ESRF

Experiment title:

Structural and oxidation state studies in the $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_x$ cuprate superconductors using resonance X-ray diffraction

Experiment number: CH 254

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Report.

Experiments were carried out on samples of compositions $(Pb_{0.5}Cu_{0.5})Sr_2Y_1Cu_2O_{7.0}$, $(Pb_{0.5}Cu_{0.5})Sr_2Y_1Cu_2O_{7.1}$, $(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7.0}$, $(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7.1}$ at ambient temperature and ambient pressure. Samples were contained in 0.5 mm borosilicate capillaries. Four energy settings were chosen for analysis: ~25 keV (~0.5 Å), ~16 keV Sr-K edge (~.77 Å), ~13 keV Pb-L_{III} (~0.95 Å) and ~9 keV Cu-K (~1.38 Å). 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.

The 1212 phases may be fully indexed using the P 4/mmm space group (No.123), the Pb/Cu atoms are displaced from the ideal (0,0,0) site to an (x,0,0) site, where x<0.1. The rocksalt Oxygen O(3) is also displaced from the ideal (½,½,0) position to a fourfould (x,½,0) site, where x is -0.35.

Samples $(Pb_{0.5}Cu_{0.5})Sr_2Y_1Cu_2O_{7.0 \text{ and } 7.1}$

Both samples were of single phase and the only difference is a small excess of Oxygen in the (0,½,0) site which cannot be detected using x-rays. Selected results are shown below,

	$(Pb_{0.5}Cu_{0.5})Sr_2Y_1Cu_2O_{7.0}$				$(Pb_{0.5}Cu_{0.5})Sr_2Y_1Cu_2O_{7.1}$			
a (Å)	3.814711(20)				3.819381(30)			
c (Å)	11.81244(7)				11.80678(11)			
	X	**Y**	**Z**	**ITF*100**	**X**	**Y**	**Z**	**ITF*100**
Pb/Cu	.0511(9)	0	0	.82(5)	.0559(8)	0	0	.55(6)
O(3)	.312(5)	½	0	2.71(10)	.316(8)	½	0	5.03(38)
O(2)	0	0	.1644(6)	1.36(20)	0	0	.1638(8)	2.17(28)

The excess Oxygen causes the unit cell dimensions to increase slightly and also intoduces more disorder into the structure. This affects the ITF's of the other Oxygens in and around the rocksalt layer and causes a slight change in the position of the Pb/Cu atom. There is no evidence for cation disorder in these samples, since no statistically meaningful results are obtained from the resonance edge data sets.

Samples $(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7.0 \text{ and } 7.1}$

Neither sample was single phase, a $(Ca,Sr)CuO_y$ impurity was present, and the only difference is a small excess of Oxygen in the (0,½,0) site which cannot be detected using x-rays. Selected results are shown below.

	$(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7.0}$				$(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7.1}$			
a (Å)	3.816231(26)				3.821506(6)			
c (Å)	11.84791(10)				11.84796(4)			
	X	**Y**	**Z**	**ITF*100**	**X**	**Y**	**Z**	**ITF*100**
Pb/Cu	.0502(15)	0	0	1.42(7)	.0552(15)	0	0	4.06(11)
O(3)	.368(10)	½	0	2.97(32)	.396(11)	½	0	6.52(41)
O(2)	0	0	.1721(9)	1.70(32)	0	0	.16764(8)	3.40(32)

Replacing Y^{3+} with Ca^{2+} leads to an increase in the c axis length and there is also an expansion of the **a** cell parameter upon excess Oxygen introduction. These samples, unsurprisingly, show a greater degree of disorder and the resonate diffraction results confirm this. On the Pb/Cu rocksalt layer, there is approximately 7% Pb defeciency. Mostly Ca and possibly some Sr substitutes onto the Pb/Cu layer in place of the Pb. However, the site is not fully occupied. On the Y/Ca site there is ~6% Pb substitution and instead of the ideal 0.6 Y/0.4 Ca occupancy, a 0.06 Pb/0.65 Y/0.29 Ca occupancy is found to give the best fit to the experimental data.