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 $0.7 \times 10^{16}$ α-event/mg, although severely damaged, still preserve single-crystal appearance. Such areas, noticeably consisting of relics 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 $(Y_{0.55}Fe_{0.22}Ca_{0.10}U_{0.09}Mn_{0.07})_2O_6$–$(Nb_{1.07}Ta_{0.07}W_{0.06})_2O_6$. If this finding can be confirmed and extended to the other members of the group [namely samarskite-(Y), calciosamarskite, and ishikawaita], 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

INTRODUCTION

Most niobium-tantalum-titanium oxide minerals, common accessory minerals of granitic pegmatites, contain yttrium, rare earths, iron, and manganese, together with relatively high amounts of radioactive elements such as uranium and thorium, whose decay causes their structure to become metamict over geological times. As a consequence, the identification of these minerals is not trivial, since many of them are so structurally compromised by radiation damage that their crystallographic determination is impossible. Other diagnostic features may be either not present (e.g., crystal forms, cleavage), common to several minerals (e.g., surface luster, color), or heavily altered by the metamictization process (e.g., birefringence). As such, phase identification is commonly done on the basis of mineral-chemistry alone.

However, especially for some oxide minerals where yttrium is the dominant metal, mineral identification via compositional data alone is often ambiguous, and over time has given origin to confusion in their naming, systematics, and crystal chemistry (e.g., Ewing 1976; Ercit 2005; Škoda and Novák 2007). In fact, many diverse mineral groups show compositional overlapping, e.g., fergusonite vs. samarskite and euxenite vs. aeschynite. There are doubts about the proper cation site assignment, which is distinctive for some minerals, as well as about the knowledge of the valence state of iron and uranium, which is impossible to determine by electron microprobe, i.e., the most common analytical technique in mineral sciences. Moreover, the presence of additional, partially occupied sites that originate from the metamictization process, further complicate the task (Bonazzi and Menchetti 1999).

For these reasons, the identification of metamict minerals is usually done through X-ray diffraction of recovered material after heating and recrystallization at high temperature. Also in