Supplementary Information for "Superconducting-insulating quantum phase transition associated with valence change in compressed perovskite bismuth-oxides"

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1. Single crystal growth

Single crystals of $Ba_{1-x}K_xBiO_3$ were grown by a modified electrochemical method, in which KOH is served as a flux, as reported in Ref. [1-4]. The samples were prepared by the following steps. First, KOH (~ 45 g) was put into a 100 ml Teflon crucible, and then placed the crucible in a glass reactor which is equipped with electrical heater and magnetic stirrer. Second, the reactor was heated up to 250-255 °C, and then spined at this temperature with a rate of 160 rpm in the continuous flowing of nitrogen gas for several hours. Third, $Ba(OH)_2\times8H_2O$ (~1.5g) and Bi_2O_3 (~3.25g) powder were added into the crucible and then the mixture was spined with a rate of 50-60 rpm for six hours. Fourth, Pt electrodes with diameter about 1mm and Pt tape with dimension of 8 mm × 0.5mm were inserted into the solution to ~ 1.5 cm in depth. The distance between the two electrodes was controlled about 2 cm. During the single crystal growth, a DC current of 1mA-2mA was applied, in which the Pt wire serves as the anode and the Pt tape as the cathode. After growing for 1-2 days, the crystals were grown on the Pt wire, which can be mechanically removed and washed in water.

2. Experimental details for high pressure measurements

High pressure was generated by a diamond anvil cell made of BeCu alloy.

2.1 High-pressure resistance measurements

In the high-pressure resistance measurements, standard four-probe method was applied. Diamond anvils with 300 μm and 400 μm culets (flat area of the diamond anvil) were applied for independent measurements. Au foil was used as electrodes, rhenium plate as a gasket and cubic boron nitride as an insulating material. To keep the sample in a quasi-hydrostatic pressure environment, NaCl powder was employed as the pressure transmitting medium.

2.2 High pressure X-ray diffraction (XRD) measurements

High-pressure XRD experiments were carried out at room temperature at beamline 4W2 at the Beijing Synchrotron Radiation Facility. A monochromatic X-ray beam with a wavelength of 0.6199 Å was employed for the measurements.

2.3 High pressure absorption measurements

High pressure X-ray absorption spectroscopy (XAS) experiments were performed at room temperature at Dynamic and 15U beamlines at the Shanghai Synchrotron Radiation Facility, respectively. Diamonds with culets of 300 μm and low birefringence were selected for the experiments. In the measurements, we used Bi_2O_3 and $NaBiO_3$ as reference materials to identify the peak position of Bi^{+3} and Bi^{5+}, respectively.

Pressure in all measurements is determined by the ruby fluorescence method[5].

3 Extended data and analysis

3.1 Reproducible resistance measurements on the $Ba_{0.57}K_{0.43}BiO_3$ sample

We performed the same high-pressure measurements on the x=0.43 samples that were cut from different batches. As shown in Fig.S1, the results of resistance versus temperature of the measured sample exhibit a similar behavior to that of the samples shown in Fig.2 and Fig.3, *i.e.* a pressure-induced quantum phase transition from superconducting to insulating states presents at the pressure above P_{c2}.

