Electron Irradiation Induced Transformation of (Pb₅Ca₅)(VO₄)₆F₂ Apatite to CaVO₃ Perovskite

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Crystallochemical changes of (Pb₅Ca₅)(VO₄)₆F₂ apatite under electron irradiation were examined by transmission electron microscopy. The apatite, a synthetic analog of vanadinite, was moderately stable towards a less intense 300-keV LaB₆ source, while it changed rapidly in structure when exposed to the higher flux of a 200-keV field emission gun. The electron beam induced transformation of vanadinite proceeds sequentially by (i) migration and loss of fluorine, (ii) lead volatilization and conversion to 2–5-nm platelets of a glaserite-type structure, and (iii) the reduction of V⁵⁺ to V⁴⁺ with the removal of lead and calcium oxide that leads to single-crystal CaVO₃ perovskite as the ultimate product. The phase transformations are interpreted based on the crystallographic relations among the CaVO₃ perovskite, the (Pb₅Ca₅)(VO₄)₆F₂ apatite and the glaserite-type structures, and compositional changes under electron irradiation.

I. Introduction

Soil contaminants such as lead, arsenic, mercury, and cadmium that degrade groundwater quality are subsequently absorbed by plants and animals, and can promote a variety of acute and stochastic medical conditions. Metal mobilization is therefore a problem of long standing. Typically, the treatment of heavy metal bearing wastes are studied on a case-by-case basis, and many thermal, biological, and physical/chemical treatment technologies have been used to manage industrial wastes and contaminated sites containing pollutants at low levels. For highly concentrated toxic metals and radioactive isotopes crystallochemical immobilization is often considered the technology of choice. Numerous studies have demonstrated the effectiveness of fixing hazardous inorganic materials in durable ceramics that can sustain high loadings and density. However, the diversity of such ceramics and the complexity of their environmental reactivities require the systematic study of each stabilization system under development.

Apatite-based ceramics have been widely investigated as their capacity to incorporate toxic heavy metals is inherently high. Apatites also have low dissolution rates that in favorable circumstances of reuse or disposal can meet stringent environmental regulations. In general, the group can be described as [A(1)₂][A(2)₃](BO₄)₃X with complete or partial filling of the A-sites by Na, Mg, Ca, Sr, Ba, Pb, Cd, La, or Ce, the B-site by V, P, As, S, Si, Ge, Cr, or B and X commonly by a halide or hydroxyl ion. Some minerals (e.g., belovite) retain Th and U and their disintegration products. Within the group, hydroxapatite (HAp) is the most thoroughly studied, as it is the main inorganic component of bones and teeth and its potential to concentrate lead, cadmium, and radionuclides is also well documented. It has also been found that HAp degrades rapidly when exposed to high-energy electrons during transmission electron microscopy (TEM) studies. This may have implications for the stabilization of β-emitting nuclides such as Sr-90 (average emission energy 196 keV) or Cs-132 (157 keV).

This report extends an earlier investigation which noted that vanadinite was more resistant than its phosphate analog to electron irradiation, although the dose dependence and ultimate transformation products were not determined. In the present study, crystallochemical damage of the vanadinite (Pb₅Ca₅)(VO₄)₆F₂ was studied by a 200 keV TEM with a field emission gun (FEG-TEM) and a 300-keV TEM with a lanthanum hexaboride (LaB₆-TEM) source with less intense electron flux. Using this approach, the dose dependence of electron irradiation on damage ingrowth could be investigated, and in the case of the LaB₆-TEM simultaneous collection of microchemical and crystallographic information was possible. Even though the rate of modification is quite different in these two experiments, the transformation mechanism and final product are identical.

II. Structure of Mixed Metal Apatites

The crystal structures of [A(1)₂][A(2)₃](BO₄)₃X P₆₋ₙm apatites possess two distinct A-sites, A(1) and A(2). In mixed metal compounds, the A(2) interstice is the preferred location for relatively larger cations while smaller cations enter the A(1) position. However, such partitioning is observed only in natural specimens or materials that have been subjected to long heat treatment. The (Pb₅Ca₅)(VO₄)₆F₂ vanadinite in its equilibrated state has such a structure and its crystallographic data is given in Table I. The dominant crystallographic features are isolated VO₄ tetrahedra that are corner-connected to [Pb/Ca(1)]O₆ metaprism columns aligned parallel to [001] to form one-dimensional tunnels in this direction (Fig. 1). The idealized [Pb/Ca(2)]O₄F octahedra has its coordination sphere expanded to seven, and is the preferred location for Pb²⁺ leading to a partitioning coefficient (kₚ₈) of 0.17 rather than 0.66, as implied by the compositional formula. The A(2) tunnels are rich in lead, is mobile due to the larger anion-coordination sphere and proximity to F⁻, and readily exchange with species of similar size in dilute salt solutions. The X sites are also the loci for the activation of electron beam damage.