control samples (with no La):

- $\text{Pb}_{4.97(6)}\text{Na}_{0.01(2)}(\text{PO}_4)_{3.01(2)}\text{Cl}_{1.01(9)}$
- $\text{Pb}_{5.01(8)}\text{K}_{0.01(1)}(\text{PO}_4)_{3.01(2)}\text{Cl}_{1.15(10)}$

La-doped samples yielded elongated needle-like crystals with hexagonal cross sections in the size range of 100–500 μm (Figure 2), whereas those containing no La yielded two generations of crystals: needle-like crystals elongated parallel to the [001] of 200 μm and hexagonal rods of less than 10 μm (Figure 2).

Crystal structures were solved and refined in space group $\text{P6}_3/\text{m}$. No reflections characteristic of a monoclinic superstructure were noted. All structures were refined to $R_1 = 0.0140$ – 0.0225 . Table 1 shows the variations in selected bond lengths, bond angles, polyhedral volumes, and twist angles for all analyzed samples.

Table 1. Selected bond lengths (Å), bond angles (°), and twist angles (°) for all analyzed samples.

	La-Na-Pym	Na-Pym	La-K-Pym	K-Pym
Pb1-O1 (×3)	2.572(3)	2.580(5)	2.581(4)	2.578(5)
O2 (×3)	2.671(3)	2.672(5)	2.674(4)	2.675(5)
O3 (×3)	2.877(3)	2.878(5)	2.881(5)	2.879(5)
Mean	2.707	2.710	2.712	2.711
Polyhedral volume (Å ³)	38.515	38.688	38.777	38.729
Pb2-O1	3.065(3)	3.086(7)	3.079(4)	3.08619(11)
O2	2.357(4)	2.359(7)	2.356(6)	2.352(6)
O3 (×2)	2.630(3)	2.633(5)	2.625(4)	2.634(5)
O3 (×2)	2.637(3)	2.637(5)	2.636(5)	2.635(5)
Cl (×2)	3.10891(18)	3.1109(6)	3.1131(2)	3.1103(3)
Mean	2.772	2.776	2.773	2.774
Polyhedral volume (Å ³)	36.941	37.138	37.019	37.085
P-O1	1.528(4)	1.523(7)	1.519(6)	1.522(7)
O2	1.555(4)	1.559(7)	1.557(6)	1.562(7)
O3 (×2)	1.534(3)	1.538(5)	1.539(4)	1.537(5)
Mean	1.538	1.540	1.536	1.540
Polyhedral volume (Å ³)	1.862	1.869	1.866	1.869
O1-P-O2	110.6(3)	110.5(4)	110.5(4)	110.3(4)