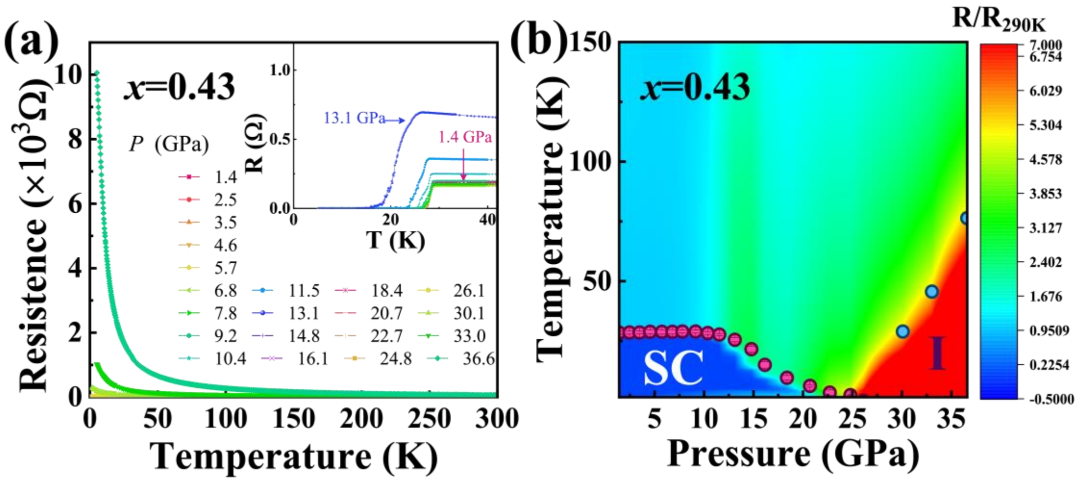

Fig.S1 Temperature dependence of resistance for the x=0.43 samples at different pressures.

3.2 Observation of reversible superconducting-insulating transition measured from the $Ba_{0.57}K_{0.43}BiO_3$ superconductor

To study the possibility of the reversible behavior in $Ba_{1-x}K_xBiO_3$ superconductors, we conducted the high-pressure resistance measurements in the process of releasing pressure for the $Ba_{0.57}K_{0.43}BiO_3$ sample. As shown in Fig.S2, releasing pressure from 23.9 GPa, where the sample shows an insulating state (see violet plot), down to 5.4 and 1.7 GPa, a superconductivity with a zero-resistance state (see red and black plot) was observed. These results clearly indicate a reversible transition between the superconducting state and the insulating state.

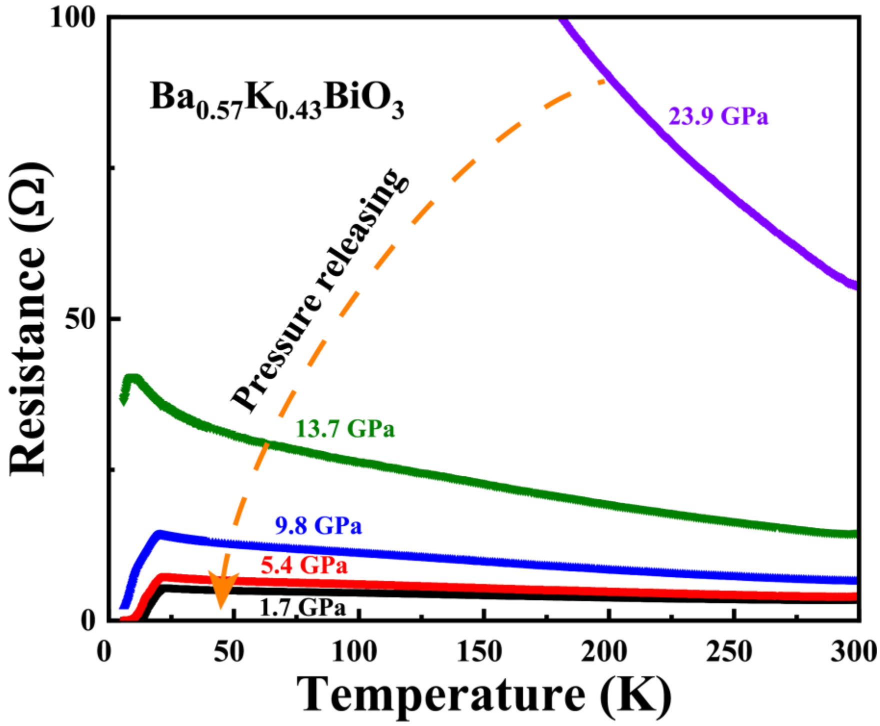

Fig. S2 The temperature dependence of resistance measured from the pressure releasing for the $Ba_{0.57}K_{0.43}BiO_3$ sample.

