Pb-valence studied by XPS and chemical analysis

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The Pb $4f_{7/2}$ binding energy is compared with Pb valence determined by $K_2Cr_2O_7$ titration for $(PbCu)(SrLa)_2CuO_y$ and $(PbCu)Sr_2(CaY)Cu_2O_y$ superconducting oxides. A linear relationship with a negative slope is found between them, which indicates that the quantitative analysis of the Pb valence is possible by x-ray photoelectron spectroscopy (XPS) for these materials. The Pb $4f_{7/2}$ binding energy is also compared with those for some simple lead oxides and discussed in terms of chemical states of Pb atoms.

1. Introduction

To determine the valence of ions is very important for understanding the fundamental mechanisms creating properties of many materials such as semiconductors, ceramics, catalysts, and unti-corrosion products. For the *high-T_c* superconducting oxides , it is a key to design materials with higher superconducting transition temperature (T_c) since the number of carriers (movable electrons or holes) directly controls the T_c and carrier concentration is often controled by substituting ions with different valence. There are two common ways to estimate the valence of ions, namely chemical analysis such as titration method and spectroscopy such as x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). The former method is known to be more quantitative but destructive while the latter method is non-destructive but, in many cases, only qualitative.

We have studied Pb valence by XPS and $K_2Cr_2O_7$ titration for Pb based copper oxide superconductors, $(PbCu)(SrLa)_2CuO_y$ [1] and $(PbCu)Sr_2(CaY)Cu_2O_y$ [2] in which the Pb valence changes with oxygen content (y) and

Table 1 Pb valence determined by $K_2Cr_2O_7$ titration and binding energy of Pb$4f_{7/2}$ and O 1s for $(PbCu)(SrLa)_2CuO_y$, $(PbCu)Sr_2(CaY)Cu_2O_y$, and some lead oxides.

sample	Pb valence by titration*	binding energy (eV) Pb $4f_{7/2}$	O 1s	binding energy correction**	Ref.
$Pb_{0.5}Cu_{0.5}SrLaCuO_{5.20}$	+3.92	137.20	528.54	A	this work
$Pb_{0.5}Cu_{0.5}SrLaCuO_{5.03}$	+3.63	137.34	528.59	A	this work
$Pb_{0.5}Cu_{0.5}Sr_{1.2}La_{0.8}CuO_{5.01}$	+3.22	137.58	528.66	A	this work
$Pb_{0.7}Cu_{0.3}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7.20}$	+3.94	137.22	528.64	A	this work
$Pb_{0.7}Cu_{0.3}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7.05}$	+3.84	137.27	528.66	A	this work
$Pb_{0.7}Cu_{0.3}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{6.97}$	+3.61	137.43	528.78	A	this work
PbO_2	+4	137.16	528.91	B	this work
PbO (sputtered PbO_2)	+2	137.52	528.76	A	this work
PbO_2	+4	137.2	528.6	C	[5]
PbO (rhombic)	+2	137.6	529.4	C	[5]
Pb_3O_4	+4	137.6	529.5	C	[5]
	+2	138.6	529.5	C	[5]

* formal valences are assumed for PbO, Pb_3O_4 and PbO_2

** A: Au 4f = 83.96 eV, B: C 1s = 284.9 eV (average value for the studied samples), C: the values in Ref.[5] were corrected as Au 4f = 84.0 eV

atomic ratios. These materials are suitable to compare valence of ions between two methods, because it was found that the electronic properties of the materials are well explained by the Pb valence determined by $K_2Cr_2O_7$ titration [1,3]. The purpose of the present paper is to clarify whether the proper Pb valence for these materials can be estimated by XPS or not.

2. Experimental

$(PbCu)(SrLa)_2CuO_y$ and $(PbCu)Sr_2(CaY)Cu_2O_y$ belong to a homologous oxide series which consists of a stack of a single (PbCu)O blocking layer and a perovskite - type $(SrLaCaY)_{n+1}Cu_nO_y$ structure including Cu-O_2 planes. These oxides listed in Table 1 were prepared, in pellet form, by solid-state reaction method in air. Oxygen content of the samples was changed by hot isostatic pressing (HIP) and annealing followed by quenching into liquid N_2. The oxygen content was determined by iodometric titration. The Pb valence was determined by $K_2Cr_2O_7$ titration [3] and thus obtained results are shown in Table 1. The samples are superconductors with T_cs of 20 - 60 K except for $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7.20}$. The details of sample preparation and other properties are reported in the previous papers [1,2].

XPS measurements were carried out with an SSX spectrometer (Surface Science Instruments). The binding energy scale of the spectrometer was corrected as Au $4f_{7/2}$ = 83.96 eV. Measured surfaces were obtained by scraping pellets under ultra high vacuum condition (< 10^{-8} Pa) and cleanness of the surfaces was confirmed by a weak intensity of higher-binding-energy lines in O 1s spectra and of C 1s lines. Spectra for PbO_2 and PbO mounted on indium sheet were also recorded under the same experimental conditions. PbO was prepared by reduching PbO_2 powder surface with Ar-ion sputtering [4].

