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X-ray emission and photoelectron spectra, and the location of fluorine atoms in strontium and calcium copper oxyfluorides

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Abstract. X-ray emission and photoelectron spectra of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, $\text{CaSrCuO}_2\text{F}_{2+\delta}$, and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ cuprates are presented. It is found that the XPS F 1s binding energies of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ are different ($\Delta E \sim 1.3$ eV) and those of $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ and $\text{CaSrCuO}_2\text{F}_{2+\delta}$ have intermediate values. These differences in x-ray photoelectron spectra are attributed to the different preferential location of fluorine atoms in structures related to La_2CuO_4 and Nd_2CuO_4 . The results obtained are in accordance with measurements of F $K\alpha$ x-ray emission spectra of the same compounds.

1. Introduction

The alkaline-earth cuprates Sr_2CuO_3 and Ca_2CuO_3 both have K_2NiF_4 -type structures, with an ordered arrangement of oxygen vacancies in the equatorial coordination sites around the Cu ions. Although it has recently been shown that extra oxygen can be incorporated into Sr_2CuO_3 under high O_2 pressure, with superconductivity resulting under appropriate conditions [1, 2, 3, 4], there have been no reports of similar behaviour for Ca_2CuO_3 . However, we have recently demonstrated that fluorine can be successfully incorporated into both Sr_2CuO_3 and Ca_2CuO_3 to give the oxyfluorides $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, with the former exhibiting superconductivity with a T_c of 46 K [5, 6]. These oxyfluorides were prepared by reaction of the alkaline-earth cuprates with fluorine gas at low temperatures (200 °C). This method of preparation was, however, not considered ideal, due to the toxicity and handling problems associated with F_2 gas, and the fact that samples could be prepared only in relatively small (≈ 200 mg) batches. Therefore new routes to these oxyfluorides were sought, which could overcome these problems.

Firstly it was demonstrated that $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ could be prepared from the reaction of Sr_2CuO_3 with NH_4F [7], and this route was used to demonstrate that Ba doping raised T_c up to 64 K for $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$. Unfortunately this method generally results in the production of significant numbers of SrF_2 impurities, and it appears ineffective for the synthesis of $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$. A second route was then discovered, involving the low-temperature reaction of the alkaline-earth oxides with transition metal difluorides (e.g. CuF_2 ,

ZnF₂) [8]. This method is simple and efficient, and can be used to prepare large samples of the whole range of oxyfluorides, including Ca₂CuO₂F_{2+δ}. In addition, no SrF₂ impurity is produced provided that the reaction conditions are carefully controlled, in particular that the reagents are dry. The only limitation of this method is that a transition metal oxide impurity (e.g. CuO, ZnO) is present in the sample arising from the decomposition of the transition metal difluoride.

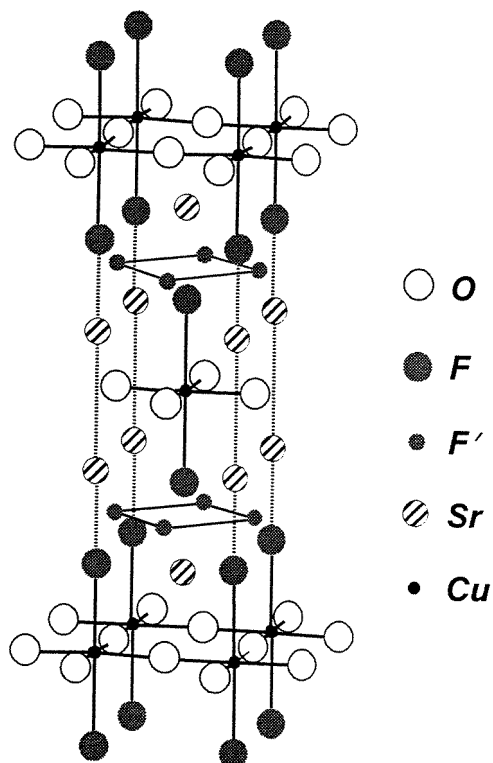


Figure 1. The structural model for Sr₂CuO₂F_{2+δ}. F' denotes the partially occupied interstitial fluorine site.

