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Metal-dielectric transition in $Ba_{0.6}K_{0.4}BiO_{3-y}$ single crystals studied by scanning photoelectron microscopy

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The electronic structure of $Ba_{0.6}K_{0.4}BiO_{3-y}$ single crystals has been studied using a scanning photoelectron microscope with a lateral resolution in the one micrometer range. It is possible to change the oxygen content (y) and convert the surface from the metallic to the dielectric state presumably by breaking the Bi-O bonds by using the focused zero-order light to irradiate the sample surface. The electronic states close to the Fermi level after such a treatment show a different doping dependence as compared to the case of potassium doping. By imaging the surface on the micrometer scale we find significant variations in the valence band intensity over the surface and observe a rather large intensity of the density of states close to the Fermi level. This will have a large impact on the discussions of dynamical lattice distortion and pseudogap behavior in the metallic phase. [S0163-1829(97)51634-1]

Cubic $Ba_{1-x}K_xBiO_3$ demonstrates the highest superconducting critical temperature (T_c) among oxide superconductors not containing copper. As compared to the copper-oxide high-T_c materials, the characteristic properties of this compound are the absence of local magnetic moments and two-dimensional metal-oxygen planes; both are widely believed to be essential factors in producing a high T_c in the cuprates. Despite numerous studies (Ref. 1 and references therein) of $Ba_{1-x}K_xBiO_3$ the metal-dielectric transition is not fully understood hitherto. This is mainly due to the fact that along with potassium concentration, oxygen stoichiometry is also a key factor in producing the optimal superconducting parameters. The semiconducting regime of $Ba_{1-x}K_xBiO_3$ has been related to the distortion of the crystal structure which results in a band splitting around the Fermi level. In the intermediate doping range $0<x<0.3$ the band filling of the semiconducting $Ba_{1-x}K_xBiO_3$ is steadily reduced until a critical doping level at about $x=0.3$ is reached. At this critical level the energy gained by the distortion of the crystal structure is lost and a phase transition to the metallic cubic phase occurs. This doping behavior is consistent with the assignment of the x-dependent core level shifts of $Ba_{1-x}K_xBiO_3$ to a shift of the chemical potential or ''rigid-band'' shift. Thus it is thought that the dielectric-metal transition in this system is related to the corresponding crystallographic phase transition causing a closing of a band gap. With this picture the role of

