Bismuth valences in a $Tl_{0.7}Bi_{0.3}Sr_{1.6}Ba_{0.4}CaCu_2O_y$ superconductor from X-ray photoemission spectroscopy

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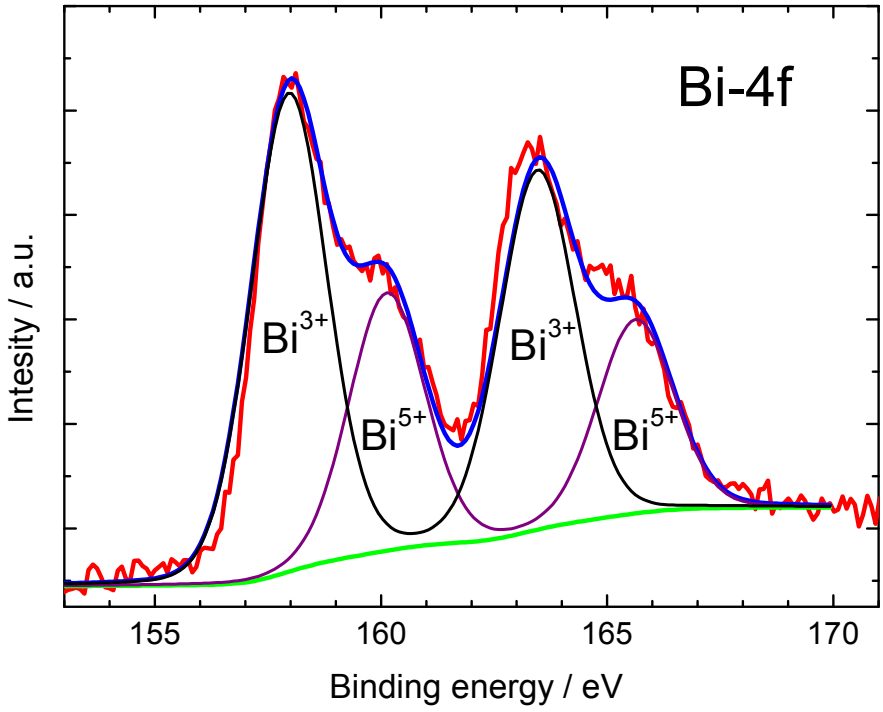
The X-ray electron photoemission spectra of a $Tl_{0.7}Bi_{0.3}Sr_{1.6}Ba_{0.4}CaCu_2O_y$ superconductor with Al K_α and Mg K_α radiations at room temperature were measured. The ratio of trivalent Bi^{3+} to pentavalent Bi^{5+} bismuth ions was calculated from the quantitative analysis of the spin-orbit split spectrum of the Bi 4*f* photoelectrons. We found out that the spin-orbit split spectrum of the Bi 4*f* electrons was enough intensive and resolved for the analysis. The *4f* Bi spectrum was compared to the same spectra of Bi-2223 superconductor and to the $Tl_{0.6}Pb_{0.4}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$ superconductor without bismuth [1]. In Bi2223 only one type of Bi^{+3} ions is present. The *4f* Bi spectrum in the $Tl_{0.7}Bi_{0.3}Sr_{1.6}Ba_{0.4}CaCu_2O_y$ superconductor consists two contributions due to the different valences. We have decomposed the spectrum by the XPS Peak program version 4.1 [2] to get the ratio of Bi^{3+} to Bi^{5+}. The component from Bi^{5+} lines is in higher binding energy than from Bi^{3+} (see the figure below).



The conclusion is that Bi is present in trivalent and in pentavalent form. The ratio of Bi^{3+} to Bi^{5+} was determined as the ratio of the respective peak areas of the fitted spectrum and is equal to 1.87 ± 0.02.

References:

[1] R.Zalecki, A.Kołodziejczyk, W.Koenig, G.Gritzner, Acta Phys. Polon., A 98 (2000) 513
[2] R.W.M. Kwok, Department of Chemistry, The Chinese University of Hong Kong.