Structural studies of the oxyfluorides Sr₂CuO₂F_{2+δ} and Ca₂CuO₂F_{2+δ} have shown that the former adopts the La₂CuO₄ structure (figure 1) [5], whereas the latter appears to adopt the Nd₂CuO₄ structure (figure 2) [6]. Madelung energy calculations on both systems strongly support the conclusion that O/F interchange occurs during fluorine incorporation to give complete CuO₂ layers, and this has been confirmed by measurements of x-ray emission and photoelectron valence band spectra of Sr₂CuO₂F_{2+δ} [9]. The structures differ in the location of the F sites: in Sr₂CuO₂F_{2+δ} the F atoms are located in the apical sites, whereas in Ca₂CuO₂F_{2+δ} they are located between the Ca bilayers. It has been proposed that in the mixed Sr/Ca copper oxyfluorides (Sr_{2-x}Ca_xCuO₂F_{2+δ}), a gradual migration of the F atoms from the apical (La₂CuO₄) sites to the bilayer (Nd₂CuO₄) sites occurs [6].

It is, however, difficult to confirm conclusively the above assumptions concerning the location of O and F sites by using x-ray or neutron diffraction, because of the similarity of the scattering factors of O and F atoms. Therefore, in the present paper, we present the F Kα x-ray emission spectra (XES) and XPS core-level measurements of

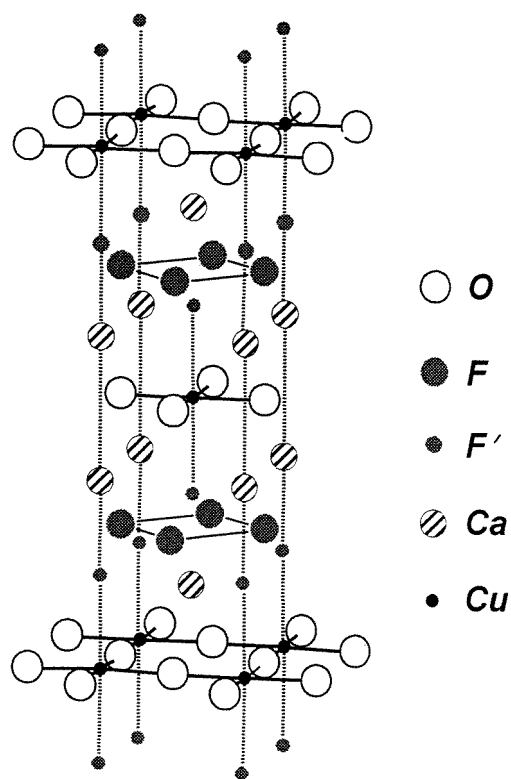


Figure 2. The structural model for $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$. F' denotes the partially occupied interstitial fluorine site.

$\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, as well as those for the phase with the highest T_c , $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$. These measurements are sensitive to the local structure of the constituent atoms in non-equivalent positions, and we have used both techniques [9, 10, 11] for the determination of the location of oxyanions in multicomponent high- T_c superconductors.

2. Experimental details

High-purity SrCO_3 , BaCO_3 , CaCO_3 , and CuO were used to prepare four samples, Sr_2CuO_3 , Ca_2CuO_3 , SrCaCuO_3 , and $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_3$. The intimately ground powders were heated in air at a temperature between 950 and 1000 °C for 14 hours, reground, and then reheated at the same temperature for a further 14 hours. Fluorination to give the oxyfluorides, $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$ and $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, was achieved by reaction with ZnF_2 (1.1 moles per mole of $\text{Sr}_{2-x}\text{A}_x\text{CuO}_3$, $\text{A} = \text{Ca}, \text{Ba}$) at a temperature between 230 and 280 °C [8]. It was essential that all reagents were pressed into pellets for XES and XPS measurements by using cold high-pressure treatment.

XPS spectra of the four oxyfluorides were measured using a Perkin–Elmer ESCA spectrometer (a PHI 5600 ci multitechnique system with monochromatized $\text{Al K}\alpha$ radiation) with an energy resolution of about 0.35 eV. The samples (pressed pellets) were cleaved in

high vacuum before the measurements. All spectra were calibrated using Au foil with $E_b(\text{Au } 4f_{7/2}) = 84.0$ eV. Since the method of fluorination, reaction with ZnF_2 , yields ZnO as an impurity, particular emphasis has been placed on the XPS core-level F 1s spectra. This method of fluorination was used since it is simplest method for the synthesis of large quantities of the oxyfluorides, and it produces negligible Sr/Ca/BaF₂ impurities, which would affect the analysis of the F 1s spectra.

F K α XES spectra (the 2p \rightarrow 1s transition) were measured with a JCXA-733 electron-probe microanalyser with a fully focused Johan-type spectrometer and a TAP (thallium phthalate) crystal analyser ($2d = 25.76$ Å) curved to $R = 280$ mm. The energy resolution was about 1.8 eV. A soft operation mode ($V = 5$ keV, $i = 100$ nA) was chosen for the x-ray tube and the electron beam focused on the sample surface was changed for every scan to avoid sample decomposition during the measurements.