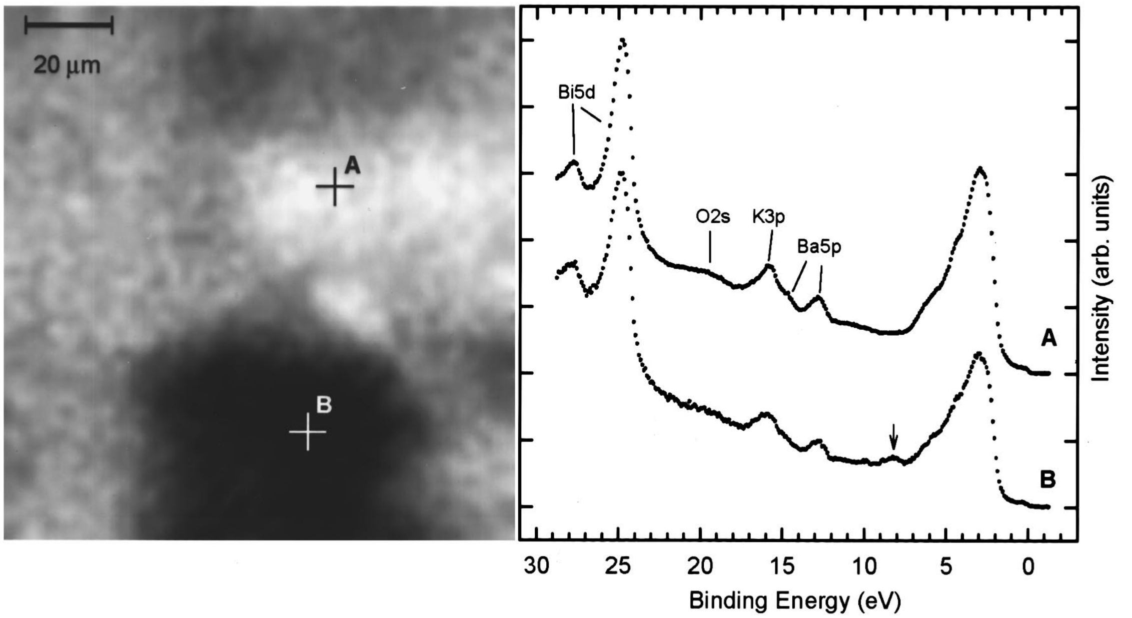

FIG. 1. Left: $120\times120\ \mu m^2$ surface area image obtained by scanning the sample through the photon beam, $h\nu=57.38$ eV. Electron analyzer was locked to $E_{kin}=54.2$ eV, corresponding to the maximum intensity of the VB. Right: two photoelectron spectra recorded from different positions of the surface (marked by crosses A and B in the figure). Spectra were normalized to the Bi $5d_{5/2}$ intensity. The arrow in the spectrum B recorded in the ''black'' area marks a structure due to surface contamination.

