Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1010–1012. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1074–1077.

Valence States of Lead and Bismuth Atoms in the High-Temperature Superconductor $BaPb_{1-x}Bi_xO_3$

G. P. Kostikova, D. V. Korol'kov, and Yu. P. Kostikov

St. Petersburg State University, St. Petersburg, Russia

Received February 17, 2000

Abstract—X-ray photoelectron spectra of valence bands and core levels of $BaPb_{0.8}Bi_{0.2}O_3$, PbO, PbO_2, $BaPbO_3$, $BaBiO_3$, $NaBiO_3$, and Bi_2O_3 were studied. Comparison of the electron binding energies of the Pb $4f_{7/2}$ or Bi $4f_{7/2}$ core levels for all the oxides studied showed that the high-temperature oxide superconductor $BaPb_{0.8}Bi_{0.2}O_3$ contains simultaneously two different valence forms of lead atoms (Pb^{IV} and Pb^{II}) and two different valence forms of bismuth atoms (Bi^V and Bi^{III}). Parameters of the X-ray photoelectron spectra of the valence bands do not contradict the conclusion on heterovalent states of lead and bismuth atoms in $BaPb_{0.8}Bi_{0.2}O_3$.

Various models have been used to interpret the high-temperature superconductivity of ceramic multicomponent oxides. Among them are traditional models based on the concept of electron pairing via electron–electron or electron–phonon interaction, as well as new models, based on the concept of resonance valence bonds or states with spontaneous magnetic flux. However, none of such models is capable of comprehensively describing the properties of high-temperature oxide superconductors. As shown in our previous works [1, 2], the high-temperature superconductivity of multicomponent oxides is provided by an oscillating (periodic) redox reaction which is responsible for the activation-free electron transfer in the solid. In the cited works we could demonstrate on a qualitative level that high-temperature nonclassical superconductors are fully analogous to known systems with oscillating redox reaction in such important properties as critical temperature and concentration, effects of magnetic field and paramagnetic additives, isotopic effect, correlation length, temperature dependence of heat capacity, and effect of ionizing radiation. On the basis of thermochemical and crystal-chemical data we revealed a unique role of copper in the formation of high-temperature superconductivity in multicomponent oxides.

A characteristic feature of these substances is that they contain at least two elements which both are necessarily present in two different valence states. This is the case with high-temperature oxide superconductors including transition metal atoms. For example, in $YBa_2Cu_3O_7$ these are simultaneously bivalent and univalent copper atoms, and also oxygen atoms in the form of the usual O^{2-} anions and simultaneously of the O_2^{2-} peroxide anions [3]. This regularity seems to be prerequisite for such multicomponent oxides to exhibit superconducting properties. The coexisting oxidized and reduced forms of each of the two elements in the structure of multicomponent oxides created conditions for redox reaction and thus gives rise to stable oscillations of the concentrations of heterovalent forms (in particular, copper and oxygen in $YBa_2Cu_3O_7$). These concentration oscillations encompass the whole sample (or each crystallite, if polycrystalline materials are considered) and predetermine the possibility for a homogeneous solid-phase oscillating (periodic) redox reaction. This reaction ensures electron transfer in the sample.

The aim of this work was to find out whether this regularity (simultaneous presence of heterovalent atoms of each of the two elements in the same structure) is valid for high-temperature oxide superconductors containing no transition metal atoms. Below are given the results of studying lead and bismuth valence states in $BaPb_{1-x}Bi_xO_3$ which has the highest T_c value among superconductors containing no transition metal atoms.

To determine the valence states of lead and bismuth atoms in $BaPb_{1-x}Bi_xO_3$, we measured the X-ray photoelectron spectra of valence bands and core levels of $BaPb_{0.8}Bi_{0.2}O_3$, PbO, PbO_2, $BaPbO_3$, $BaBiO_3$, $NaBiO_3$, and Bi_2O_3. These compounds were synthesized by published procedures [4]. The X-ray photoelectron spectra were recorded on an HP-5959A spectrometer. The binding energies of the Pb $4f_{7/2}$ and Bi $4f_{7/2}$ core levels (with the accuracy of 0.1 eV) are given relative to the standard

1070-3632/01/7107-1010 $25.00 © 2001 MAIK "Nauka/Interperiodica"

Au $4f_{7/2}$ level with the binding energy 84.08 eV [5].

The binding energies of the $4f_{7/2}$ Pb and $4f_{7/2}$ Bi electrons of the indicated lead and bismuth oxides, determined from the crystal X-ray photoelectron spectra of core levels (Fig. 1), are given in the table. First we point out that the resulting binding energies fall in the ranges of the corresponding values, given in the handbook [6]. The data in the table and Fig. 1 allow the following conclusions.