3. Results and discussion

Figure 1 shows Pb 4f spectra for $(PbCu)(SrLa)_2CuO_y$:(a) and$(PbCu)Sr_2(CaY)Cu_2O_y$:(b) with different oxygen contents and atomic ratios. The difference in binding energy of Pb 4f line is about 0.4 eV (a) and 0.2 eV (b) among three samples of each oxide series. This binding-energy difference reflects mainly the valence states of Pb since the binding-energy difference were less than 0.1 eV for the La 3d and Y 3d lines. The binding energy of Pb $4f_{7/2}$, and O 1s are listed in the light-side column of Table 1 for $(PbCu)(SrLa)_2CuO_y$ and $(PbCu)Sr_2(CaY)Cu_2O_y$ with those for the lead oxides.

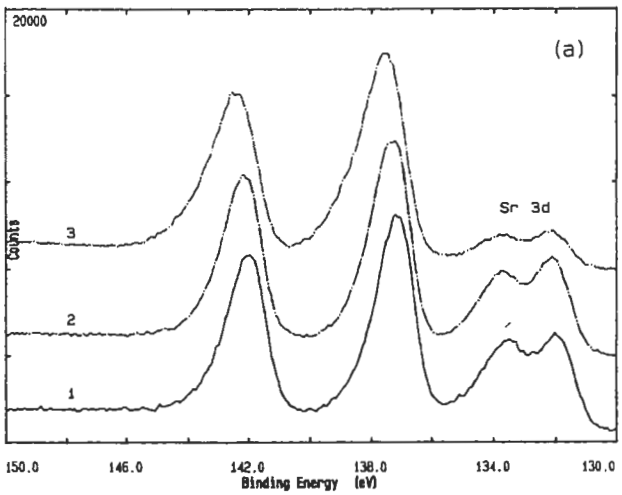

Fig.1(a) Pb 4f spectra for $Pb_{0.5}Cu_{0.5}Sr_{1-x}La_xCuO_y$.
1: HIPed, Pb = + 3.92 (x=1, y = 5.20)
2: as-sintered, Pb = + 3.63 (x=1, y = 5.03)
3: quenched, Pb = + 3.22 (x=0.8, y = 5.01)

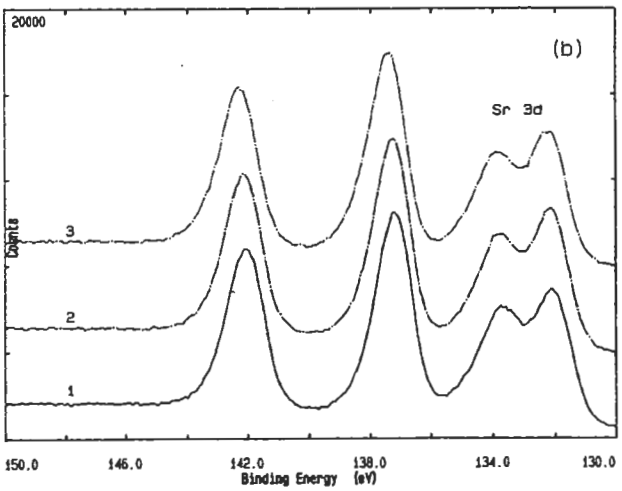

Fig.1(b) Pb 4f spectra for $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_y$.
1: HIPed, Pb = + 3.94 (y = 7.20)
2: as-sintered, Pb = + 3.84 (y = 7.05)
3: quenched, Pb = + 3.61 (y = 6.97)

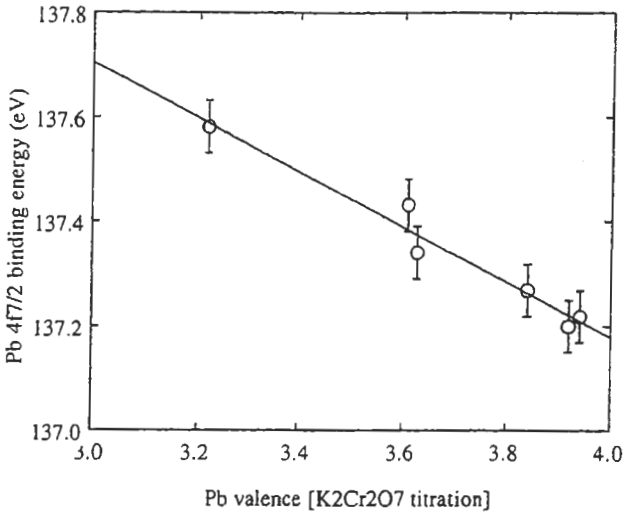

Fig.2 Relationship between Pb $4f_{7/2}$ binding energy and Pb valence estimated by $K_2Cr_2O_7$ titration for $(PbCu)(SrLa)_2CuO_y$ and $(PbCu)Sr_2(CaY)Cu_2O_y$.

