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## X-ray emission spectra and valence state of sulphur atoms of $\text{YBa}_2[(\text{CuO})_{1-x}(\text{NiS})_x]_3\text{O}_{4-\delta}$

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**Abstract.**  $\text{SK}\alpha_{1,2}$  and  $\text{SK}\beta_1$  fluorescence x-ray emission spectra of  $\text{YBa}_2[\text{CuO}_{1-x}(\text{NiS})_x]_3\text{O}_{4-\delta}$  ( $x = 0.01; 0.03$ ) are investigated. According to analysis of their energy position and fine structure one can conclude that sulphur atoms enter the lattice of Y123 compounds and form oxyanion groups. The oxidation state of S atoms in these compounds depends on their concentration and varies from 4+ to 6+.

### 1. Introduction

Superconducting cuprates containing oxyanions of carbon, phosphorus, sulphur and some other elements have been synthesized recently [1–6]. According to structural studies, light elements substitute copper atoms in chains of Y123 crystal structure and form oxyanion groups. Owing to such substitution, it is possible to change the concentration of carriers in  $\text{CuO}_2$  layers. Moreover, the introduction of the oxyanions is favorable for preparation of  $\text{YSr}_2\text{Cu}_3\text{O}_{7-\delta}$  under ambient pressure [5] (this compound usually can be synthesized only at high pressure [7]).

In our previous papers [8–10] we have studied x-ray emission spectra of impurity S atoms for three series of S-doped Y123 compounds. It is found for  $\text{YBa}_2[\text{CuO}_{1-x}(\text{NiS})_x]_3\text{O}_{4-\delta}$  ( $x = 0.01; 0.03$ ) compounds prepared by ceramic technology from a mixture of  $\text{Y}_2\text{O}_3$ , BaO, CuO and NiS and annealed in  $\text{O}_2$  at 600 °C that sulphur atoms have 6+ valency and form sulphate groups [8]. For another set of compounds,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\text{S}_y$ , which were synthesized by solid-phase reaction of the initial Y123 and pure sulphur with subsequent low-temperature annealing in a vacuum-sealed tube under  $T = 300$  °C it is observed that sulphur can substitute oxygen atoms for  $y \leq 0.5$  and form isolated sulphate groups for  $0.5 < y < 2.0$  [8, 9]. For the third series of S-doped Y123 compounds,  $[\text{Y}_{0.89}\text{Sr}_{0.11}]\text{Sr}_2\text{Cu}_{2.78}(\text{SO}_4)_{0.22}\text{O}_{6.12}$ , which were prepared by ceramic technology from highly purified  $\text{Y}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and CuO and finally cooled slowly (24 h) in  $\text{O}_2$  from 930 °C, it is concluded that S atoms enter Y123 compounds in the oxyanion form, and 0.2 vol.% of CuS is present as an additional phase [10].

In the present paper we continue the characterization of the local electron structure and valence state of impurity atoms of S-doped Y123 compounds by means of x-ray emission spectroscopy. A new series of  $\text{YBa}_2[(\text{CuO})_{1-x}(\text{NiS})_x]_3\text{O}_{4-\delta}$  ( $x = 0.01; 0.03$ ) compounds

was prepared for these measurements using low-temperature annealing at  $T = 350$  °C in air and  $O_2$ .

Table 1.

Compound	Energy of intensity maxima (eV)			
	S $K\alpha$	S $K\beta_1$		
		A	B	C
Y123:(NiS) <sub>0.01</sub>	2308.7	—	—	—
Y123:(NiS) <sub>0.03</sub>	2308.9	2466.7	2462.9	2452.5
Y123:(NiS) <sub>0.01</sub> (pO <sub>2</sub> )	2308.7	2466.6	2462.9	2452.5
Y123:(NiS) <sub>0.03</sub> (pO <sub>2</sub> )	2308.9	2467.0	2462.9	2452.5
Y <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2308.9	2467.3		2453.5
CuSO <sub>4</sub>	2308.9	2467.0		
CuS	2307.8			
Na <sub>2</sub> SO <sub>3</sub>	2308.65			