3.3 High pressure X-ray diffraction results

To clarify whether the quantum phase transition observed in the $Ba_{1-x}K_xBiO_3$ superconductors is related to a pressure-induced crystal structure phase transition, we conducted the high-pressure synchrotron X-ray diffraction measurements on the

$Ba_{0.6}K_{0.4}BiO_3$ sample at 300 K. As shown in Fig. S3a, all peaks can be indexed well by the cubic structure with space group Pm-3m (No.221), and no new peak was observed up to 37.4 GPa. These results indicate that the sample does not undergo any structure phase transition in the pressure range studied. Based on the results, we extract lattice parameter (*a*), volume (*V*) and distance between Bi-O bond as a function of pressure (Fig.S3b-3d). It is seen that *a*, *V* and the distance between Bi-O show a consistent change in the pressure range below P_{c1} and P_{c2}, as well as in the range above P_{c2}.

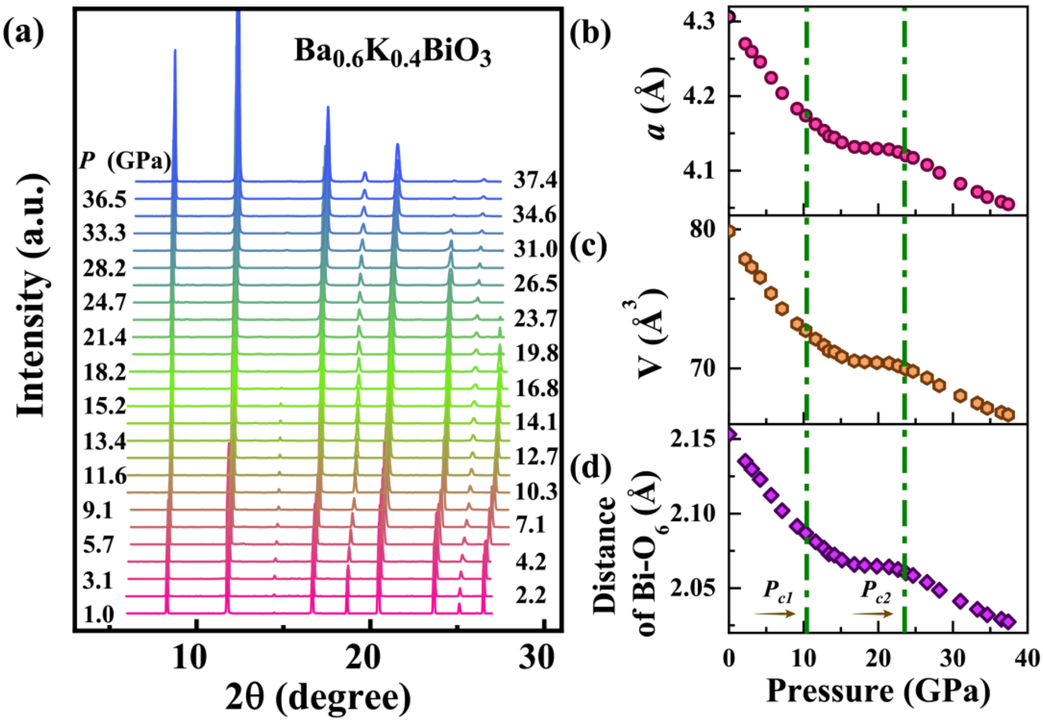

Fig.S3 (a) X-ray diffraction patterns of $Ba_{0.6}K_{0.4}BiO_3$ collected at different pressures, showing no structure phase transition over the pressure range investigated. (b), (c) and (d) Pressure dependences of the lattice parameter (*a*), volume (*V*) and distance between Bi-O bond of $Ba_{0.6}K_{0.4}BiO_3$, respectively.

3.4 Evidence of weak link superconductivity of the compressed sample at pressure between P_{c1} and P_{c2}.

We conducted resistance measurements upon cooling for the x=0.4 sample subjected at 21.5 GPa, the pressure of which is close to P_{c2}, and swept the magnetic field (Fig.S4). It is seen that the compressed sample loses its zero-resistance state. When the magnetic field is applied to 4 T, the superconductivity is completely suppressed. This is quite different from the superconducting behavior of the sample subjected to pressure below P_{c1}, where the sample possesses its superconductivity with zero-resistance at 8 T (Fig.1e). These results indicate that the sample subjected to the pressure close to P_{c2} has a weak link superconductivity.