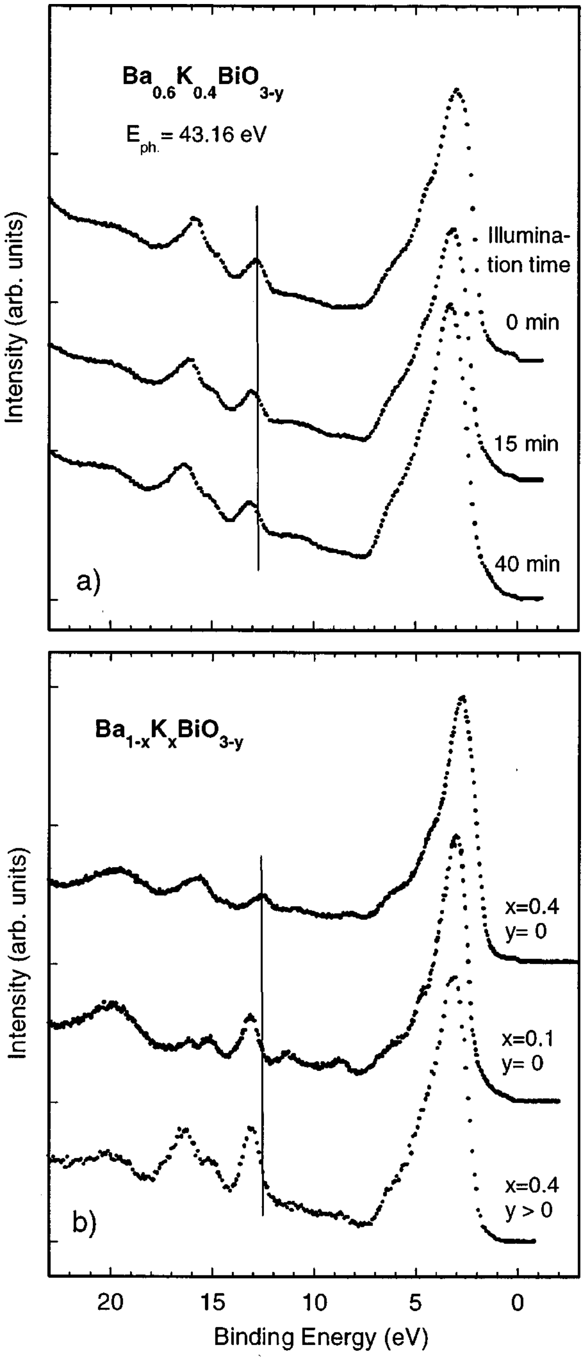

FIG. 2. Valence band and shallow core level photoelectron spectra for $Ba_{1-x}K_xBiO_{3-y}$. (a) $Ba_{0.6}K_{0.4}BiO_{3-y}$ at different illumination doses corresponding to the different oxygen content. The intensity supression at the Fermi level and chemical shift for the VB and core levels with time of illumination can clearly be seen. (b) Comparison of different dopings in $Ba_{1-x}K_xBiO_{3-y}$. The bottom spectrum was recorded from the microscope beamline for $x=0.4$ after a short (15 min) ZOL treatment, $E_{ph}=86.7$ eV. The upper two spectra were recorded at BL22 (beam spot 3×1 mm^2), $E_{ph}=80$ eV, for potassium content $x=0.1$ (dielectric, middle spectrum), $x=0.4$ (superconductor, upper spectrum). The weak features at 8.5 and 11.5 eV BE in the upper two spectra are from Ba 4*d* excited by second-order radiation.

oxygen stoichiometry remains unclear, although some experimental results[2–4] show the importance of oxygen defects on the metallic and superconducting parameters. For example, maximum conductivity and critical temperature for the optimal potassium content of $x=0.4$ is realized at an oxygen content of $3-y=2.95$.[4]

Another problem in surface sensitive studies of high-temperature superconductors (HTSC) is the surface homogeneity, which also is fundamentally important in practical applications. Suitable experimental techniques to address this problem are still scarce and the most powerful spectroscopies typically lack spatial resolution.

Different kinds of data can be obtained with scanning photoelectron microscopy using a focused light probe. First, surface scans of the photoelectron yield of different core levels may carry chemical information on compositional homogeneity. The main obstacle in these measurements is the presence of topographically induced features in the images, particularly important in the case of crystals having no natural cleavage planes, obscuring the chemical information in the images. Second, at selected microscopic areas photoelectron spectra can be recorded. In the present study of BaKBiO we find that there is a difference in the Fermi level intensity distribution over the surface on the micrometer scale, and on some crystals we observe an intensity three times larger than has been measured so far on high-quality single crystals by ordinary photoelectron spectroscopy,[1,5] which probes the surface on a millimeter scale. These results shed new light on the discussion of dynamic lattice distortion and pseudogap behavior[5] in the metallic phase of $Ba_{1-x}K_xBiO_3$. Finally, after illuminating the sample with zero-order light (ZOL), concentrated into an area of a few micrometers in diameter by the focusing optics, both images and spectra change markedly in dependence of illumination dose. The BaKBiO compound (and perhaps other HTSC), which are extremely sensitive to the oxygen stoichiometry, may be converted from the metallic to the dielectric state by exposure to the focused ZOL beam. By recording spectra from the ZOL illuminated areas it is possible to follow the changes in chemical composition and, what is particularly attractive, to trace the metal-dielectric transition as a function of illumination dose, which causes a decrease in the oxygen content.

The crystals used in the present study were grown from a KOH fluxed melt using the electrodeposition technique introduced by Norton.[6] Potassium content was $x=0.4$ as determined by neutron activation analysis and x-ray diffraction measurements using the reference ''lattice parameters-concentration'' dependence.[7] The critical temperature $T_c=29$ K ($T_c^{\text{onset}}=30$ K, $\Delta T_c=3$ K) was determined by AC susceptibility measurements. The crystals were glued to copper sample holders with the naturally formed {100} plane of the crystal as base. The crystals were cleaved by fracturing *in situ* at a pressure around 10^{-10} Torr and were kept cooled (~130 K) during cleavage and measurements.

