ESRF	**Experiment title:** **Cation site disorder studies in the $[Pb_{(2-x)}Sr_2(Y_{1-x}Ca_x)Cu(3-y)O_z$ cuprate superconductors using X-ray diffraction**	**Experiment number:** CH 343
Beamline: BM 16	**Date of experiment:** **from:** 08/07/97 to: 12/07/97	**Date of report:** 13/03/98
Shifts: 12	**Local contact(s):** GAVIN VAUGHAN	*Received at ESRF':*

Names and affiliations of applicants (* indicates experimentalists):

*Brian J. Mitchell University of St.Andrews, North Haugh, StAndrews. FIFE.
Dr P.R. Slater University of St.Andrews, North Haugh, St.Andrews. FIFE
Dr J.T.S. Irvine University of St.Andrews, North Haugh, St.Andrews. FIFE

Report.

Diffraction experiments were carried out on two samples of nominal composition $Pb_3Sr_4Y_2Cu_5O_y$ (sample 1) and $Pb_3Sr_4Y_1Ca_1Cu_5O_y$ (sample 2) at ambient temperature and ambient pressure. Samples were contained in either 0.5 mm or 0.2 mm borosilicate capillaries depending on the energy selected. Five energy settings were chosen for analysis: -25 keV (-0.5 A), -16 keV Sr-K edge (~.77 A), -16 keV Y-K edge (-0.73 A) -13 keV Pb-L_{III} (-0.95 A) and ~9 keV Cu-K (-1.38 A). The resonance edges were selected by scanning the particular edge and examining the fluorescence signal. After setting the edge, a Si standard was used to determine the exact wavelength value.

After a low pO_2 synthesis both samples were found to posses the orthorhombic 3212 type of structure discovered by Cava[1] and co-workers, where a ~5.38 Å, b ~5.42 Å and c ~15.75Å. There was no evidence to indicate a monoclinic structure[2] through peak broadening was apparent. Since instrumental broadening contributions have effectively been eliminated, only anisotropic peak broadening was detected. This is common in such layered materials and may be attributable to stacking faults.

Sample 1 was found to have an onset of superconductivity at 67K from magnetic measurements. Rietveld analysis using the GSAS[3] routine indicated that the sample composition of the main product phase (>96%) is much closer to the ideal $(Pb_2Cu_1)Sr_2Y_1Cu_2O_8$ rather than its nominal composition, The sample contains stacking faults as confirmed by HREM analysis, while the oxygen content was determined from neutron diffraction on DlA at ILL to be at the ideal value of 8.0.

The results of the Rietveld refinement, table 1, show the sample to have a slight deficiency of Pb on its ideal site with Sr compensating for this deficiency. The calculated amount of Sr is small, close to the limits of quantitative determination. There was no indication of cation deficiency/disorder on the SrO and CuO_2 layers. There was, however, a clear deficiency on the Cu layer (sandwiched between) the PbO layers. The results indicate that Y is present on this site. Again the amount is small and should really only be taken as clear evidence of cross-substitution rather than as a quantitative value.

Table 1. Cation composition determined by Rietveld refinement

a (Å)	b (Å)	c (Å)	R_{wp} (%)	R_p (%)	Chi^2
5.3926(2)	5.4276(2)	15.7459(4)	12.86	10.26	5.24
Atom	x	y	z	Frac	U_i/U_e*100 (Å²)
Pb(1)	0.5	0	0.3875(4)	0.943(4)	0.72(2)
Sr(2)	0.5	0	0.3875(4)	0.040(8)	0.72(2)
Y(1)	0	0	0	1.00	0.83(5)
Sr(1)	0	0	0.2204(2)	1.00	0.78(7)
Cu(1)	0	0	0.5	0.877(7)	0.36(9)
Y(2)	0	0	0.5	0.036(7)	0.36(9)
Cu(2)	0.5	0	0.1031(5)	1.00	0.91(7)
O(1)	0.5	0	0.2541(4)	1.00	1.5
O(2)	0.022(7)	0.092(3)	0.388(10)	0.25x4	1.5
O(3)	0.25	0.25	0.0912(7)	1.00	1.5

Sample 2, summarized in table 2, shows many of the same problems as sample 1 i.e. stacking faults, composition not same as nominal, and cation disorder. The phase purity was slightly less than in the Ca free sample but was found to have an onset of superconductivity at 76K from magnetic measurements. Since there was no neutron diffraction measurement on this sample, the Oxygen content was assumed to be 8.0, although an Oxygen deficiency should be considered. There was no evidence for significant substitution on the Pb site. The sample is Ca deficient and the calculations did show only a tiny amount of Pb on the Y/Ca site.

Table 2. Cation composition determined by Rietveld refinement

a (Å)	b (Å)	c (Å)	R_{wp} (%)	R_p (%)	Chi^2
5.3827(2)	5.4172(2)	15.7748(4)	12.35	11.62	8.76
Atom	x	y	z	Frac	U_i/U_e*100 (Å²)
Pb	0.5	0	0.3873(2)	1.00	0.64(3)
Sr	0	0	0.2205(5)	1.00	0.62(5)
Y(1)	0	0	0	0.762(8)	1.07(10)
Ca	0	0	0	0.248(8)	1.07(10)
Cu(1)	0	0	0.5	0.799(6)	0.36(6)
Y(2)	0	0	0.5	0.036(6)	0.36(6)
Cu(2)	0.5	0	0.1072(3)	1.00	0.53(3)
O(1)	0.5	0	0.2638(14)	1.00	1.5
O(2)	0.039(4)	0.084(5)	0.3856(12)	0.25x4	1.5
O(3)	0.25	0.25	0.0960(8)	1.00	1.5

There is evidence that cations are displaced from their ideal sites on the Pb-0, Sr-0 and Y/Ca layers from anisotropic temperature factor refinements and difference Fourier maps from these samples and neutron diffraction data.