In oxides, where lead atoms are surrounded by oxygen atoms, the binding energy of the $4f_{7/2}$ levels of bivalent lead atoms is close to 137.9 eV (PbO), and that of tetravalent atoms, to 136.9 eV (PbO_2). The weak shoulder at 137.7 eV in the spectrum of the Pb $4f_{7/2}$ levels of PbO_2 is assignable to ionization of the $4f_{7/2}$ core levels of Pb^{II} (E_b ~137.9 eV) in PbO which is always present in PbO_2 as an admixture. The binding energy of $4f_{7/2}$ core levels decreases in going from a low-valence state of lead atoms (Pb^{II}) to a high-valence state (Pb^{IV}). This fact was earlier noted by other authors [6]. At the same time, for the majority of atoms (first for transition metal atoms) the reverse tendency is known. The destabilization of the Pb $f_{7/2}$ core levels in higher lead oxides, as compared to its lower oxides, results from changing internal screening with increasing number of valence electrons of lead atoms bonded with ligands (oxygen atoms). This destabilization correlates with the decreased contribution of core levels [7] into the energy of Pb–O chemical bonds in going from Pb^{II} to Pb^{IV}, with the lower stability of higher lead oxides, and with the thermodynamic instability of higher lead oxides with respect to reduction. The phenomenon of destabilization of the core levels under consideration with increasing oxidation state should be characteristic of all heavy nontransiton elements of the 6 period (Tl, Pb, Bi, Po, At, and Rn).

Lead atoms in the perovskite-like oxide $BaPbO_3$, as expected from its composition and structure, exist in two different states: Pb^{II} and Pb^{IV}. This is proved by the presence of two lines of the Pb $4f_{7/2}$ core levels at 137.8 and 136.6 eV, respectively, in the X-ray photoelectron spectrum. The presence of an additional shoulder (~137.0 eV) in the region of the Pb^{IV} line in this spectrum is explained as follows. In fact, $BaPbO_3$ has a composition close to $BaPbO_{2.8}$ and has a perovskite-like structure with an incompletely filled sublattice of oxygen atoms, as is the case of $BaFeO_{2.5}$, $SrVO_{2.5}$, and $SrVO_{2.7}$ [8]. The observation of the additional shoulder in the X-ray photoelectron spectrum points to the fact that Pb^{IV} atoms in this crystal are in nonequivalent positions and differ in coordination numbers. This is the pattern which should be observed in the case when the sublattice of oxygen atoms contains structural vacancies.

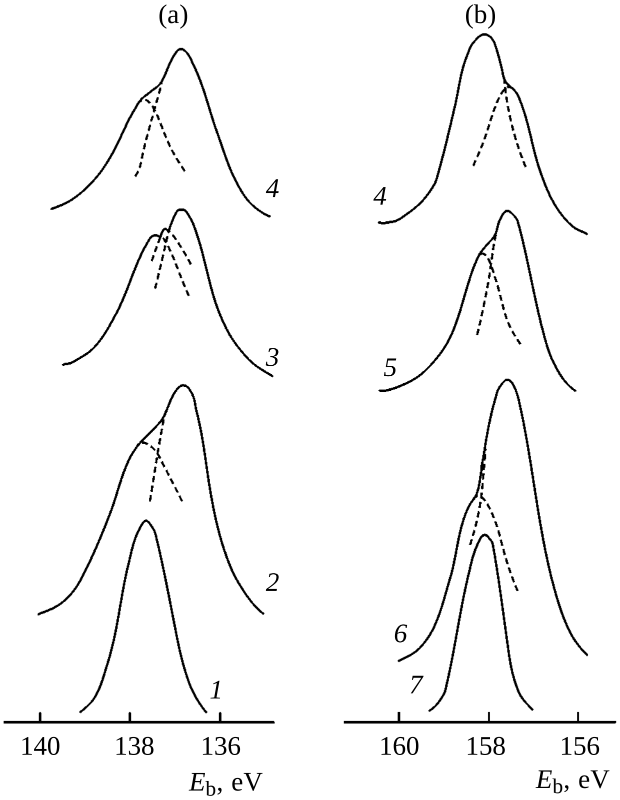

Fig. 1. X-ray photoelectron spectra of the $4f_{7/2}$ core levels of (a) lead and (b) bismuth atoms in the oxides (*1*) PbO, (*2*) PbO_2, (*3*) $BaPbO_3$, (*4*) $BaPb_{0.8}Bi_{0.2}O_3$, (*5*) $BaBiO_3$, (*6*) $NaBiO_3$, and (*7*) Bi_2O_3.

In bismuth oxides, where bismuth atoms are surrounded by oxygen atoms, the bindung energy of the $4f_{7/2}$ core levels of tetravalent bismuth atoms is close

Binding energies (E_b, eV) of the $4f_{7/2}$ electrons of lead and bismuth atoms in oxides

Compound	Lead	Bismuth
PbO	137.9	–
PbO_2	136.9	–
$BaPbO_3$	137.8	–
	136.6	
$BaPb_{0.8}Bi_{0.2}O_3$	137.7	158.2
	136.9	157.4
$BaBiO_3$	–	158.4
		157.5
$NaBiO_3$	–	157.6
Bi_2O_3	–	158.2