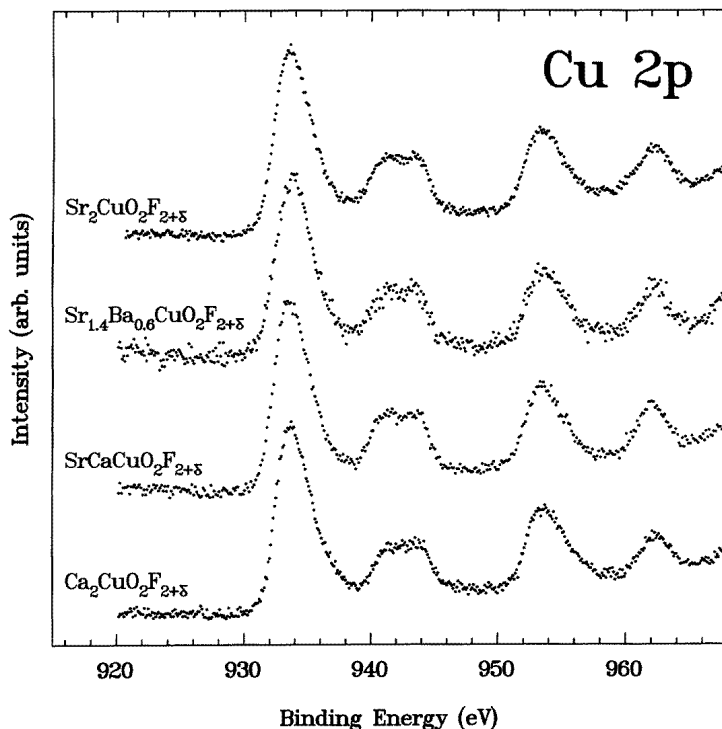


Figure 3. XPS Cu 2p_{3/2,1/2} spectra of Sr₂CuO₂F_{2+ δ} , Ca₂CuO₂F_{2+ δ} , SrCaCuO₂F_{2+ δ} , and Sr_{1.4}Ba_{0.6}CuO₂F_{2+ δ} .

3. Results and discussion

XPS Cu 2p spectra measurements of Sr₂CuO₂F_{2+ δ} , Sr_{1.4}Ba_{0.6}CuO₂F_{2+ δ} , SrCaCuO₂F_{2+ δ} and Ca₂CuO₂F_{2+ δ} compounds are presented in figure 3. Since the binding energies and relative intensities of the Cu 2p_{3/2} and Cu 2p_{1/2} lines and their satellites are very close to those of various cuprates and CuO [12], it can be concluded that the chemical state of the Cu ions in the oxyfluorides is close to Cu²⁺. Two broadened lines are observed in the XPS O 1s spectra of strontium and calcium copper oxyfluorides (figure 4). The most intense O

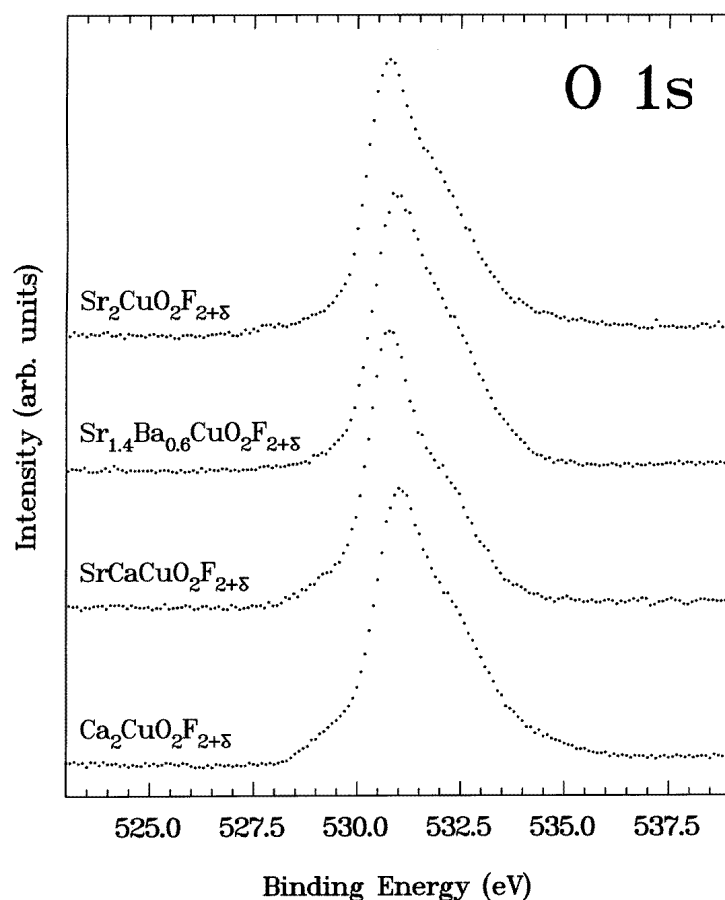


Figure 4. XPS O 1s spectra of $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$, and $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$.

