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Electron-beam (5–10 keV) damage in triplite-group phosphates: Consequences for electron-microprobe analysis of fluorine

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ABSTRACT

The F*K*α emission in samples of triplite-group phosphates (TGP) submitted to electron beams routinely used for electron-probe microanalysis of light elements (5–10 keV, 30 nA, 5 μm in diameter) evolves anisotropically with time. The intensity variations consist of an initial rise of the signal (time constants on the order of few tens of seconds), by up to 20–30% of the zero-time value, followed by a longer-time-constant increase or decrease. The initial signal rise is interpreted as an enhancement of the fluorescence yield of the F ions due to bond breaking. Halogen-formed lattices are known to be sensitive to radiolysis, i.e., destabilization of the atomic arrangement due to perturbations of the electronic structure induced by particle irradiation, leading often to bond breakage and lattice-ion displacements. In strongly ionic structures (alkali halides and alkaline-earth fluorides, notably), bond breakage results from the decay of metastable states in which transient molecular ions (e.g., F_2^-) are formed. Molecular ions preexisting within ionic lattices under the form of halogen-halogen bonds (e.g., F^0-F^- bonds) are likely involved in the degradation processes under irradiation of materials such as fluoro-phosphates. High-resolution studies of the F*K*α emission band in TGPs reveal that lattice F ions may have an average fractional charge of $-x$ ($0.5 < x < 1$, instead of $x = 1$ for ideally ionic lattices) consistent with the presence of F^0-F^- bonds.

Other longer-time-constant processes are attributed to the production of F^- interstitials beneath the specimen surface that can accumulate (increasing signal) or desorb (decreasing signal) when they have enough energy to overcome the surface potential barrier. The role of the energy stored within the lattice by charging is critical to the understanding of both the anisotropy of the F*K*α intensity and the accumulation-desorption processes of the produced F^- interstitials. Owing to the differences between specimens in (1) the effective charge of the F ions and (2) the electron-stimulated desorption (ESD) mechanisms leading to the emission of F^- and F^+ ions, it is concluded that standards with structural properties close to those of unknowns should be selected for accurate analysis of F in beam-sensitive minerals or glasses.

Keywords: Fluorine analysis, crystal structure, point defects in solids, electron microscopy, electron microprobe, polytypism, triplite-group phosphates