

**Experiment title:**

study of disorder in Ni substituted to calcium orthovanadates through analysis of low temperature diffraction data

Experiment number:

MA-5217

Beamline:

ID22

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Report:

The goal of experiment was analyze disorder in $\text{Ca}_{10}\text{Ni}_{0.5}(\text{VO}_4)_7$ sample at low temperatures, and compare it with $\text{Ca}_{10.5}(\text{VO}_4)_7$ and also $\text{Ca}_{9.5}\text{Ni}(\text{VO}_4)_7$, where only a disorder due to structural vacancies is present.

Calcium orthovanadate ($\text{Ca}_3(\text{VO}_4)_2$), is known to crystallize in $R3c$ space group with structure similar to that of whitlockite mineral, $\text{Ca}_{18}(\text{Mg,Fe})_2(\text{PO}_4)_{12}(\text{PO}_3\text{OH})_2$. Unsubstituted $\text{Ca}_3(\text{VO}_4)_2$ crystals, which contain five cationic Ca sites (named M1–M5), can be modified by replacing a small fraction (typically up to ~10%) of Ca atoms by other ones, with valences from +1 to +4, without any change in the structure. In such a case, the corresponding structural modification consists of full or partial replacement of Ca atoms at one or more M sites by the substituting atom, leading to the formation of substitutionally disordered compounds; in such materials, an additional disorder may also occur due to the presence of structural vacancies.

Using the diffraction data from low temperatures, can confirm the hypothesis that the structure at low temperatures is the same (and with the same site-occupation scheme) as at room temperature, and then determine and model both the thermal expansion and to separate the static disorder from the thermal one on the basis of the Debye expression describing the atomic displacements.

The expected opportunities of evaluation of the disorder at specific cationic sites will open the door to use the described method for other materials of complex structure, including other whitlockite related materials. One publication exploiting a fraction of the obtained data has been submitted.

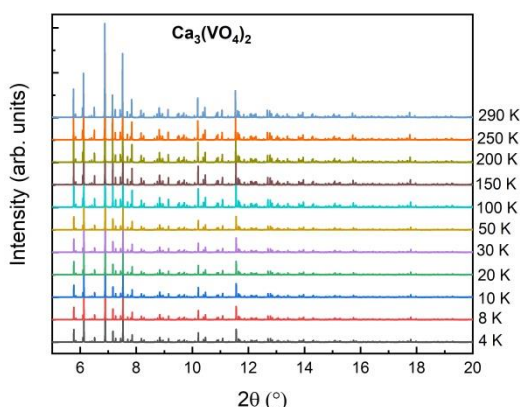


Figure 1. Variable-temperature diffractograms of $\text{Ca}_3(\text{VO}_4)_2$ in temperature range of 4(1) – 292(1) K