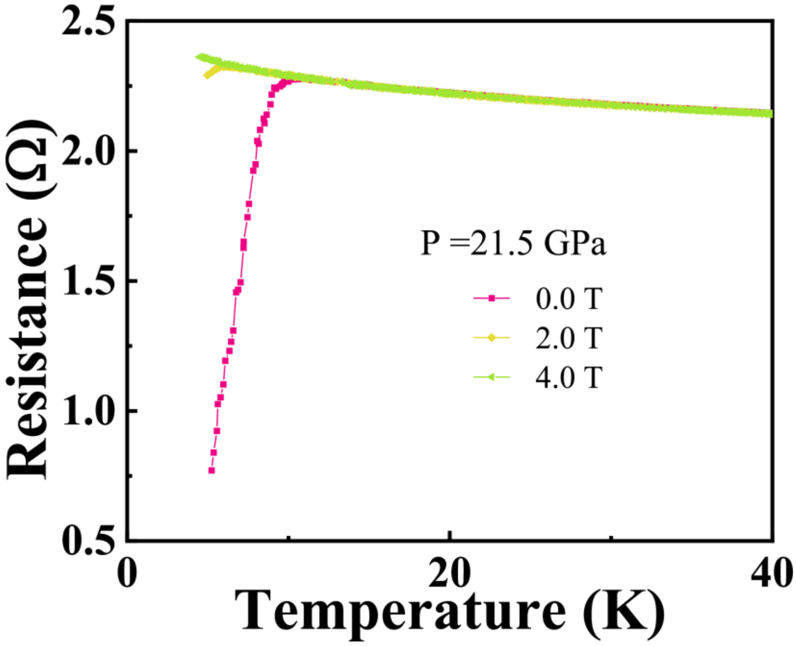

Fig. S4 Temperature dependence of resistance for the compressed sample at 21.5 GPa.

3.5 High-pressure X-ray absorption measurements on the $Ba_{1-x}K_xBiO_3$ (x=0.40 and 0.52) superconductors and data analysis

To clarify the valence change induced by external pressure, high-pressure X-ray absorption measurements on L_{III}-Bi absorption edge were performed at Dynamic and 15U beamlines at Shanghai Synchrotron Radiation Facility. Fig. S5 show the energy dependence of absorption data for the x=0.40 and x=0.52 samples, respectively. In the experiments, we took Bi_2O_3 and $NaBiO_3$ as reference materials to indicate the peak position of Bi^{3+} and Bi^{5+}. We found that the spectra of the x=0.40 and x=0.52 samples displayed the same trend – the peak shifts to the higher energy upon increasing pressure. Subsequently, we estimated the mean valence (ν) of Bi ions by the method reported in Ref. [6] for the compressed sample at each pressure, and plot ν versus pressure (Fig.4d). We found that ν increases with elevating pressure and reaches 5^+ at the pressure around P_{c2}, where a quantum phase transition occurs. Significantly, ν returns to 3.8^+ from 5^+ when the pressure is released down to 3.7 GPa (pink plot in Fig. S5a). The result is in accordance with our resistance measurements for the sample released from high pressure, whose superconductivity recovers as the pressure is released down to 5.7 GPa (Fig.S2).

We also extracted pressure dependence of the mean valence (ν) of Bi ions for the second sample (x=0.52) and plotted it with its T_c as a function of pressure (Fig.S6). Although its P_{c1} and P_{c2} are slightly different from that of the x=0.4 sample, the change trend of ν with pressure is the same for the two samples (Fig.4d). ν shows an increase with elevating pressure and approach to 5+ at P_{c2}, where the superconducting state is destroyed and the insulating state emerges.