1s line ($E_b \sim 530.8\text{--}530.9$ eV) is ascribed to O–Cu bonds and the next one at the higher binding energy is due to oxygen of contaminating ZnO, hydroxides and carbonates [12]. The contributions from O–Sr(Ca) bonds (at the lower binding energies) which are seen in XPS O 1s spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [12] are absent in the oxyfluoride O 1s spectra (figure 4), which is in accordance with the structural models for $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ (figures 1 and 2) in which F atoms not O atoms are located closest to Sr (Ca).

The XPS F 1s spectra of $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$, and $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ are given in figure 5. As can be seen, the F 1s binding energies of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ are different ($\Delta E \sim 1.3$ eV) and those of $\text{SrCaCuO}_2\text{F}_{2+\delta}$ and $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ are at intermediate values. It is not surprising that non-equivalent fluorine atoms in fluorinated cuprates have different binding energies. The higher binding energy observed for $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ can be attributed to the different preferential location of fluorine atoms in this material (Nd_2CuO_4 -like structure) compared with $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ (La_2CuO_4 -like structure), in accordance with the structural models previously reported for these compounds [5, 6]. In the simplest structural model for $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, the dominant F species is bonded to one Cu (2.42 Å), and five Sr (four at 2.80 Å, one at 2.53 Å) which

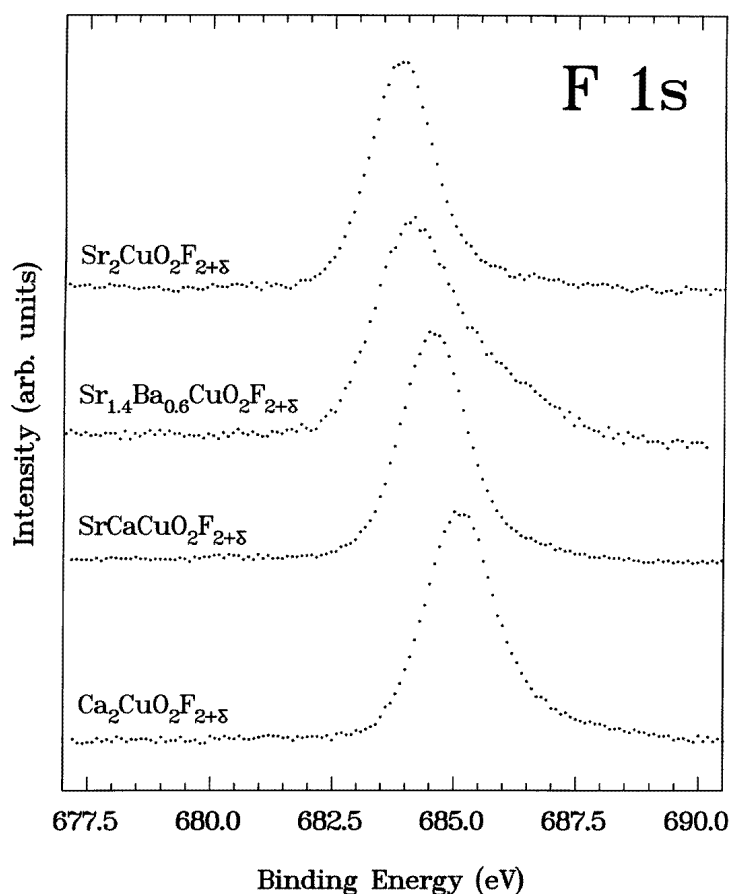


Figure 5. XPS F 1s spectra of $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$, and $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$.

contrasts markedly from the primary F environment in $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, which has just four Ca neighbours at 2.33 Å. According to these models one can expect that the subsequent substitution of Ca for Sr in $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ will correspond to some intermediate situation and will be accompanied by chemical shifts of F 1s lines in between these two limiting cases, and this is found to be the case for the oxyfluoride $\text{SrCaCuO}_2\text{F}_{2+\delta}$ (figure 5). It would be expected, however, that the F 1s spectrum might be broader for this sample, encompassing both extremes, but this is found not to be the case, with the peak width comparable to that of the end-members, $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$. This may be the result of some ordering of the F atoms in both types of site in this case.

