Proposal Code: **HS-3337**
Proposal Title: Cation Order and Microstructure of Columbites: in situ high resolution XRPD investigation

Synopsis. Experiment HS3337 allowed a novel type of microstructure formation and self-assembly mechanism to be revealed in columbite oxides. Spontaneous separation of phases characterised by same structure and chemical composition but different degree of intracrystalline cationic order occurs at high temperature.

Experimental. A chemically homogeneous natural columbite coming from Kragero (Norway) [composition determined by EMPA/WDS $(Mn_{0.85}Fe_{0.15})(Nb_{1.8}Ta_{0.2})O_6$] was used. Pure columbite crystals were selected, hand-ground in an agate mortar under acetone, sieved, and washed to give a powder with grain sizes in the range 10–40 μm. Samples were loaded in 0.7 mm diameter quartz capillary, mounted on the axis of the diffractometer and spun during measurements in order to improve powder randomization. A wavelength of λ = 0.39466(3) Å was selected with a double-crystal Si(111) monochromator, calibrated and refined using Si NIST powder (a = 5.43094 Å) from the position of the first ten Si reflections. Series of diffraction patterns were collected in the $0 \le 2\theta \le 22°$ interval at different temperatures. In particular: 28 patterns (30' each) at 650 °C; 8 patterns (30' each) at 700 °C; 7 patterns (30' each) at 730 °C; 9 patterns (30' each) at 750 °C; 10 patterns (15' each) at 850 °C and 4 patterns (15' each) at 900 °C. The same sample was quenched to room temperature three times: i) after 2 hours at 650 °C; ii) after the measurements at 750 °C; iii) after the measurements at 900 °C. After each quenching procedure a pattern was collected in the $0 \le 2\theta \le 118°$ interval. An XRPD pattern in the same 2θ range was also collected on a different portion of the same untreated natural sample. Rietveld refinements were performed using the GSAS software suite (Larson and Von Dreele 2004) and its graphical interface EXPGUI (Toby 2001).

Results. Figure 1 shows selected regions of the powder diffraction patterns acquired at high temperature. The natural starting material is a single columbite with a low degree of cation order. After a few minutes of annealing the development of a second phase is clearly evident: reflections split and a single-phase model no longer gives a satisfactory fit to the data. Two similar but distinct columbite phases characterised by different degrees of order are now present. In the last stages of annealing, split reflections merge into single peaks and the pattern is again that of one single columbite phase which is now almost completely ordered. Long-range ordering of Fe and Mn on the A site and of Nb and Ta on the B site of the columbite crystal structure is also evidenced by the development of superlattice reflections ($h \neq 3n$).