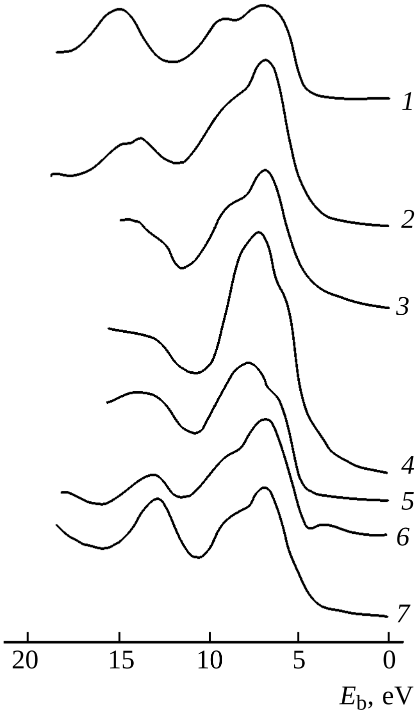

Fig. 2. X-ray photoelectron spectra of valence bands of the oxides (*1*) Bi_2O_3, (*2*) $NaBiO_3$, (*3*) $BaBiO_3$, (*4*) $BaPb_{0.8}Bi_{0.2}O_3$, (*5*) $BaPbO_3$, (*6*) PbO_2, and (*7*) PbO.

to 158.2 eV (Bi_2O_3), and that of quin-quevalent atoms, 157.6 eV ($NaBiO_3$). Again, like with lead oxides, the binding energy of the $4f_{7/2}$ core levels decreases in going from a low-valence state of bismuth atoms (Bi^{III}) to a high-valence state (Bi^{V}).

In the perovskite-like oxide $BaBiO_3$, according to the known concept of its structure, bismuth atoms exist in two different states, namely, tetravalent and quinquevalent. Indeed, the X-ray photoelectron spectrum of the Bi $4f_{7/2}$ levels of this oxide contains two lines at 158.4 and 157.5 eV, respectively. This result completely agrees with the neutron diffraction data in [9], indicative of ordering of tri- and quinquevalent bismuth atoms in the structure of $BaBiO_3$. This structure should be classed as composite perovskites $A_2B'B''O_6$ with ordered arrangement of different valence forms of B atoms in the B sublattice.

Analysis of the electron energy distribution in the valence band of the studied oxides (Fig. 2) shows first that the valence band of the "mixed" oxide $BaPb_{0.8}Bi_{0.2}O_3$ is a superposition of valence bands of $BaPbO_3$ and $BaBiO_3$. The transition from the individual oxides $BaPbO_3$ and $BaBiO_3$ to the "mixed" $BaPb_{0.8}Bi_{0.2}O_3$ oxide is accompanied by a noticeable change in the Bi $4f_{7/2}$ spectrum (the fraction of trivalent bismuth essentially increases) at a practically invariable Pb $4f_{7/2}$ spectrum. No special features are observed in the region of the Fermi level in the experimental X-ray photoelectron spectra of valence bands (excitation by $AlK_{\alpha1}$ radiation). On the whole, the parameters of the X-ray photoelectron spectra of valence bands of the compounds under study do not contradict our conclusion on the valence states of lead and bismuth atoms in $BaPb_{0.8}Bi_{0.2}O_3$.

Thus, the results of our X-ray photoelectron experiments clearly demonstrate that two different valence states of lead atoms (Pb^{IV} and Pb^{II}) and two different valence states of bismuth atoms (Bi^{V} and Bi^{III}) are simultaneously present in the high-temperature oxide superconductor $BaPb_{0.8}Bi_{0.2}O_3$.

REFERENCES

1. Kostikova, G.P., Korol'kov, D.V., and Kostikov, Yu.P., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 5, pp. 728–735.
2. Kostikov, Yu.P., Korolkov, D.V., and Kostikova, G.P., *Solid State Ion.*, 1997, vol. 101–103, pp. 471–474.
3. Kostikov, Yu.P., Rubal'skii, G.D., Strykanov, V.S., and Yarmarkin, V.K., *Sverkhprovodimost': Fiz., Khim., Tekhnika*, 1990, vol. 3, no. 3, pp. 527–530.
4. *Handbuch der prapärativen anorganischen Chemie*, Brauer, G., Ed., Stuttgart: Enke, 1954.
5. Siegbahn, K., *Rev. Mod. Phys.*, 1982, vol. 54, pp. 709–718.
6. Nefedov, V.I., *Rentgenoelektronnaya spektroskopiya khimicheskikh soedinenii* (X-ray Electron Spectroscopy of Chemical Compounds), Moscow: Khimiya, 1984.
7. Kostikova, G.P., Kostikov, Yu.P., and Korol'kov, D.V., *Dokl. Akad. Nauk SSSR*, 1986, vol. 287, no. 3, pp. 671–675.
8. Krebs, H., *Grüdzüge der anorganischen Kristallchemie*, Stuttgart: Enke, 1968.
9. Sakuma, H. and Hashizumo, H., *Acta Crystallogr., Sect. B*, 1990, vol. 46, no. 4, pp. 693–702.