	Experiment title: Study of the high-temperature phase $In_4Sn_3O_{12}$	**Experiment number**: ME-1053
Beamline: ID 15B	**Date of experiment**: from: 04/05/2005 to: 10/05/2005	**Date of report**: 23/10/2005
Shifts: 18	**Local contact(s)**: Gabriela GONZALEZ AVILES	*Received at ESRF:*

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Report:

Indium oxide, tin oxide and tin-doped indium oxide are the most commercially used transparent conducting oxides due to their electrical and optical properties. Since the 1980's, several authors have reported the presence of an intermediate In-Sn-O phase at temperatures higher than 1200 ^oC [1-8]. Some literature reports index that phase as cubic [1,3], and others as rhombohedral with a wide range of lattice parameters and stoichiometries [2,4,5,7]. There is also discrepancy on its formation temperature, ranging from 1200 ^oC to 1380 ^oC.

In order to study the structural nature and the formation temperature of this phase, we carried out *in situ* high-temperature, x-ray diffraction experiments at ID15B. The starting materials were pellets of nano-SnO_2 and nano-In_2O_3 powders pressed into pellets with a diameter of 5 mm and 1 mm thick. A furnace surrounding the pellet heated the sample while a MAR image plate collected *in situ* diffraction images to determine when the phase transformation took place. The x-ray energy was about 90 keV, and the beam size was 0.2 x 0.2 mm. Diffraction rings were collected up to a d-spacing of approximately 1.1 Å. Three isothermal annealing experiments were performed at 1335 ^oC, 1375 ^oC and 1400 ^oC. The 2D diffraction images were analyzed and integrated. The integrated x-ray diffraction patterns were then fitted using the Rietveld method to obtain sample compositions and structural information for each of the existing phases.

The In-SnO intermediate phase was indexed as rhombohedral $In_4Sn_3O_{12}$ with lattice parameters a= 9.5601(1) Å and c= 9.0391(1) Å at 1400 ^oC. This phase was observed at 1375 ^oC and 1400 ^oC but not at 1335 ^oC, even after 45 hours of annealing. Future annealing experiments between 1335 ^oC and 1375 ^oC will help us determine the lowest formation temperature of this phase. $In_4Sn_3O_{12}$ grains formed within 3 minutes of annealing at 1400 ^oC and 13 minutes at 1375 ^oC. Figure

1 represents a region of the diffraction pattern showing the evolution of phases during a heating experiment from 1105 °C up to 1400 °C. Figure 2 shows the composition of the sample as a function of annealing time at 1400 °C. The slow decrease in $In_4Sn_3O_{12}$ and increase of bixbyite phase after 12 hours is the result of preferential evaporation of tin, as confirmed by x-ray fluorescence analysis of the sample.

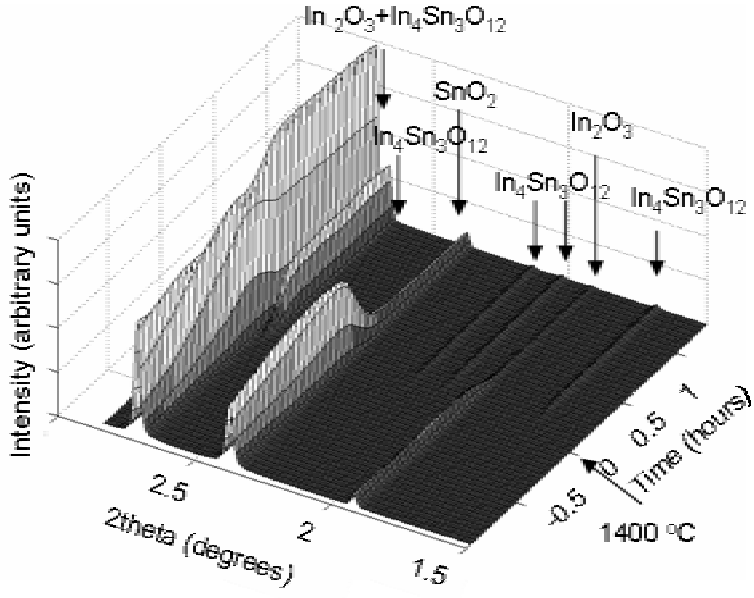

Figure 1. Evolution of phases during annealing from 1105 °C to 1400 °C

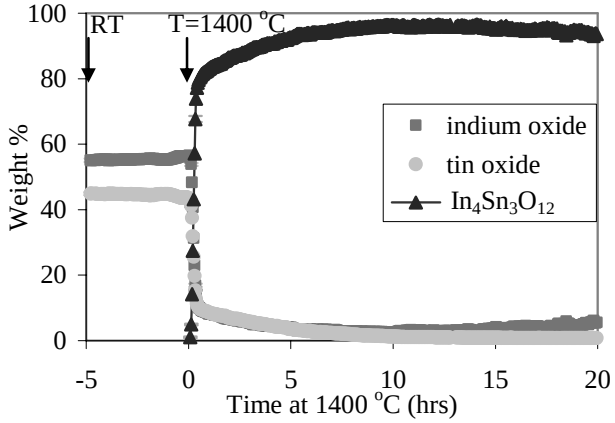

Figure 2. Sample composition from room temperature up to 1400 °C

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