The XPS F 1s spectrum of the Ba-doped oxyfluoride $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ might be simulated by a superposition of those of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$. This is somewhat surprising at first sight, but could suggest a possible mixture of F in the two sites in this material, or a larger excess F content, δ , in the Ba-doped phase. It must also be noted that the actual defect structures of these materials are very complex, and significant local distortions occur to minimize unacceptable F–F contact distances [5]. In the absence of detailed reliable information on the extent of such local interactions, and the way that they are influenced

by substitutions of Ca or Ba for Sr, it is not possible at present to provide a definitive interpretation for the enhanced F 1s binding energy observed for $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$.

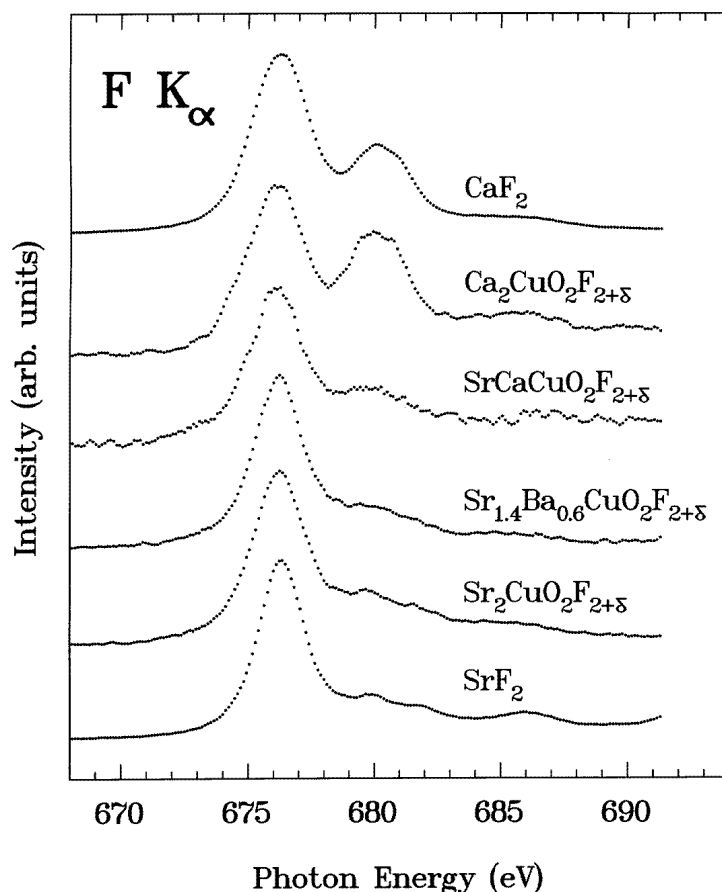


Figure 6. F $K\alpha$ XES of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$, $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ and the reference compounds CaF_2 and SrF_2 .

F $K\alpha$ x-ray emission spectra of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$, $\text{SrCaCuO}_2\text{F}_{2+\delta}$, and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ fluorinated cuprates and some reference binary compounds (CaF_2 , SrF_2) are presented in figure 6. These spectra correspond to the dipole transition $2p \rightarrow 1s$ (vacancies on the F 1s core level are filled by valence F 2p electrons) and give information about the F 2p density of states in the valence band. It is shown in our previous publications [13, 14] that these spectra are very sensitive to the chemical bonding and show a different energetic position and intensity of the high-energy satellite (at $E \sim 680\text{--}682$ eV) according to the chemical bonding. It is seen from the spectra given in figure 6 that F $K\alpha$ XES of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ are different and, on the other hand, are very similar to the spectra of SrF_2 and CaF_2 , respectively. The F $K\alpha$ XES of $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ and $\text{SrCaCuO}_2\text{F}_{2+\delta}$ have some intermediate intensities of the high-energy satellite. These data serve as additional confirmation of the structural models of $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ and $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ shown in figures 1 and 2. For $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ (figure 1), F atoms have strong bonds with Sr atoms within F–Sr planes, and the F $K\alpha$ XES of this compound are very close to that of

SrF₂, with typical low intensity of the high-energy satellite (see figure 6). In the case of Ca₂CuO₂F_{2+δ}, F atoms are bonded with Ca atoms (figure 2), and this is accompanied by high intensity of the satellite structure of F Kα XES (figure 6). F Kα XES of Sr_{1.4}Ba_{0.6}CuO₂F_{2+δ} and SrCaCuO₂F_{2+δ} have intermediate intensities of the high-energy satellites in comparison with those of Sr₂CuO₂F_{2+δ} and Ca₂CuO₂F_{2+δ}.

Acknowledgments

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