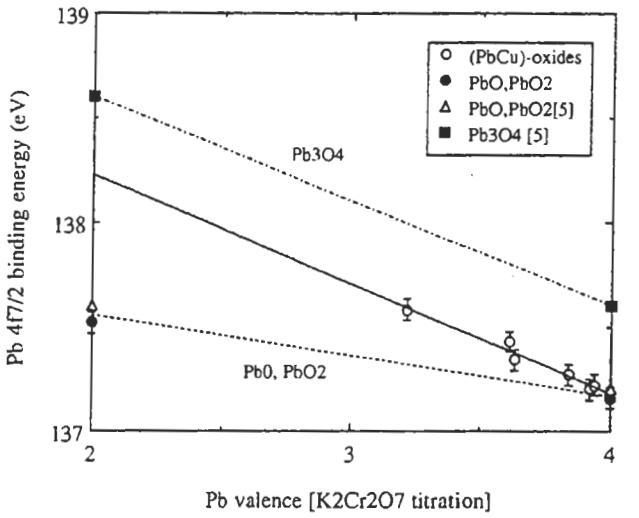

Fig.3 Relationship between Pb $4f_{7/2}$ binding energy and Pb valence estimated by $K_2Cr_2O_7$ titration for PbO, Pb_3O_4, and PbO_2 with the results in Fig.2.

The relationship between the Pb $4f_{7/2}$ binding energy (as Au $4f_{7/2}$ = 83.96 eV) and the Pb valence determined by $K_2Cr_2O_7$ titration is shown in Fig.2. The Pb $4f_{7/2}$ binding energy linearly decreases with the increase of the Pb valence. Kim et al [5] reported that the Pb 4f binding energy for Pb^{4+} is lower than that for Pb^{2+} from the XPS study for PbO, Pb_3O_4, and PbO_2. Therefore, the chemical shift of Pb $4f_{7/2}$ for the studied materials is in good agreement with the change of the Pb valence determined by the titration. The linear relationship in Fig.2 can be used as a calibration curve for estimating the Pb valence in the Pb-based copper oxides with the single (PbCu)O blocking layer by XPS.

Figure 3 shows the relationship between the binding energy of Pb $4f_{7/2}$ and the formal valence of Pb ions in PbO(Pb: 2+), Pb_3O_4(Pb: 2+, 4+), and PbO_2(Pb: 4+) with the results for $(PbCu)(SrLa)_2CuO_y$ and $(PbCu)Sr_2(CaY)Cu_2O_y$. The Pb $4f_{7/2}$ binding energy for PbO_2 is close to those for the studied materials with Pb valence of ~ +4. However, the slope in the linear line for the Pb-based copper oxides (about - 0.5 eV) is markedly larger than that of a linear line between PbO and PbO_2 (about - 0.2 eV). As a result, the binding energy for $Pb_{0.5}Cu_{0.5}Sr_{1.2}La_{0.8}CuO_{5.01}$ exceeds that for PbO. However, The Pb valence lower than 2+ is unacceptable for $Pb_{0.5}Cu_{0.5}Sr_{1.2}La_{0.8}CuO_{5.01}$ when the charge neutral principal is taken into consideration. These results indicate that we can not estimate the Pb valence in the studied materials quantitatively from the Pb $4f_{7/2}$ binding energy if PbO and PbO_2 are used as standard materials of Pb^{2+} and Pb^{4+}, respectively. We reported the similar results for $(Pb_2Cu)Sr_2YCu_2O_{8+d}$ which has a (PbO-Cu-PbO) blocking layer [6]. The difference in local crystal and electronic structures around Pb atoms between studied copper oxides and PbO should be considered. Pb atoms are in a six-coordination for the single (PbCu)O blocking layer in the Pb-valence range higher than + 3.2 [3]. Pb atoms are also in a six-coordination for PbO_2. These can explain the fact that the studied oxides and PbO_2 have almost identical Pb $4f_{7/2}$ binding energy (137.2 eV) in the vicinity of the Pb valence of 4+. On the contrary, in PbO which has a layered structure due to the Pb $6s^2$ lone pair, Pb ions are in a four-coordination in each PbO layer. The slope in the linear line of the Pb $4f_{7/2}$ binding energy for the studied oxides is rather close to that of a linear line between Pb^{2+} and Pb^{4+} in Pb_3O_4 (both are about - 0.5 eV in Fig.3). The interaction between PbO - and PbO_2 - type structures in Pb_3O_4 would perturb the observed binding energy from that of pure molecules PbO and PbO_2 [5]. It is suggested

that the Pb-O bonding state in the single (PbCu) blocking layer would be similar to those in Pb_3O_4.

4. Conclusion

The Pb valence in the Pb-based copper oxides with the single (PbCu)O blocking layer is quantitatively estimated by measuring the Pb $4f_{7/2}$ binding energy and using a calibration curve obtained from the Pb valence determined by $K_2Cr_2O_7$ titration. However, a calibration curve made from the Pb $4f_{7/2}$ binding energy of PbO and PbO_2 assuming Pb^{2+} and Pb^{4+}, respectively, is not applicable to the studied materials. The difference in the local crystal and electronic structures of Pb ions between PbO and the studied materials is pointed out as a reason for this failure.

5. Reference

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