X-ray spectral studies of calcium copper titanates

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Abstract. XPS and NEXAFS spectroscopy were used to study calcium copper titanates (CCTO) solid solutions doped with iron and nickel atoms. The CCTO compound spectra analysis shows that titanium atoms have +4 charge state, and copper and calcium atoms – +2, and their valency does not change when doped with iron and nickel atoms at the concentration of the latter up to 6 atomic percent. In this case, doping atoms are mainly embedded into the positions of titanium atoms and have Fe³⁺ and Ni²⁺ charge states.

1. Introduction

Calcium copper titanate CaCu₃Ti₄O₁₂ (CCTO) is a material with an unusually high dielectric constant ε (up to 10⁵). At that ε weakly depends on temperature in a wide range of temperatures (100 – 600 K) and frequencies (20 Hz – 1 MHz) [1-3]. In this case, the CCTO doping with various metals atoms leads to a significant decrease in the dielectric constant, which also highly depends on the doping degree [2]. According to [1, 4], CCTO has a cubic cell that is 2x2x2 times larger than the pyrochlore ABO₃ cell, with Ca/Cu and Ti atoms in positions A and B, respectively. Titanium atoms have an oxygen atoms octahedral environment, like in the perovskite structure and 3/4 of A atoms, i.e. Cu atoms with local symmetry mmm, are coordinated with four oxygen atoms forming a square with a copper atom in the center due to the rather large inclination of the TiO₆ octahedron. The remaining A atoms, i.e. Ca atoms with local m3 symmetry, have BCC arrangement, and each of them is surrounded by a 12-oxygen icosahedral environment. When doping with 3d atoms, the questions remain open are in what position (A or B) these atoms are implanted and what is the degree of their oxidation (charge state).

2. Experiment details

The solid solution samples of calcium copper titanate CaCu₃Ti₄₋₄ₓMₓO₁₂₋₈ (M=Fe, Ni, 0 ≤ x ≤ 0.06) and CaCu₃₋₃ₓTi₅ₓMₓO₁₂₋₆ (M=Fe, Ni, 0 ≤ x ≤ 0.06) were obtained via the standard ceramic procedure from “special pure” grade CaCO₃ and Ti(IV), Cu(II), Fe(III), Ni(II) oxides using staged calcination at 650, 850, 950 and 1000 °C varied from 6 to 60 hours.

The near-edge X-ray absorption fine structure (NEXAFS) spectra of the CaCu₃Ti₄O₁₂ and oxides were obtained by means the synchrotron radiation source (Russian-German Laboratory at BESSY II). Each spectrum was registered in the total electron yield (TEY) mode [5]. X-ray photoelectron spectroscopy (XPS) studies were carried out at the resource center "Physical methods of surface investigation" (Saint Petersburg University Research park). XPS analysis was performed on a Thermo
Scientific ESCALAB 250Xi X-ray spectrometer. The X-ray tube with AlKα radiation (1486.6 eV) was used as the ionizing radiation source. During the experiments an electron-ion charge compensation system was used to neutralize the charge of the sample. All peaks were calibrated with respect to the C1s peak at 284.5 eV. The experimental data were processed using the ESCALAB 250 Xi spectrometer software.

3. CCTO samples spectral features
Consider the samples of non-doped CCTO, prepared with different calcination times. Figures 1-2 show the NEXAFS and XPS spectra of the samples. In particular, Fig. 1a shows the titanium NEXAFS spectra in CCTO and titanium oxides Ti$_2$O$_3$ [6] and TiO$_2$ [7] in various crystalline modifications of anatase, rutile and amorphous titanium oxide. It is known that all titanium oxides modifications have the following crystal structure: titanium atoms with an octahedral oxygen atoms environment. Though, their crystal lattice depends on modification: TiO$_2$ anatase and rutile – tetragonal, TiO$_2$ brookite – rhombic, and Ti$_2$O$_3$ – trigonal. In amorphous oxide, the oxygen atoms environment of titanium is also octahedral.

![Figure 1](image-url)  
**Figure 1.** a) NEXAFS Ti2p spectra of CCTO and titanium oxides [6-7]; b) NEXAFS Cu2p spectra of CCTO and copper oxides; c) NEXAFS Ca2p spectra of calcium in CCTO, CaO and atomic calcium [8].

