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Structure Modification of $Pb_xCa_{10-x}(VO_4)_6F_2$ Apatite under Electron Beam Irradiation

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Apatite-based ceramics have been widely investigated as their capacity to incorporate toxic heavy metals is inherently high [1,2]. The group crystallochemical formula can be expressed as $[A(1)_4][A(2)_6](BO_4)_6X_2$ with complete or partial filling of the A-sites with Na, Mg, Ca, Sr, Ba, Pb, Cd, La or Ce and the B-site occupied by V, P, As, S, Si, Ge, Cr or B [3]. Moreover, some minerals (e.g. belavite) retain Th and U and their disintegration products. Apatites have low dissolution rates that in favorable circumstances of reuse or disposal can meet stringent environmental regulations.

This investigation is focused on the apatite structure modification induced by electron beam irradiation that could happen in the stabilization of β-emitting nuclides such as Sr-90 (average emission energy 196 keV) or Cs-132 (157 keV). Radiation damage experiments were undertaken in two parts. First, a 200 keV field emission gun (FEG) transmission electron microscope (TEM) was used to accelerate the induction of crystallochemical damage. Second, a 300 keV lanthanum hexaboride (LaB_6) source exposed vanadinite to a less intense electron flux that tempered damage ingrowth and permitted the simultaneous collection of microchemical and crystallographic information from partially evolved products. While the rate of modification is quite different in these two experiments, the transformation mechanism and final product are identical. Experimental results showed that $(Pb_5Ca_5)(VO_4)_6F_2$ apatite, a synthetic analogue of vanadinite, was moderately stable towards a less intense 300 keV LaB_6 source, but modified rapidly when exposed to the higher flux of a 200 keV field emission gun (Fig.1). As reported in our previous study [4], the electron beam induced transformation of vanadinite proceeds sequentially by (i) migration and loss of fluorine, (ii) lead volatilization and conversion to a glaserite-type structure, and (iii) the reduction of V^{5+} to V^{4+} with removal of lead and calcium oxide. The ultimate product is $CaVO_3$ perovskite (Fig.2). The glaserite intermediary exists as ~5nm platlets (Fig.1). The unit cell volume of $CaVO_3$ derived geometrically from the lattice metric of $(Pb_5Ca_5)(VO_4)_6F_2$ differs by only 2.9% from those obtained by X-ray diffraction refinement. This relatively small discrepancy allows the external form of single crystals to be preserved during conversion from apatite to perovskite.

References

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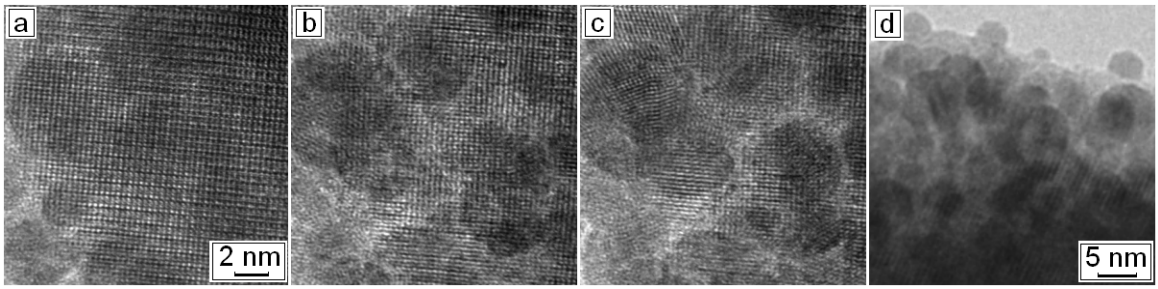

Fig. 1. The formation of calcium-rich 2-5 nm domains after irradiation for (a) less than 2 min, (b) 5 min and (c) 10 min. A lower magnification image (d) shows the migration of more volatile phases, presumed to be lead-rich glaserite and lead oxide, prior to vaporization.

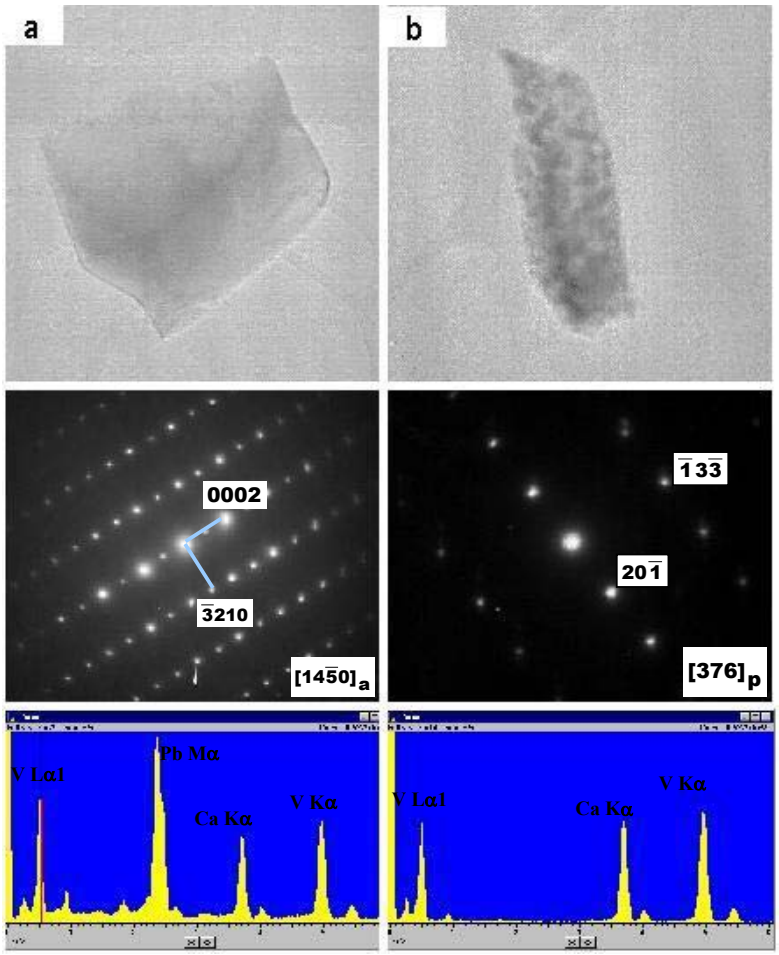

Fig.2. Formation of $CaVO_3$ perovskite crystal from a $(Pb_5Ca_5)(VO_4)_6F_2$ apatite crystal during irradiation under LaB_6 emission as monitored by bright-field microscopy, electron diffraction and energy dispersive X-ray analysis. (a) An apatite crystal prior to electron beam irradiation, (b) Perovskite structure formed after electron beam irradiation for 100 min.

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