## 2. Experimental details

The samples were prepared using ceramic technology from highly purified Y<sub>2</sub>O<sub>3</sub>, BaO, CuO and NiS as described in [11]. Two series of samples of the same composition; YBa<sub>2</sub>[(CuO)<sub>1-x</sub>(NiS)<sub>x</sub>]<sub>3</sub>O<sub>4- $\delta$</sub>  ( $x = 0.01; 0.03$ ) were synthesized in air and  $O_2$  at  $T = 350$  °C. S  $K\alpha_{1,2}$  (1s–2p transition) and S  $K\beta_1$  (1s–3p transition) x-ray emission spectra (XES) were measured with help of a Johari-type vacuum x-ray tube spectrometer with a position-sensitive detector [12]. A quartz crystal (10 $\bar{1}$ 1) was used as a crystal analyser and curved to  $R = 1.3$  m. The instrumental distortion was estimated to be  $\Delta E = 0.25$  eV and energy was measured with accuracy  $\pm 0.05$  eV. The spectra were excited by photon radiation; the x-ray tube was operated under  $V = 50$  keV,  $I = 50$  mA. S  $K\alpha_{1,2}$  XES were accumulated up to 2000 impulses in maxima of intensity and the signal/noise ratio was 40. S  $K\beta_1$  XES were accumulated up to 700–1000 impulses in maxima of intensity and the signal/noise ratio was three.

## 3. Results and discussion

The local electronic structure and chemical bonding of impurity sulphur atoms in NiS-doped Y123 compounds were studied using the x-ray-emission-spectroscopy method. This technique was recently efficiently used for analysis of substitution effects of other light elements (P, B and F) in high- $T_c$  superconductors [10, 13–16].

In the present experiment, the x-ray transitions into sulphur 1s initial vacancies created by photon irradiation were examined. It is known that x-ray emission spectra are sensitive only to states with angular-momentum quantum numbers separated by one from those of the initial core-vacancy states according to dipole selection rules. Thus, for radiative transitions into the initial S 1s core level a measure of the p-type local density of states is obtained.

We have studied two types of x-ray transition: 1s–2p and 1s–3p which are accompanied by generation of S  $K\alpha_{1,2}$  and S  $K\beta_1$  x-ray emission spectra, respectively. S  $K\alpha_{1,2}$  XES corresponds to transition between two core levels and its chemical shift is sensitive to oxidation state (see [17]). In the second case the intensity distribution of S  $K\beta_1$  XES gives direct information about the S 3p local-density-of-states distribution in the valence band and about the hybridization of S 3p states of emitting atoms with electron states of other atoms which are situated in the first coordination sphere of emitting atoms.

