ESRF	**Experiment title:** **Structure determination of the new superconducting phase $Sr_{1-x}K_xBiO3$ as a function of K content and temperature by powder synchrotron diffraction**	**Experiment number:** CH-332
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Report:

Ye have recently reported the synthesis and structural study of a new bismuth oxide based Superconducting compound in the Sr-K-Bi-O system [I]. The new $SrBiO_3$ compound was Synthesized at high oxygen pressure, and doping by potassium was realized by high pressure high temperature synthesis in a belt type apparatus. While $SrBiO_3$ is insulating, potassium loping leads to the appearance of a metallic state and superconductivity at ≈ 12K for x=0.45-0.6 in $Sr_{1-x}K_xBiO_3$. As for the baryum analogues, the structures of these compounds are characterized by a weak distortion from that of cubic perovskite, with unit cell $\approx a_p\sqrt{2}$ x $a_p\sqrt{2}$ x $2a_p$ (where a_p is the cubic perovskite cell parameter). A preliminary neutron powder diffraction study performed at the ILL at room temperature on a potassium free, and a Superconducting sample, indicated a change in symmetry, the latter being tetragonal I4/mcm), while the former could be either orthorhombic (Pnma) or monoclinic (P2l/n). The experimental resolution did not allow us to conclude safely. It is generally believed that the conducting behaviour of such systems is closely related to charge localisation effects : the presence of two inequivalent Bi sites leads to an ordered disproportionation of the Bi cations into Bi^{3+} and Bi^{5+} ones localized on different crystallographic sites, and to insulating properties. If these cations are randomly distributed over a single site, the compound becomes metallic and possibly superconducting at low temperature. In the case of $SrBiO_3$, the Pnma or P21/n space groups would correspond to either one or two crystallographic sites. The unambiguous determination of the symmetry of this compound was thus of the highest importance for the understanding of the physical properties in this system. It was also very interesting to study the evolution of symmetry and structure as function of potassium content and temperature, in order to have a better knowledge of' the complex phase diagram of the system, in relation with its physical properties.

The synchrotron powder diffraction experiment was carried out by using the multi analyzer stage at 30 and 40 KeV to limit absorption effects, on rotating capillary samples mounted inside the new BM16 cryostat. Four samples with different potassium contents were measured, and for two of them data were collected between room temperature and 4K. The refinements have been carried out using the GSAS program, including the Finger, Cox and Jephcoat correction for low angle peak shape asymmetry, which proved to work quite well even for reflections with Bragg angles as low as ≈ 2°.

The analysis of the SrBi03 sample data down to 4K indicate without doubt that the symmetry is monoclinic P2l/n, with a monoclinic angle β≈90.04°, almost constant in the whole temperature range. This result, corresponding to two independant Bi sites, is in agreementt with the insulating nature of this compound. Despite the presence of two parasitic phases, the quality of refinement was extremely good, and allowed us to determine that part (-20%) of the: Bi sites are occupied by Sr cations. This observation has already allowed us to prepare single phase material with $Sr_{1.2}Bi_{0.8}O_3$ stoichiometry, while obtaining pure samples starting from stoichiometric SrBi03 mixtures was impossible.

The tetragonal I4/mcm structure was confirmed down to 4K in the superconductig region of the phase diagram, and no phase with a different symmetry could be detected in the K-doping range investigated.

[1] Discovery of a second family of bismuth-oxide-based superconductors,
S M. Kazakov, C. Chaillout, P. Bordet, J.J. Capponi, M. Nunez-Regueiro, A. Rysak, J.L. Tnolence, P.G. Radaelli, S.N. Putilin and E.V. Antipov.
Nature, 390, 145, 1997