ESRF	**Experiment title:** Revealing of the crystal structure of NaBiO3*xH2O	**Experiment number**: HC-3346
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Scientific background. In recent years, a new type of semiconductor material, $NaBiO_3$ has attracted great attention of researchers due to high photocatalytic activity, low cost and environment friend features. It can compete with TiO2, which is the most extensively studied photocatalyst [1].

Theoretical analysis of electronic structure of Bi-based compounds and composites has shown, that these materials can be considered as a family of photocatalysts driven by visible-light [5]. $NaBiO_3$ is one of few compounds where Bi has a greatest oxidation state: 5+ [2]. Due to wide applications of the bismuth materials (e.g. in superconductors), understanding of Bi-centres electronic structure is very important. One of the best ways to get such information is performing X-ray absorption spectroscopy experiments. $NaBiO_3$ is very useful as reference sample, where five-fold oxidized Bi ion is in octahedral environment.

NaBiO3 is highly hygroscopic and can be find only in crystallohydrate form. There are two kinds of them. The first one is $NaBiO_3*2H_2O$, while the second is $NaBiO_3*xH_2O$ [1-3]. Heating of the $NaBiO_3*2H_2O$ results in a phase transformation with formation of the $NaBiO_3*xH_2O$ at ~180ºC. The pattern of powder diffraction of $NaBiO_3*xH_2O$ is identical to the ilmenite-type ($FeTiO_3$) like in water free niobium oxides α-$NaSbO_3$ [4], while the structure of the $NaBiO_3*2H_2O$ is still unknown. The crystallographic position of water molecule is unknown for the both phases. The crystal structure refinement using neutron powder diffraction data led to Rwp = 11.6 and Gp = 9.18% for $NaBiO_3$. Such big values may be related to the neglecting of water molecule inside structure of $NaBiO_3*xH_2O$ [5].

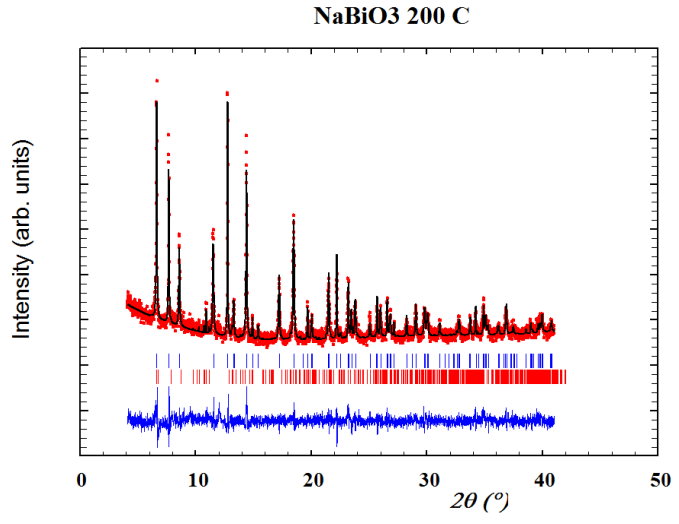

Fig. 1. Diffraction pattern of Sigma Aldrich sample of $NaBiO_3$ obtained at 200 C. Red points are experimental data. Black curve is the result of analysis.

Samples and experimental techniques. There were three series of samples which have been measured: $NaBiO_3$, obtained from water solutions by oxidation and consequent annealing at temperatures up to 160ºC (3 samples), $NaBiO_3$ obtained by oxidation process without any hydrothermal synthesis (3 samples), commercially available samples from Sigma Aldrich and Vecton companies (2 samples). All the samples have been measured during the heating up to 400 ºC. Besides that, $AgBiO_3$ compound has been studied, since it should be structurally identical to $NaBiO_3$.

Results. We have obtained diffraction patterns at room temperature for all the samples, which have been studied. Unfortutantly, diffraction patterns only for commercial samples have shown the features of $NaBiO_3$, while in other samples some different compounds have been detected (e.g. Bi_2O_3). Probably, the initial compounds used in the synthesis were not pure enough.

For the Vecton sample it has been shown, that the diffraction pattern is similar to the ones, which were obtained e.g. in neutron experiement, but the width of Bragg peaks is too high. It means, that the crystallites are too small, and the sample is not appropriate for the good structural analysis. Because of that, the main attention has been paid to the Sigma Aldrich sample.

We have performed the measurements in the temperature range from -40 to 400 C. An example of diffraction pattern is presented in Fig. 1. We have observed co-existance of $NaBiO_3*2H_2O$ and $NaBiO_3*xH_2O$ phases at temperatures below 180 C, only $NaBiO_3*xH_2O$ phase between 180 C and 385 C and some other structure above 385 C. Profile analysis has shown, that the $NaBiO_3*xH_2O$ phase is indeed of ilmenite-type. The other structures have been not yet resolved. We suppose, that the important role in understanding of the structure of $NaBiO_3*2H_2O$ plays determination of the water molecules positions. We have applied for the neutron beamlines in order to perform simultaneous analysis of diffraction patterns and revel finally the structure of the sodium metabismuthate.

References

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