

What is the actual structure of samarskite-(Y)? A TEM investigation of metamict samarskite from the Garnet Codera dike pegmatite (Central Italian Alps)

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ABSTRACT

We investigated, by scanning and transmission electron microscopy (SEM, TEM), wavelength- and energy-dispersive spectroscopy (WDS, EDS), and electron diffraction tomography (EDT), several (Y-REE-U-Th)-(Nb-Ta-Ti) oxides from the Garnet Codera dike pegmatite (Central Italian Alps). These oxides have compositions in the samarskite-(Y) field and yield an amorphous response from the single-crystal X-ray diffractometer. Backscattered electron images reveal that the samples are zoned with major substitutions involving (U+Th) with respect to (Y+REE). At the TEM scale, the samples show a continuous range of variability both in terms of composition and in radiation damage, and the amount of radiation damage is directly correlated with the U-content. Areas with high U-content and highly damaged show crystalline, randomly oriented nanoparticles that are interpreted as decomposition products of the metamictization process. On the other hand, areas with lower U-content and radiation dose contained within 0.7×10^{16} α -event/mg, although severely damaged, still preserve single-crystal appearance. Such areas, noticeably consisting of relicts of the original samarskite structure, were deeply investigated by electron diffraction techniques. Surprisingly, the retrieved crystal structure of untreated samarskite is consistent with aeschynite and not with ixiolite (or columbite), as believed so far after X-ray diffraction experiments on annealed samples. In particular, the resolved structure is a niobio-aeschynite-(Y), with *Pnma* space group, cell parameters $a = 10.804(1)$, $b = 7.680(1)$, $c = 5.103(1)$ Å, and composition $(Y_{0.53}Fe_{0.22}Ca_{0.10}U_{0.09}Mn_{0.07})_{\Sigma=1}(Nb_{1.07}Ti_{0.47}Fe_{0.34}Ta_{0.07}W_{0.06})_{\Sigma=2}O_6$. If this finding can be confirmed and extended to the other members of the group [namely samarskite-(Yb), calciosamarskite, and ishikawaite], then the samarskite mineral group should be considered no longer as an independent mineral group but as part of the aeschynite group of minerals.

It is finally suggested that the rare crystalline sub-micrometric ixiolite domains, occasionally spotted in the sample by TEM, or the nanoparticles detected in highly metamict areas interpreted as decomposition product of the metamictization process, which may have in fact the ixiolite structure, act as seeds during annealing, leading to the detection of ixiolite peaks in the X-ray powder diffractograms.

Keywords: Samarskite-(Y), niobioaeschynite-(Y), TEM, electron diffraction tomography