03 Synthesis and characterisation of YBCO (Superconductor)

Aim: Prepare the superconductor $YBa_2Cu_3O_{7-\delta}$ with different oxygen content.
Characterization: Powder diffraction and resistivity measurements.
Technique: Solid state reaction of oxide materials
Material properties: Superconductor.
Chemicals: Y_2O_3
BaO_2
CuO

Instructions:
1) The powders are weighed stoichiometrically to obtain the correct ratio between Y:Ba:Cu, which is 1:2:3, the resulting oxygen content nominally exceeds 7.
2)a) The powders are ground and packed loosely into an Al_2O_3 crucible.(eller blot i beholder)
Hertil kan forberedes på gymnasiet

Rest foregår på Universitetet
2)b) The crucible is placed in a furnace and heated to 940°C, and held there for 12 hours. The product is furnace cooled.
3) The powder is reground and pressed into pellets. Use ~2 cm dies for pressing. The pressed pellet is furnace heated to 940°C and slowly cooled to room temperatures. Samples are removed at temperature intervals to introduce oxygen deficiencies (e.g. in steps of 100°C from 600-500°C down to room temperature).
4) Powder diffraction investigation to establish unit celle size
5) Phase transition temperature is measured utilizing the Meissner effect.
6) Oxygen content is determined by volumetric method.

Relevant literature:
Superconductivity at 93 K in a new Mixed phase Y-Ba-Co-O compound system at ambient pressure
M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang
Phys. Rev. Lett. 58, 908-910 (**1987**)
Oxygen determination from cell dimensions in YBCO superconductors
Benzi P, Bottizzo E, Rizzi N
J. Crystal Growth 269, 625-629 (**2004**)
Superconductivity at 39 K in magnesium diboride
Jun Nagamatsu, Norimasa Nakagawa, Takahiro Muranaka, Yuji Zenitani and Jun Akimitsu
Nature 410, 63-64 (**2001**)
Bonding Nature in MgB_2
E. Nishibori, M. Takata, M. Sakata, H. Tanaka, T. Muranaka and J. Akimitsu
J. Phys. Soc. Jpn. 70, 2252-2254 (**2001**)

Determination of oxygen content using iodiometric titration

Iodiometric titration can be used to determine the Cu^{2+} and Cu^{3+} concentration. The Cu^{3+} concentration is proportional to the amount of oxygen in the sample.

$$Y^{3+}Ba_2^{2+}Cu_{3-x}^{2+}Cu_x^{3+}O_y^{2-}$$

In principle these experiments should be performed under inert atmosphere to avoid oxidation by air, but this unfortunately we cannot do.
We need two experiments to determine x. Experiment A) YBCO is boiled in HCl to transform Cu^{3+} to Cu^{2+} the titration gives the total amount of Cu in the sample. B) the sample is dissolved in HCl and titrated directly giving the concentration of Cu^{2+} and Cu^{3+}, now since Cu^{3+} produces more I_2 is possible to extract the Cu^{3+} concentration of the sample and thus the oxygen content.
Three experiments of each titration are done to allow calculation of mean and average value – this gives a total of 6 titrations.

A) Total concentration of Cu^{2+}.
   About 30 mg of YBCO is dissolved in approximately 5ml 1M HCl and boiled for 10 min. Cu^{3+} is hereby reduced to Cu^{2+}.
   10 ml 0.7 N KI is added.
   Titration using thiosulfat see concentration in the lab – should be around 0.1 M (so you need approximately 1 mL).
   Close to the equivalence point starch is added.

   The processes taking place are

   $$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
   $$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

B) The YBCO is dissolved in 7 ml of 0.7M HCl.
   Add 7 ml of 1M KI
   Start titration using thiosulfate

   The processes taking place are

   $$Cu^{3+} + 3I^- \rightarrow CuI + I_2$$
   $$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
   $$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

The titration of Cu^{3+} corresponds to the double concentration compared to Cu^{2+} Subtracting the used volumes of $S_2O_3^{2-}$ in A and B gives the concentration of Cu^{3+}. Using the oxidation state of the individual elements in YBCO and neutrality – the total oxygen concentration can be found.