The scanning photoelectron microscope[8] on BL31 at the 550 MeV MAX I storage ring at MAX-lab, Lund, Sweden, was used in these studies. It utilizes an undulator based focused beam of monochromatized photons in the energy range from 15 to 150 eV. The beam on the sample, focused by a ring-shaped ellipsoidal mirror, has a diameter (FWHM) of 1.5 μm with 10^9-10^{10} photons/sec and a typical bandwidth of 0.1 to 0.2 eV. The emitted photoelectrons from the sample are detected by a hemispherical sector electron energy analyzer mounted in an angle of 47 degrees from the sample normal. The microscope can be operated in two

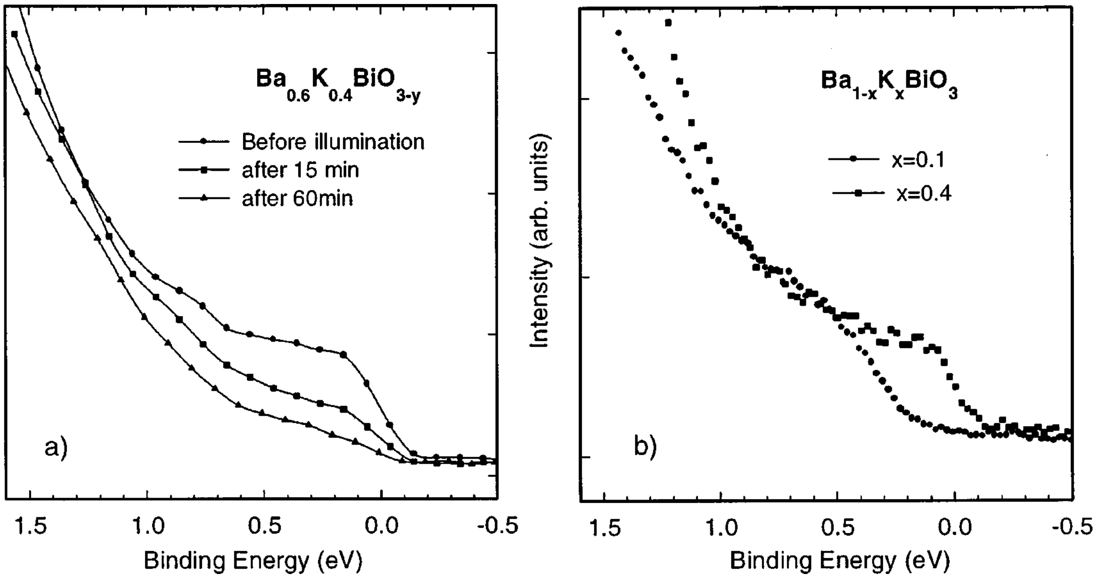

FIG. 3. Photoelectron spectra of $Ba_{1-x}K_xBiO_{3-y}$ in the vicinity of the Fermi level. (a) Illumination dose dependence of the intensity close to the Fermi level for $Ba_{0.6}K_{0.4}BiO_{3-y}$ recorded at the microscope beamline, $E_{ph}=43.2$ eV. (b) Potassium concentration dependence of the intensity close to the Fermi level for $Ba_{1-x}K_xBiO_3$ recorded at BL22 (beam spot $3\times1\ mm^2$), $E_{ph}=95$ eV. All spectra were normalized to the maximum intensity of the VB.

modes; either image is obtained by scanning the sample through the photon beam with the electron analyzer locked to a specific kinetic energy that records the photoelectron intensity, or a selected spot on the sample surface is positioned into the focused photon beam to record a laterally resolved photoelectron spectrum of the surface layer. Images were recorded using the photoelectron signal from the valence band (VB) and all the shallow core levels of Bi, K, Ba, and O. Photoelectron spectra of the VB and shallow core levels were recorded from several different microscopic areas on the sample surface. For comparison photoemission data from semiconducting and superconducting $Ba_{1-x}K_xBiO_3$ with $x=0.1$ and $x=0.4$, respectively, were recorded at photon energies 80–100 eV at BL22 (beam spot-size $3\times1\ mm^2$) which is equipped with a modified Zeiss SX-700 plane grating monochromator[9] and a Scienta-type hemispherical electron energy analyzer.[10]