In the presented titanium NEXAFS spectra, the main absorption bands are associated with transitions of 2p titanium electrons to 3d free states. These bands are split into two series 2p3/2 and 2p1/2, due to spin-orbit interaction. In an octahedral crystalline field, the 3d states split, which results in the bands splitting, in the simplest case, into bands A and B. The former are described as transitions of 2p electrons to t$_{2g}$-symmetry states, and the latter (bands B) to e$_g$-symmetry states. These features
can be observed in all titanium oxides spectra (both TiO$_2$ and Ti$_2$O$_3$). Moreover, the splitting (energy difference between bands A and B) in Ti$_2$O$_3$ is higher, what apparently indicates a more significant effect of the crystalline (octahedral) field. It should also be noted that the band B$_3$ in anatase and rutile is split into two bands, with the different intensity ratio, which indicates that their titanium atoms environment are not completely equivalent. In amorphous titanium oxide, this split is also exists, but in the form of asymmetry on the peak right side (as in anatase) due to the peaks overlap. Consider the titanium spectra it should be mentioned that the obtained CCTO spectra coincide in the number of basic features and their energy positions with the TiO$_2$ spectra, which indicates that the titanium atom in the CCTO has a Ti$^{4+}$ charge state. The presence of the CCTO spectra band B$_3$ splitting in the form of asymmetry in the low-energy side indicates the similarity of the titanium atoms environment in CCTO and in rutile. Indeed, in both compounds, the TiO$_6$ octahedra are in contact with each other by separate nodes, i.e. one oxygen atom belongs to two neighboring octahedra, while in the anatase case, the TiO$_6$ octahedra have common edges. At the same time, it should be noted that the band B asymmetry in the CCTO spectra described above is somewhat diffuse in nature as in the amorphous TiO$_2$ spectra. This fact can be interpreted as a distortion of the titanium octahedral environment.

Consider the copper NEXAFS spectra presented in Figure 1b. Here, for comparison, the obtained Cu2p spectra of copper oxides CuO and Cu$_2$O are presented. The spectra comparison shows that, according to the energy position of the main absorption bands, the obtained CCTO spectra coincide with the CuO spectra, which suggest the copper atoms in the compounds under consideration have a Cu$^{2+}$ charge state. In addition, it should be noted that the copper atoms in the crystal monoclinic lattice in CuO have a planar environment of 4 oxygen atoms, as in the CCTO, while the copper atom in the cubic lattice Cu$_2$O has a coordination number of 2.

![Figure 2](image_url). XPS spectra of copper (b), titanium (c), calcium (d) and the CaCu$_3$Ti$_4$O$_{12}$ survey spectra (a).
The obtained calcium NEXAFS 2p spectra are shown in Figure 1c. For comparison, the obtained calcium spectra in the calcium oxide and atomic calcium are presented [7]. It can be seen from the presented spectra that the energy position of the main bands B coincides in the obtained CCTO and CaO, while the spectra of atomic calcium are displaced as a whole to the lower energies, which corresponds to the general rules: NEXAFS spectra of more electronegative atoms have a shift towards lower energies. In this case, the bands splitting by a crystalline field practically does not occur in the CCTO spectra, while in the CaO spectra is clearly expressed in the bands A appearance (CaO has an fcc lattice and potassium atoms have an octahedral environment of oxygen atoms). According to [1, 4], in the CCTO, the oxygen atoms environment around a calcium atom has an icosahedron symmetry, much closer to spherical than octahedral. Therefore, the splitting caused by crystalline field may be substantially less noticeable or absent as in the atomic calcium case. However, nevertheless, we observe wide influxes from the peaks B low-energy side, which is most likely due to the oxygen environment influence. In total, according to the presented results, it can be assumed that the calcium atoms in the compounds under consideration have a Ca$^{2+}$ charge state.

To clarify the charge state in the studied CCTO samples, the obtained compounds were studied by XPS. The obtained CaCu$_3$Ti$_4$O$_{12}$ spectra are shown in Figure 2. A comparison of the binding energies of the atoms under consideration with their oxides binding energies [9] allows to conclude that titanium atoms have a +4 charge state in the studied superconducting compounds, and copper and calcium atoms – +2, which coincides with the NEXAFS spectra analysis results presented above. It should be noted that the XPS spectra under study correlate well in the main energy features with the similar spectra of the CCTO samples prepared both by the traditional sintering technique [10-11] and thin deposited films spectra [12-13].

However, based on the interpretation of the XPS spectra data, the authors [10-13] conclude that copper atoms exist in the structure of the CCTO in two charge states Cu$^2+$ and Cu$,+$ which is inconsistent with our results based on the analysis of not only XPS, but also NEXAFS -spectra. This result is in good agreement with the spectral studies of doped CCTO presented below.