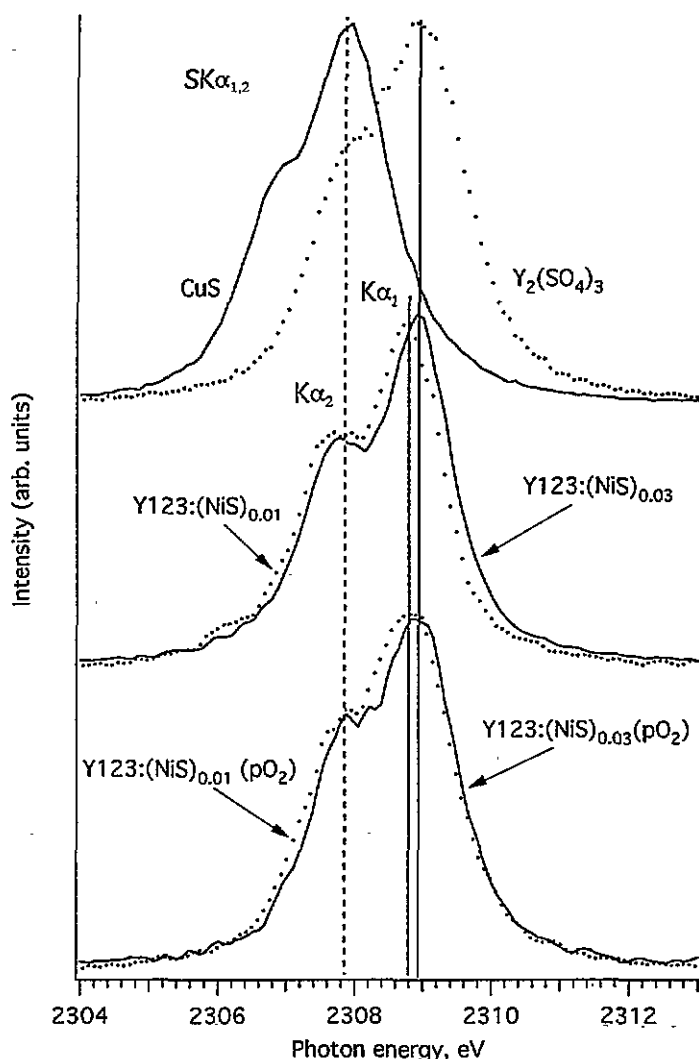


Figure 1. S  $K\alpha_{1,2}$  XES of  $Y123:(NiS)_x$  ( $x = 0.01; 0.03$ ) annealed in air and  $O_2$ . The spectra of reference compounds ( $CuS$ ,  $Y_2(SO_4)_3$ ) are given for comparison.

The results of the measurements of x-ray emission spectra are presented in figures 1–3 and table 1.

### 3.1. S $K\alpha_{1,2}$ XES

According to data presented in figure 1 and table 1, the energy difference of S  $K\alpha_{1,2}$  XES between  $CuS$  ( $S^{2+}$ ) and  $Y_2(SO_4)_3$  ( $S^{6+}$ ) is about 1.1 eV. This chemical shift of S  $K\alpha_{1,2}$  XES is usually used for determination of the oxidation state of S atoms in different compounds [17]. The energy position of S  $K\alpha_{1,2}$  XES of  $Y123:(NiS)_{0.03}$  is equal to that of  $Y_2(SO_4)_3$  and  $CuSO_4$ . This means that S atoms in these compounds have 6+ valency. The simple shape of the S  $K\alpha_{1,2}$  XES doublet of  $Y123:(NiS)_x$  compounds gives evidence of the absence of any contribution of other S-containing phases (for instance, sulphides). It is necessary to