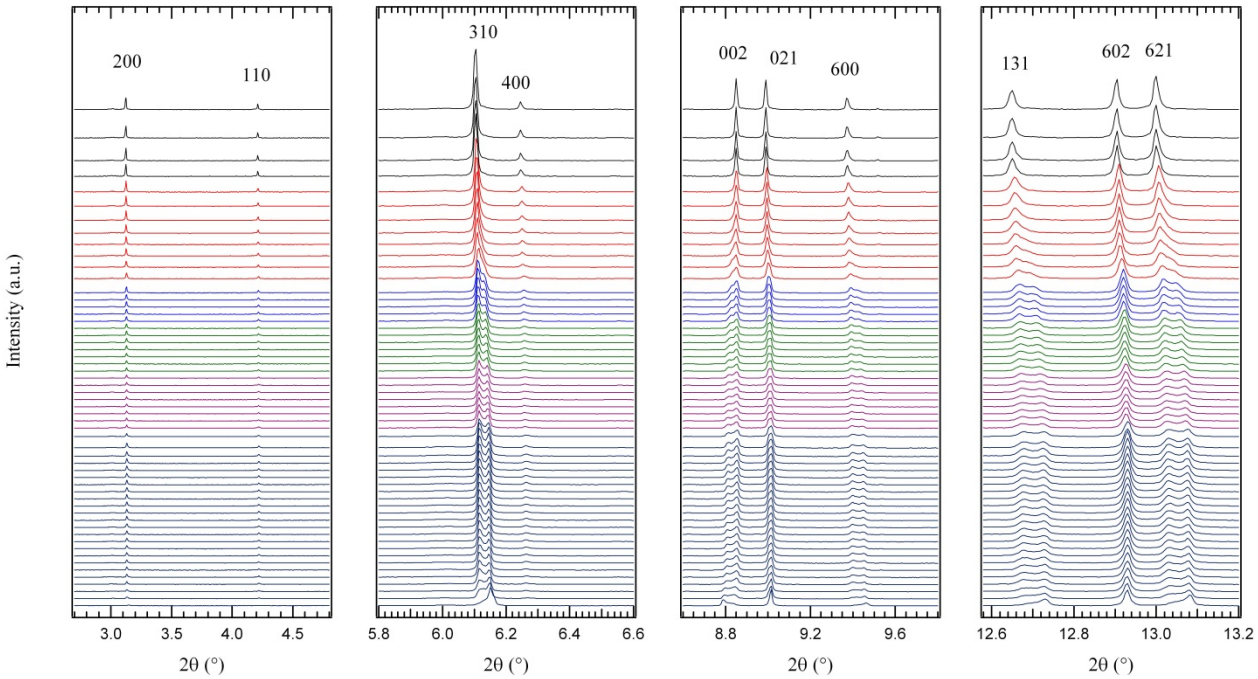

Fig. 1

Synchrotron datasets were analyzed in sequence using the Rietveld method. All the patterns but those from the untreated sample and from the last stages of annealing are well described by a model comprising the initial partially ordered (hereafter labelled P) columbite phase and a second largely ordered phase (labelled O). Both evolve with annealing time. This two-phase model was subsequently refined for all the runs, yielding the evolution of the phase fraction, unit cell parameters, and peak widths for the P and O phases. Variations of the degree of order of both phases, calculated from unit-cell parameters (Ercit et al. 1995; Tarantino et al. 2003), are reported in Figure 2. Neither the proportion of the partially ordered phase O, as given by the ratio of the refined scale factors, nor the dimensions of the nanodomains, from peak width, change during the annealing process.

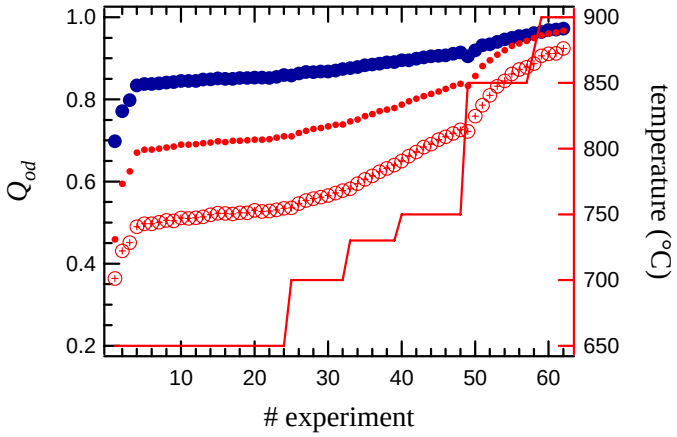

Fig. 2

Discussion. High-resolution synchrotron X-ray diffraction data collected at ID31, together with transmission electron microscopy data, have shown that ordering in columbite crystals involves two discrete phases with different degrees of order but the same composition. A highly unusual distribution of ordered rhombic-shaped domains within a disordered matrix becomes established on a nano scale and remains relatively stable over a prolonged period of annealing. Progressive ordering takes place within the ordered domains and the disordered matrix but the domains maintain more or less constant shape and distribution. We can speculate, therefore, that new families of microstructures might appear during ordering under metastable conditions of other oxide phases with strongly first order cation ordering transitions.

Data collected during experiment HS3337 at ID31 are part of a paper published with journal American Mineralogist: S.C. Tarantino, M. Zema, G. Capitani, M. Scavini, P. Ghigna, M. Brunelli, M.A. Carpenter, Rhombic-shaped nanodomains in columbite driven by contrasting cation order, *American Mineralogist*, **96**, 374-382, 2011.

Additional beamtime would be necessary in order to complete the characterization of this process by i) determining the kinetics of the cation ordering and concomitant domain forming processes individually in the two phases under isothermal conditions and ii) verifying that the same unmixing process occurs in other phases satisfying the requirement of strongly first order character for the cation ordering transition by studying the cation ordering process in tapiolite oxides, belonging to the same columbite family, but characterized by a crystal structure related to that of rutile.