Figure 1 shows an example of an image from a $120\times120\ \mu m^2$ surface area recorded by electron analyzer locking to the kinetic energy corresponding to the maximum intensity of the VB. Also shown are two photoelectron spectra recorded from different areas of the surface as marked by the crosses in the image. The bright (dark) areas in the image correspond to high (low) intensity of the VB. Images recorded at kinetic energies corresponding to the different core levels of Bi, K, Ba, and O were very similar, which allows us to conclude that the main cause of the intensity distribution is a topography effect. But the important finding is that areas of low intensity (e.g. the ‘‘black’’ area B in the figure) always show an extra structure at 8.5 eV binding energy (BE) (marked by the arrow in spectrum B) which is known to be due to contamination of the surface.[1]

Figure 2(a) shows VB and shallow core level (O $2s$, K $3p$, Ba $5p$) photoelectron spectra from an area which has been exposed to different doses of ZOL. The upper spectrum in Fig. 2(a) recorded before irradiation (0 min), displays fine structures in the VB (shoulders at 4.5 and 6.2 eV binding energy) and a noticable intensity at the Fermi level, all considered to be characteristic of a clean surface[1] and in a good agreement with band structure calculations.[11] The observed large intensity at the Fermi level is of paramount importance since there has been a long discussion [Refs. 1 and 5, and references therein] concerning suppressed Fermi level intensity in the metallic phase of $Ba_{1-x}K_xBiO_3$ as compared to calculated Fermi level density of states. It has been proposed[5] that dynamical structural distortion is responsible for the observed low intensity near the Fermi level due to a pseudogap formation, an effect not accounted for in existing band theories. The present studies show that the intensity at the Fermi level is mainly determined by the surface quality, and the upper spectrum in Fig. 2(a) (0 min) has a Fermi-level intensity (normalized to the maximum intensity of the VB) at least three times larger as compared to the experimental results of Namatame *et al.*[5] under approximately the same experimental conditions ($x=0.38$, $E_{ph}=40.8$ eV). Our laterally resolved experimental results show much better agreement with existing theory[11] than previous experimental findings do.

After exposing the sample to ZOL for 15 min and 40 min [Fig. 2(a)] the spectra display some features that are characteristic of the dielectric behavior. First of all, the intensity at the Fermi level is significantly decreased [cf. Fig. 3(a)] and the whole spectrum (VB and core levels) is shifted towards higher BE by about 0.3–0.4 eV. This BE shift has previously been observed for the dielectric-metal transition due to potassium substitution.[1,5] Figure 2(b) illustrates the situation for different potassium and oxygen doping in $Ba_{1-x}K_xBiO_{3-y}$. The bottom spectrum was recorded at 86.7 eV photon energy at the microscope beamline after exposure (15 min) to ZOL when the sample was transferred to the dielectric state. The middle spectrum (dielectric sample, potassium content $x=0.1$) and the upper spectrum (superconductor, potassium content $x=0.4$) in Fig. 2(b) were recorded at BL22 at approximately the same photon energy (80 eV). The peak po-

