

Samarskite high-temperature modification recrystallisation: vibrational spectroscopy probing

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For samarskite, ideally ABO_4 ($A=Y, Fe$; $B= Nb, Ta$), two crystal structure modifications have been proposed based on XRD studies of thermally annealed metamict samples: low-temperature (LT) samarskite, crystallising around 550 °C, and high-temperature (HT) samarskite, crystallising around 950 °C (Sugitani et al., 1985). Diffraction data indicated orthorhombic symmetry ($Pbcn$) for the LT modification and monoclinic ($P2/c$), probably wolframite-related structure, for the HT modification, yet no structure has been resolved for any of the modifications.

Two metamict samples of samarskite, one from Lauvrak, Norway, and another one from Ampangabe, Madagascar, were annealed in air and reducing atmosphere (Ar/H_2) at 550 °C and 1000 °C. Unannealed and annealed samples were characterised by XRD, Raman and IR spectroscopy to get insight into low range ordering and crystal structure. Powdered samples were analysed using Jobin Yvon T64000 spectrometer working in micro-Raman mode with Ar 514.5 nm excitation line. IR absorption measurements of the samples prepared as KBr pellets were performed by Bruker Tensor 27 spectrometer.

Both samples are X-ray amorphous, indicating heavy metamictisation. When heated at 550 °C in both atmospheres they recrystallise orthorhombically, matching well with the proposed samarskite LT. At 1000 °C the proposed samarskite HT co-recrystallises with a pyrochlore phase, independent on the heating atmosphere.

Raman and IR spectra show a gradual recrystallisation of the two samples with corresponding band frequencies for both samples while the bands are best resolved at 1000 °C. A comparison to IR absorption and Raman spectra of scandium niobates and tantalates with ABO_4 stoichiometry and wolframite structure (Goundobin et al., 1977) yields a good match of bands which are attributed by normal coordinate analysis. The most prominent Raman bands occur at 815 cm^{-1} (B-O symmetrical stretching), 630 cm^{-1} (B-O anti-symmetrical stretching) and 426 cm^{-1} (A-O symmetrical stretching). IR bands are as follows: 795 cm^{-1} (B-O symmetrical stretching), 579 cm^{-1} (O-B-O anti-symmetrical stretching), 450 cm^{-1} (A-O anti-symmetrical stretching). The band around 530 cm^{-1} is both IR and Raman active. The occurrence of the pyrochlore phase is confirmed with the pyrochlore prominent band around 335 cm^{-1} in Raman and a band around 640 cm^{-1} in IR spectra.

This study indicated a relation of samarskite HT local structure to the one of wolframite-type structure with cations in octahedral coordination as implied from the vibration spectra of similar synthetic analogues. Substitutions of different cations in A-site, most notably REE and Fe in the case of samarskite, cause a shift of vibration frequencies due to mass and bond strength variations.

References:

- Goundobin N., Kondratov, V., Kravchenko, V., Petrov, K. (1977), Journal of Molecular Structure, 39, 15-23.
Sugitani, Y., Suzuki, Y., Nagashima, K. (1985), American Mineralogist, 70, 856-866.