

## Rietveld Refinement and HRTEM Simulation of Calcium-Lead Apatites

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Many investigations have been carried out in recent years on the stabilization of toxic heavy metals in wastes and soils through transformation into durable mineral forms that prevent their release into the surrounding environments [1,2]. It is known that apatite minerals, of ideal formula  $A_4^I A_6^{II} (BO_4)_6 X_2$ , are highly durable compounds capable of surviving without alteration in a variety of geological settings. In addition, its lattice can accommodate a wide range of toxic metals and metalloids. However, the paucity of fundamental data on the crystal chemistry of (non-phosphate) apatites has limited their application to a subset of hazardous metal containing wastes. In this investigation, the solid state chemistry of  $(Pb_x Ca_{10-x})(VO_4)_6 F_2$  apatite, for the immobilization of industrial sludge and incinerator ashes containing top-end toxic metals (e.g. lead and vanadium) was studied.  $(Pb_x Ca_{10-x})(VO_4)_6 F_2$  were synthesized by solid reaction route. CaO (obtained by firing and decomposing AR grade  $CaCO_3$  at  $900^\circ C$ ), PbO,  $V_2O_5$  and  $CaF_2$  powders were mixed in stoichiometric proportions and fired at  $800^\circ C$  in alumina boats at ambient atmosphere for 10 hours. The firing temperature chosen was just below the melting point of lead endmember  $Pb_{10}(VO_4)_6 F_2$ . Ten compositions of  $(Pb_x Ca_{10-x})(VO_4)_6 F_2$  with  $x = 0, 1, 2 \dots 9$  were prepared. Powder X-ray diffraction data were collected using a Siemens D5005 X-ray diffractometer at a scanning rate of  $0.12^\circ 2\theta/min$ . The average calcium/lead partitioning was quantified using full structure refinement by Rietveld X-ray analysis, which showed that substitution of lead over the two calcium-type cation-acceptor sites was not straightforward. This is because the  $Ca^{II}$  site is larger than the  $Ca^I$  site and fills preferentially with lead, resulting in a non-linear expansion of the crystallographic c-axis (FIG. 1). The direct (real space) observation of Ca/Pb partitioning was studied by HRTEM. A typical image from  $(Ca_5 Pb_5)(VO_4)_6 F_2$  after long term annealing at  $800^\circ C$  is given in FIG. 2. Combined with HRTEM image simulation results, it is believed that the contrast changes at site "A" are possibly due to the disordered structure formed during sintering. The results more fully describe the mechanism and capacities of toxic metals to be accommodated in apatite's "A", "A<sup>II</sup>" and "B" sites with high stability.

### References

- [1] Q.Y.Ma et al., Environ. Sci. Technol. 27 (1993) 1803.
- [2] P. Zhang, and J.A.Ryan, Environ. Aci. Technol. 33 (1999) 618.
- [3] The authors would like to thank the Environmental Technology Institute, Singapore for supporting this research. The authors would also like to thank Ms Wei Bing for her aid in sample sintering.

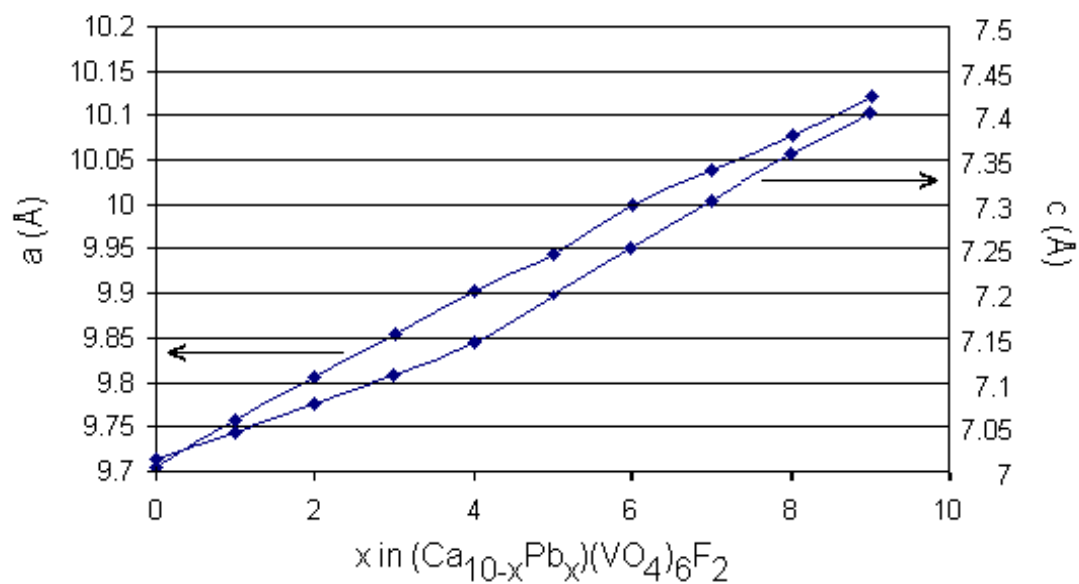


FIG. 1. Rietveld X-ray refinement result indicating lattice parameter changes of  $(\text{Pb}_x\text{Ca}_{10-x})(\text{VO}_4)_6\text{F}_2$  apatite with lead content. Heat treatment conditions: 800°C.

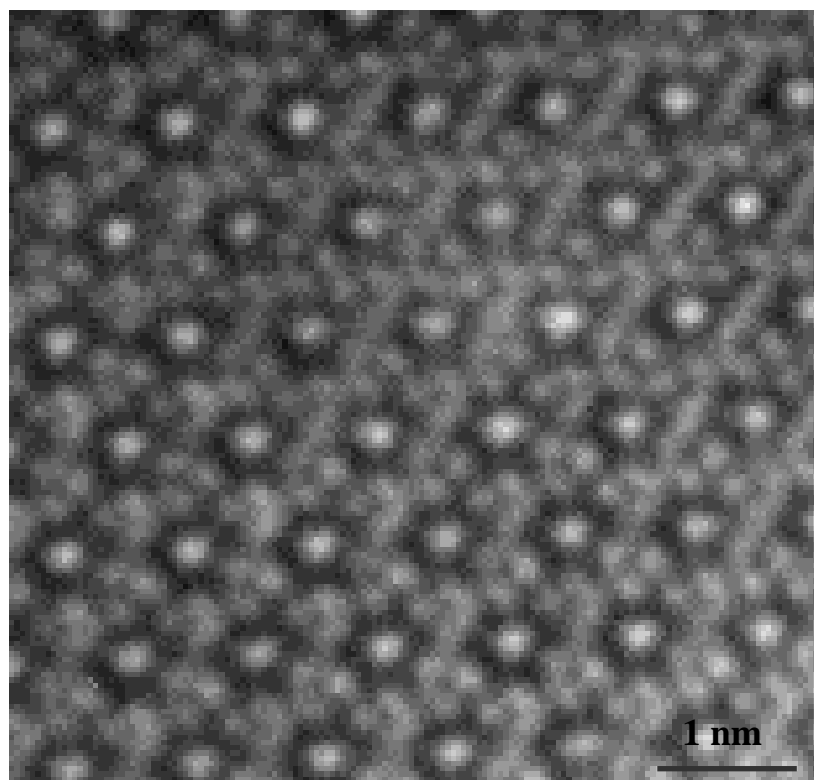


FIG. 2. HRTEM image taken from c-axis of  $(\text{Pb}_5\text{Ca}_5)(\text{VO}_4)_6\text{F}_2$  apatite after treated at 800°C for 1186 hours.