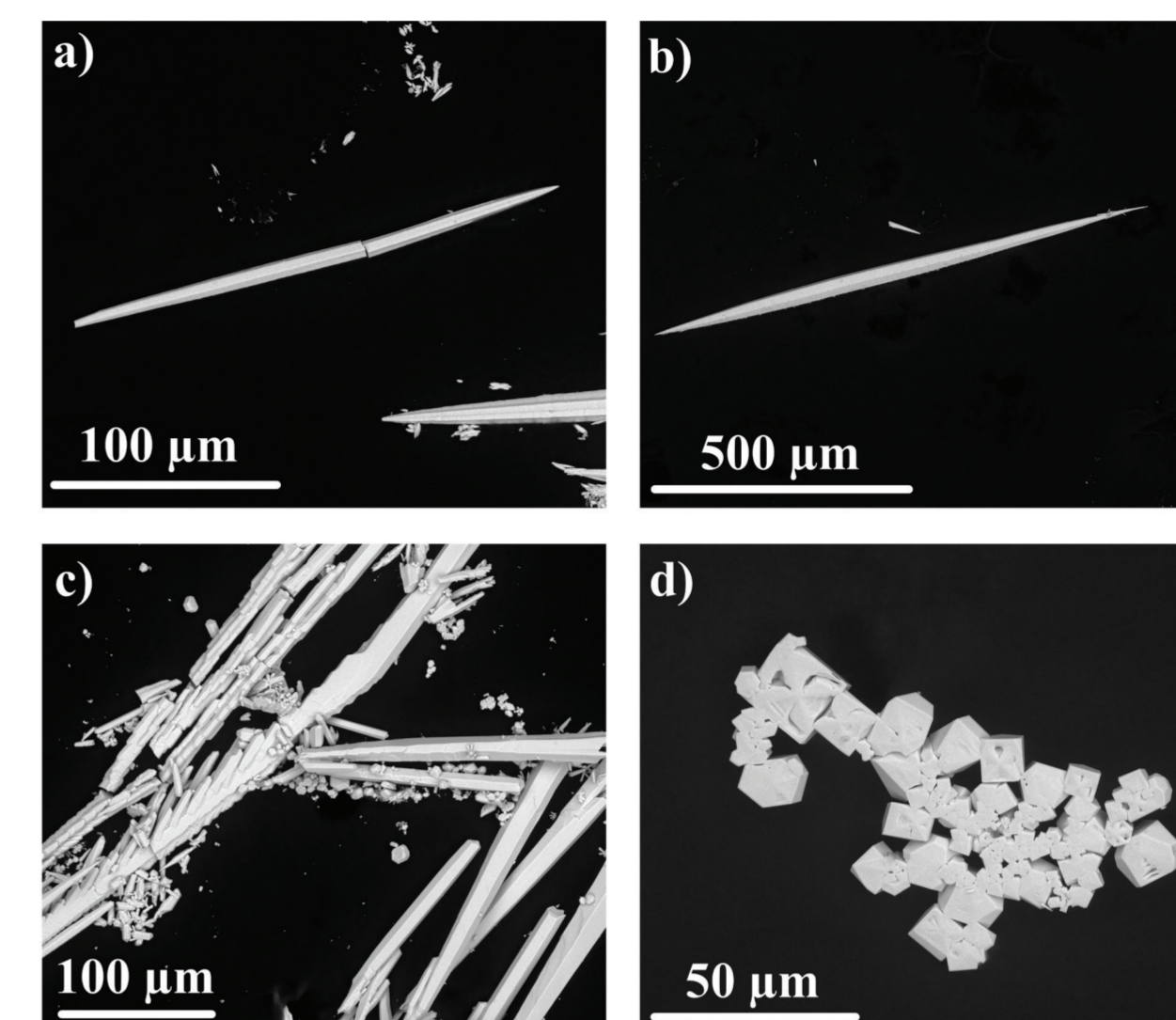


Figure 2. Scanning electron micrographs (BSE) of synthesized analogs: (a) La-Na-Pym; (b) La-K-Pym; (c) control Na-Pym; and (d) control K-Pym.

DISCUSSION:

Minor substitution of Na and K ions in the control samples slightly affected the mean Pb1–O distances, resulting in the increase in the Pb1 polyhedral volume in Na-Pym compared to K-Pym. This is consistent with the smaller ionic radius of Na than that of K. The mean Pb1–O distances for La-doped samples increased by 0.005 Å for La-K-Pym compared to those of La-Na-Pym, reflecting the polyhedral volume changes. The most sensitive bond for substitution was the Pb1–O1 bond. The Pb1 polyhedral volume for La-Na-Pym decreased by 0.173 Å³ compared to the control sample, whereas the corresponding volume in La-K-Pym increased in comparison to the control sample by 0.048 Å³. This variation may be caused by the differences in ionic radii. In the case of Na and La substitutions for Pb, both substituting ions are smaller than Pb, whereas in the case of K and La substitutions for Pb, the K ion is larger than Pb and the La ion is smaller. However, the average ionic radii of La and K is very close to that of Pb, which may be the reason for the small volume change in this polyhedron compared to the control sample (only by 0.048 Å³). Variations in individual and mean interatomic distances in Pb1 polyhedron reflect the cumulative effect of both the amount of substitution and ionic radii of substituting ions. Changes in the Pb1 polyhedron slightly affected the mean Pb2–O distances. The largest difference was visible for the weakest bond, Pb2–O1, which was shorter in both the La-doped pyromorphites compared to the control samples. A similar trend was observed for the Pb2 polyhedral volume. Substitution in Pb1 did not affect the PO₄ tetrahedron.

Changes in distances also affected the unit-cell parameters and, consequently, their volumes. The unit-cell parameter c appears to be more affected by the substitution and decreased in La-doped samples compared to the control samples. In La-Na-Pym, the unit-cell parameter a also decreased compared to the control sample. However, in La-K-Pym, a increased compared to K-Pym. This affected the volumes of the unit cell, and within the samples the smallest unit-cell volume, 630.680 Å³, was observed for La-Na-Pym. This is due to the substitution of two smaller ions (Na⁺ and La³⁺) for Pb²⁺. In the La-K-Pym sample, the La content is lower than in La-Na-Pym, and the K ion is larger than Na, which resulted in an overall increase in the unit-cell volume.

SUMMARY:

The restricted chemistry of synthetic analogs of La-doped pyromorphite allowed us to determine the effect of La substitution on the structure. From our single-crystal X-ray diffraction study, the following implications emerged. The mechanisms controlling La substitution in Pb-apatite are somewhat different from those in Ca-apatite. In both types of apatite, owing to the charge difference, heterovalent substitution of La³⁺ for Me²⁺ requires counter ions, which, in this case, were K⁺ and Na⁺. However, in contrast to natural Ca-apatite, in Pb-apatite La occupies the Me1 site and not the Me2 site. This is at least the case in pyromorphites in which the counter ion is K or Na. It is possible that a greater size of Ca2 in Ca-chlorapatite diminishes the selectivity of this position for REE relative to that of Ca1 (Fleet et al. 2000). However, considering the present stage of knowledge, it is not possible to accurately compare the results obtained for pyromorphite with its calcium chlorapatite counterpart $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ due to the difficulty in obtaining such apatite by simple synthesis from aqueous solutions. Therefore, it is difficult to clearly assess how much of this difference in substitution is due to the crystallization process and how much is due to a slight difference in structural properties, the influence of the lone-electron pair in Pb²⁺ ions, or the preference of Pb to occupy the Me2 site. Nevertheless, the magnitude of La substitution in the synthetic pyromorphites described here was larger than that reported in natural ones (see, for example, Markl et al. 2014). This substitution model appears to be the model for all REE in Pb-apatite (or at least for all LREE).