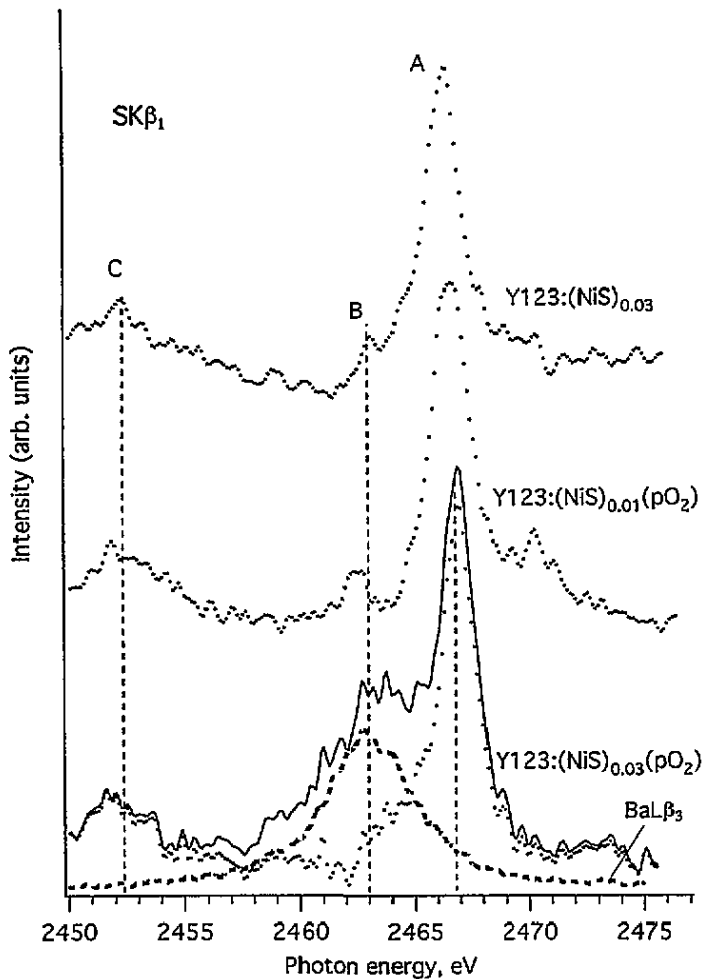


Figure 2. S  $K\beta_1$  XES of  $Y123:(NiS)_x$  ( $x = 0.01; 0.03$ ): dependence on composition and annealing conditions. In the lower part of this figure the correction of the S  $K\beta_1$  spectrum of  $Y123:(NiS)_{0.03}(pO_2)$  for the contribution of the Ba  $L\beta_3$  line is shown.

point out that a low-energy shift of S  $K\alpha_{1,2}$  XES (about 0.2 eV) takes place with decreasing  $x$  content from 0.03 to 0.01. A similar shift is observed between  $Y_2(SO_4)_3(S^{6+})$  and  $Na_2SO_3(S^{4+})$  [17] (see table 1). Hence the decrease of sulphur content in the compounds under investigation is accompanied by change of oxidation state of sulphur atoms from 6+ to 4+. No influence of atmosphere of annealing of the samples is found on characteristics of S  $K\alpha_{1,2}$  XES.

### 3.2. S $K\beta_1$ XES

S  $K\beta_1$  XES of  $Y123:(NiS)_x$  ( $x = 0.01; 0.03$ ) are presented in figure 2. Three peaks A, B and C are fixed in these spectra. The B subband does not belong to S  $K\beta_1$  XES, but results from superposition of Ba  $L\beta_3$  XES ( $2s-3p$  transition) in the second order of reflection from the Ba component of Y123 compounds. In the S  $K\beta_1$  XES spectra which are given in figure 2, Ba  $L\beta_3$  XES is strongly suppressed by using the high energy resolution of the position-sensitive