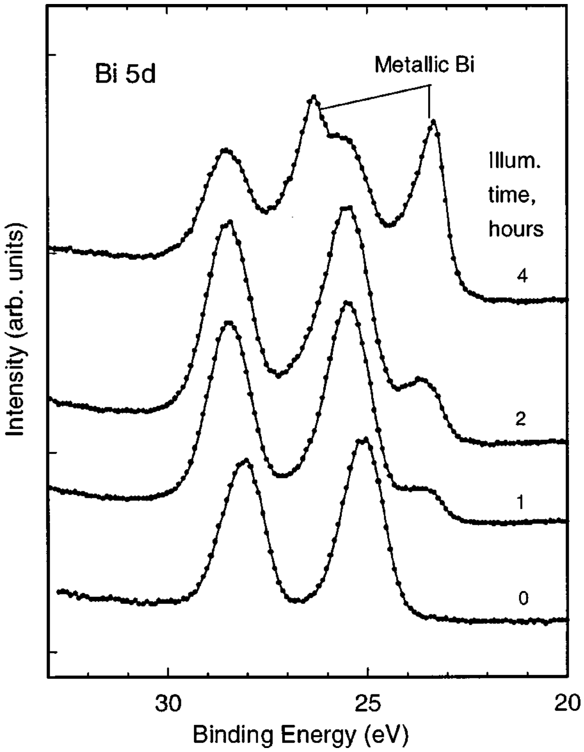

FIG. 4. Bi 5d photoelectron spectra for $Ba_{0.6}K_{0.4}BiO_{3-y}$ for different illumination doses. Appearance of metallic Bi (peaks at 2 eV lower binding energy) can be seen for heavy doses of illumination. $h\nu$=86.85 eV.

sitions for both dielectrics coincide very well, while the metallic sample has a chemical shift (~0.4 eV) towards lower BE. One should notice that the potassium content in the dielectric obtained after ZOL irradiation has not changed from the initial optimal value ($x=0.4$) for the metallic state which can be judged from the K 3p peak intensity (BE 16.5 eV). This directly shows that optimal potassium concentration is not the only condition necessary to provide the metallic conductivity in the system. We believe that the observed transition from the metallic to the dielectric state is caused by a small change of the oxygen concentration.[2–4]

Spectra showing the states close to the Fermi level in $Ba_{0.6}K_{0.4}BiO_{3-y}$ after different ZOL illumination doses are displayed in Fig. 3(a). A steady decrease in intensity, not only at the Fermi level, but also in the vicinity of about 1 eV below is observed. This oxygen doping dependence drastically differs from what has been observed for potassium substituted crystals where the position of E_f followed a ‘‘rigid band’’ behavior. To illustrate this, photoelectron spectra of $Ba_{1-x}K_xBiO_3$ recorded at BL22 for the dielectric ($x=0.1$) and metallic ($x=0.4$) composition in the same energy window as in Fig. 3(a) are presented in Fig. 3(b). One can clearly see the ‘‘rigid band’’ shift which amounts to about 0.35 eV in the case of potassium substitution. Thus, one can conclude that oxygen and potassium doping in $Ba_{1-x}K_xBiO_3$ have a different nature influencing different electronic states near the Fermi level.

As to the question of the nature of the electronic states affected by ZOL treatment, in Fig. 4 spectra within the Bi 5d energy region for a heavy-dose illuminated surface are shown. In addition to the Bi $5d_{5/2,3/2}$ peaks at BE 25 and 28 eV for superconducting $Ba_{0.6}K_{0.4}BiO_3$ a new doublet appears with 2 eV lower BE which is characteristic of metallic Bi.[12,13] Our interpretation of the effect of ZOL treatment is that Bi–O bonds are broken in the surface layer resulting in the formation of metallic Bi. This changes the optimally potassium doped BaKBiO from a metallic state to a dielectric state and this process is quite different from the case of changing the potassium doping at a fixed oxygen concentration.

To conclude, we have performed photoemission measurements on $Ba_{0.6}K_{0.4}BiO_{3-y}$ single crystals at a sample temperature of 130 K using a scanning photoelectron microscopy beamline with a lateral resolution in the micrometer range. In superconducting samples we investigated the VB intensity distribution over the surface on a micrometer scale and found a Fermi level intensity at least three times larger than has been previously reported on high quality crystals investigated by millimeter-size beam spots. Our findings further improve the agreement between band structure calculations and experiment and give no support to the proposed lattice distortion and pseudogap behavior in the metallic state. One of the benefits of using a focused beam is the possibility to affect the surface chemistry. Using ZOL we changed the oxygen content and observed a metal-dielectric transition in $Ba_{0.6}K_{0.4}BiO_{3-y}$ single crystals. We interprete this to be due to the breaking of bonds destroying the Bi-O states close to the Fermi level. This last finding may be important in terms of using a high photon flux on studying solids with easily broken chemical bonds.

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