4. Fe-and Ni-doped CaCu$_3$Ti$_4$O$_{12}$ ceramics

Consider the CCTO samples doped with iron and nickel atoms. It should be noted that both the NEXAFS and XPS spectra of titanium, copper, and calcium atoms of all doped CCTO samples are identical (these spectra are not given in this work). This allows to conclude that iron and nickel doping does not change the state of titanium, copper, and calcium atoms CCTO, i.e. their nearest environment and charge state remain unchanged. Therefore dwell only on the dopant atoms spectra presented in Figure 3. From the comparison between the CCTO samples iron NEXAFS spectra (Figure 3a), it can be seen that the compounds spectra coincide in the number and energy position of the main absorption bands A and B, and do not depend on the CCTO samples stoichiometric composition. This suggests that, in these compounds, the iron atoms are in the same chemical environment and coordination (position in the CCTO crystal lattice). From the comparing of the iron NEXAFS spectra of the studied CCTO samples with the iron oxides spectra is clearly seen that the energy position and intensity of the spectrum main features (bands A and B) correlate with the corresponding characteristics of the Fe$_2$O$_3$ iron atom spectra and Fe$_3$O$_4$, but differ from the FeO spectra [14]. It is known that in Fe$_2$O$_3$, all iron atoms are in the trivalent state, while in Fe$_3$O$_4$ iron atoms exhibit valencies of II and III depending on the position in the crystal lattice. All of the above suggests that the iron in the doped CCTO is mainly in the trivalent state (iron atoms have an effective charge of $+3$), but there is a possibility that a certain number of iron atoms carry an effective charge of $+2$.

The iron XPS spectra (Figure 3b) analysis also indicates that the iron atoms position in the CCTO does not depend on the doping degree, and a comparison with the Fe$_2$O$_3$ spectrum indicates that iron atoms most likely carry a charge of $+3$. In this case, iron atoms in accordance with the stoichiometric formula can replace both copper atoms and titanium atoms in the CCTO structure. However, taking into account the fact that the iron atoms in Fe$_2$O$_3$, like the titanium atoms in the CCTO, are in the oxygen atoms octahedral environment, while copper atoms are in the center of the oxygen atoms square, it can be assumed that iron
atoms at doping is most likely located in the positions of titanium, regardless of the doped CCTO stoichiometric composition.

Figure 3. NEXAFS (a,c) and XPS (b,d) spectra of CCTO sample doped with Fe (a,b) and Ni (c,d).

Consider the spectra of doping nickel atoms. Figure 3d shows the corresponding XPS spectra of CaCu$_3$Ti$_{4-x}$Ni$_x$O$_{12}$, CaCu$_3$Ti$_4$Ni$_x$O$_{12}$ and nickel oxide NiO. The spectra of CCTO samples are comparable in the main details both together and with the oxide spectra. This suggests that nickel atoms have a Ni$^{2+}$ charge state, which is consistent with the results of [15]. It should be noted that the CCTO are shifted as a whole towards high energies by 0.7 eV, which is usually associated with a large effective positive charge. The characteristic shift between the energy positions of the main features in the Ni$^{2+}$ (NiO) and Ni$^{3+}$ (Ni$_2$O$_3$) spectra lies in the range of 1.5 – 1.8 eV [9], which allows us to assume the nickel atom effective charge in doped CCTO of the order of +2.5. Figure 3c shows the absorption spectra of the nickel atom in the studied samples and nickel oxide. It is clearly seen that the superconductors spectra coincide in the number of basic features and their energy positions, which suggests the nickel atoms in both compounds have the same chemical state: position in the crystal...
lattice and effective charge. It should be noted that these spectra differ from the corresponding NiO spectrum. The CCTO spectra, in particular, contain an additional peak A in the low-energy region. Since the NEXAFS formation in the Ni2p spectra is dominated by dipole-allowed 2p-3d transitions, the appearance of additional band A may be due to the fact that the highest occupied molecular orbital (HOMO) in NiO turned out to be partially free in CCTO, i.e. became the lowest unoccupied molecular orbital (LUMO). This can be interpreted as follows: the 3d states in the nickel atom in this case have a lower occupation degree, i.e. carry a more positive charge than the nickel atom in NiO (more than +2). This corresponds to assumptions stated above. Moreover, the relative intensity of peak A in CaCu$_3$Ti$_{4-x}$Ni$_x$O$_{12}$ is slightly higher than in CaCu$_3$Ti$_{4-x}$Ni$_x$O$_{12}$, which most likely indicates a lower occupancy of the corresponding molecular orbital, and accordingly, the nickel atom in CaCu$_3$Ti$_{4-x}$Ni$_x$O$_{12}$ has an effective positive charge higher than in CaCu$_3$Ti$_{4-x}$Ni$_x$O$_{12}$.

Thus, from the interpretation of the obtained XPS and NEXAFS 2p spectra, we can conclude that in the studied CCTO compounds, the copper and calcium atoms have a charge state of +2, titanium atoms – +4, and doping atoms of nickel and iron – +2.5 and +3, respectively.

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