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 $A_3^I A_6^{II}$ (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 $(Pb_xCa_{10-x})(VO_4)_6F_2$ apatite, for the immobilization of industrial sludge and incinerator ashes containing top-end toxic metals (e.g. lead and vanadium) was studied. $(Pb_xCa_{10-x})(VO_4)_6F_2$ were synthesized by solid reaction route. CaO (obtained by firing and decomposing AR grade CaCO$_3$ at 900°C), PbO, V$_2$O$_5$ and CaF$_2$ powders were mixed in stoichiometric proportions and fired at 800°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 $(Pb_xCa_{10-x})(VO_4)_6F_2$ with $x = 0, 1, 2...9$ were prepared. Powder X-ray diffraction data were collected using a Siemens D5005 X-ray diffractometer at a scanning rate of 0.12° 2θ/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 $(Ca_5Pb_5)(VO_4)_6F_2$ after long term annealing at 800°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$^I$”, “A$^{II}$” and “B” sites with high stability.

References

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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: $800^\circ\text{C}$.

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 $800^\circ\text{C}$ for 1186 hours.