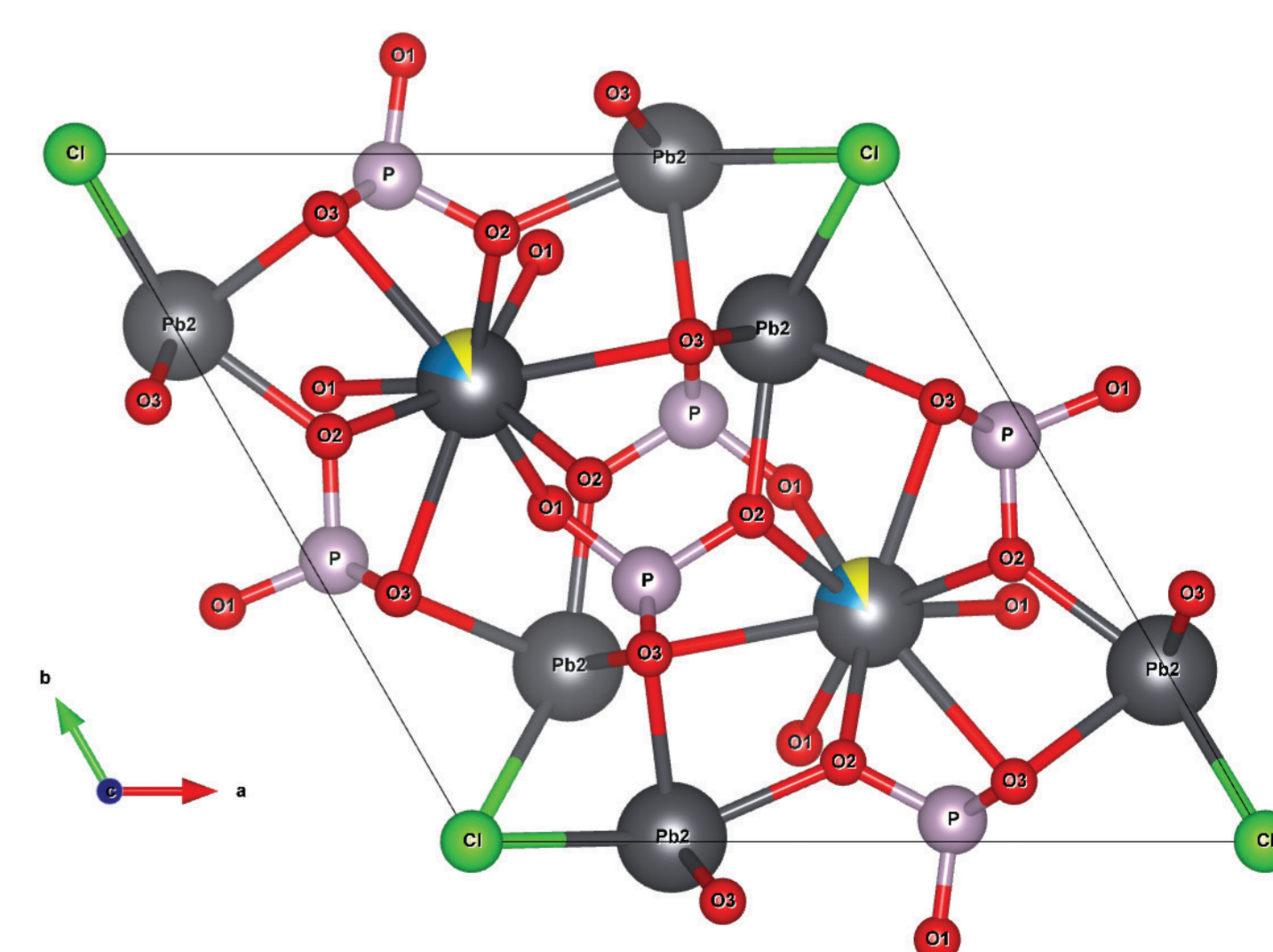


Figure 3. Graphical (ball-and-stick) representation of obtained structure of La-K-Pym. Unlabeled atom is Pb1 position occupied by Pb (grey), La (blue), and K (yellow).

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- Fleet, M.E. and Pan, Y. (1995), *Am. Min.*, 80, 329–335; Fleet, M.E. and Pan, Y. (1997a), *Am. Min.*, 82, 870–877; Fleet, M.E. and Pan, Y. (1997b), *Geochim. Cosmochim. Acta*, 61, 4745–4760; Fleet, M.E., Liu, X., and Pan, Y. (2000), *Am. Min.*, 85, 1437–1446; Markl, G., Marks, M.A., Holzäpfel, J., and Wenzel, T. (2014), *Am. Min.*, 99, 1133–1146; Pan, Y. and Fleet, M.E. (2002), *Rev. Mineral. Geochem.*, 48, 13–49; Rønso, J.G. (1989), *Am. Min.*, 74, 896–901.