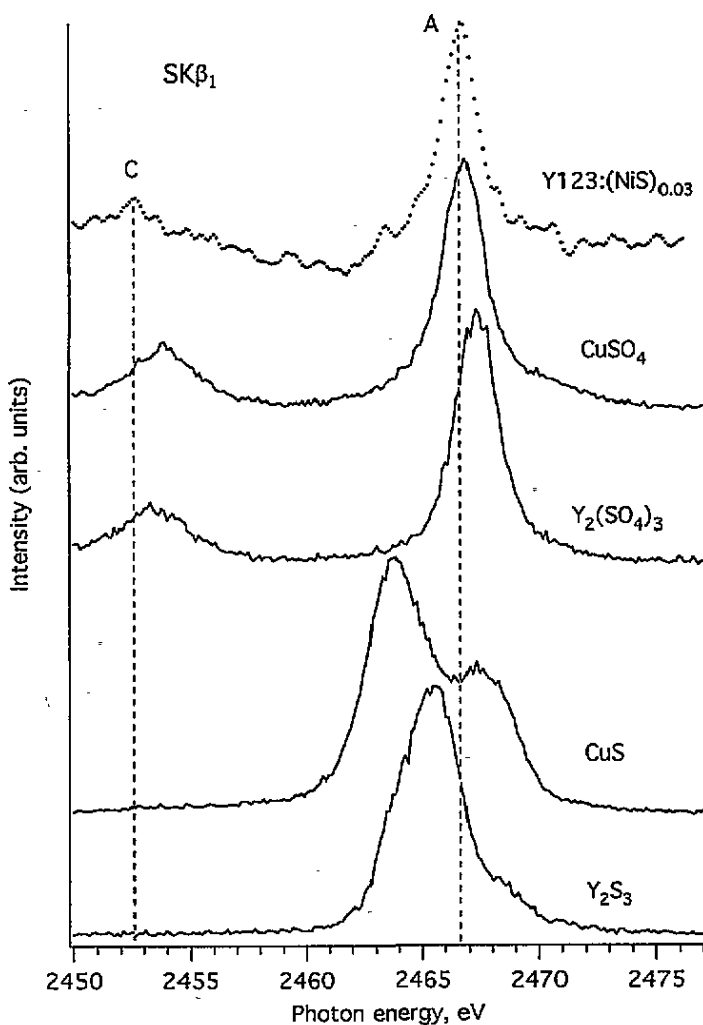


Figure 3. S  $K\beta_1$  XES of  $Y123:(NiS)_{0.03}$  and its comparison with spectra of reference compounds ( $CuSO_4$ ,  $Y_2(SO_4)_3$ ,  $CuS$  and  $Y_2S_3$ ).

detector (about 40%) and the multicannel analyser. It is necessary to point out that the B subband is absent from S  $K\beta_1$  XES of the S-doped  $YSr_2Cu_3O_{7-\delta}$  compound (bariumless Y123) [10]. S  $K\beta_1$  x-ray emission spectra of  $Y123:(NiS)_x$  which are given in figures 2 and 3 are corrected for the contribution of the Ba  $L\beta_3$  line. The contribution of the Ba  $L\beta_3$  line in each case was determined by means of the coincidence of the low-energy tails of the Ba  $L\beta_3$  line and the S  $K\beta_1$  spectrum. The procedure of such treatment is shown in figure 2 for  $Y123:(NiS)_{0.03}(pO_2)$ .

The results of comparison of S  $K\beta_1$  of  $Y123:(NiS)_{0.03}$  with spectra of reference samples ( $CuSO_4$ ,  $Y_2(SO_4)_3$ ,  $CuS$  and  $Y_2S_3$ ) are shown in figure 3. It is seen that S  $K\beta_1$  XES of  $Y123:(NiS)_{0.03}$  is very similar to that of the sulphates  $CuSO_4$ , and  $Y_2(SO_4)_3$ . It has a fine structure typical for sulphates: a narrow intense high-energy subband (A) and a low-intensity C subband. According to results of MO LCAO calculations of electron structure of oxyanions (see e.g. [18, 19]), these subbands are 'genetically' connected with O 2p and O

2s states, respectively, and are revealed in S  $K\beta_1$  XES due to hybridization with S 3p states. On the other hand, S  $K\beta_1$  XES of  $Y_{123}:(NiS)_{0.03}$  is quite different with respect to that of CuS and  $Y_2S_3$ . No contribution is fixed from these phases to S  $K\beta_1$  XES of  $Y_{123}:(NiS)_x$  which confirms the conclusion given on the basis of analysis of S  $K\alpha_{1,2}$  XES.

It is necessary to point out that C and A subbands of S  $K\beta_1$  XES of  $Y_{123}:(NiS)_{0.03}$  are shifted to the low-energy side with respect to those of  $CuSO_4$  and  $Y_2(SO_4)_3$ . One can suppose that this shift is due to non-equivalency of oxygen atoms in so-called sulphate groups which are formed under substitution of copper atoms in chains by sulphur atoms in  $Y_{123}:(NiS)_x$  compounds. This assumption is supported by data of [6] according to which S-doped  $YSr_2Cu_3O_{7-\delta}$  has a fourfold increase of the supercell unit with respect to undoped Y123 and S atoms have slightly distorted tetrahedral surroundings. Two pairs of oxygen ions forming this tetrahedron occupy the non-equivalent positions. S atoms are nearest to these oxygen atoms and the next copper atoms in the chains are situated at a distance of about 3.0 Å.

#### 4. Conclusion

We have analysed the substitution effects in  $YBa_2[(CuO)_{1-x}(NiS)_x]_3O_{4-\delta}$  ( $x = 0.01; 0.03$ ) with the help of x-ray emission spectroscopy. It is found that sulphur atoms have oxygen surroundings in NiS-doped Y123 close to those of sulphates. There is only one possibility for placement of S atoms into the Y123 lattice for realization of such a situation: to substitute copper atoms in chains. It is concluded that the oxidation state of S atoms is changed in dependence on  $x$  and varies from 4+ to 6+ for  $x = 0.01$  and 0.03, respectively.

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