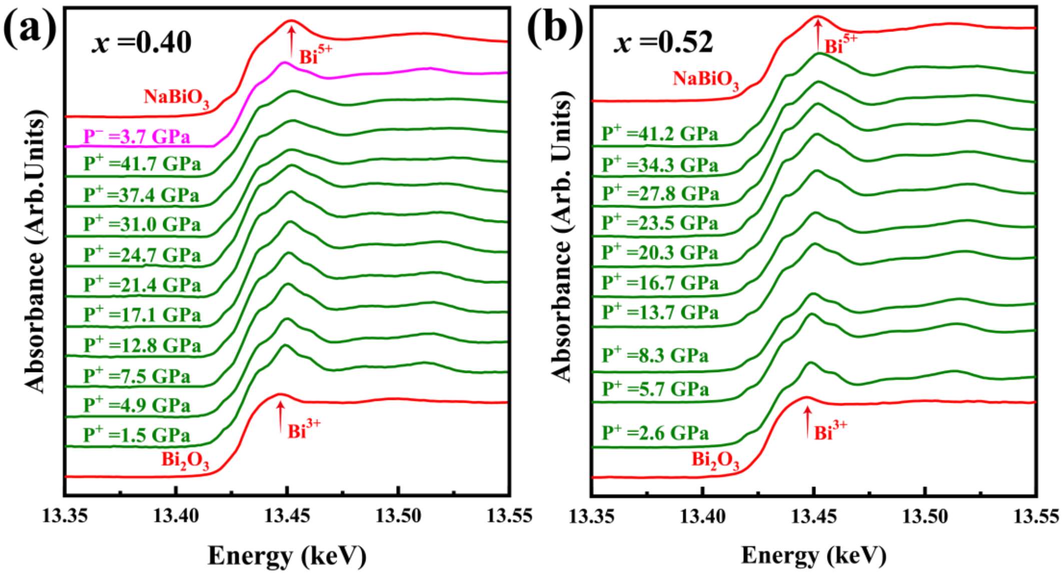

Fig. S5 X-ray absorption spectra of the $Ba_{1-x}K_xBiO_3$ (x=0.40 and 0.52) superconductors measured at different pressures. The green and pink data were collected upon increasing (P^+) and decreasing (P^-) pressures. The red data are the ambient-pressure spectra of the reference material Bi_2O_3 and $NaBiO_3$.

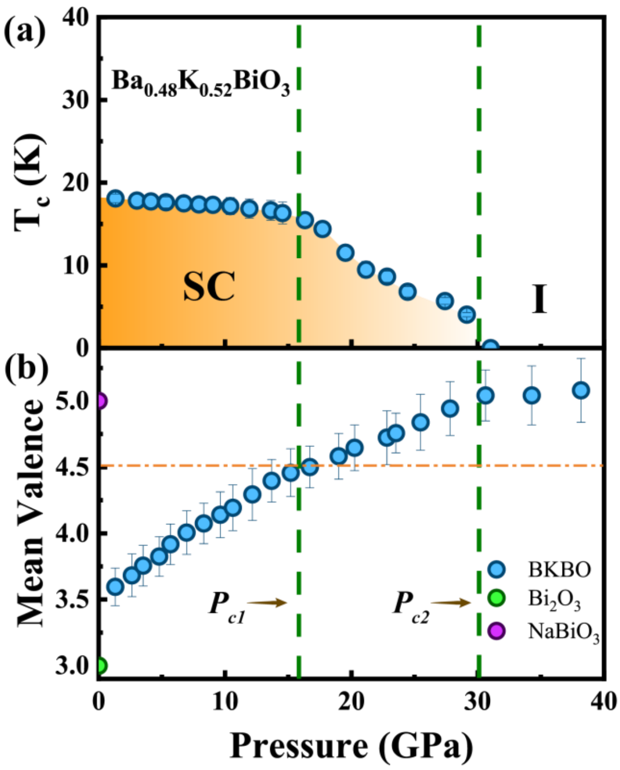

Fig.S6 (a) Pressure-T_c phase diagram for the x=0.52 sample. (b) Mean valence (ν) of Bi ions in $Ba_{1-x}K_xBiO_3$ (x=0.52) as a function of pressure.

3.6 High-pressure X-ray absorption measurements on the $Bi_2Sr_2CaCuO_{8+\delta}$ superconductor and data analysis

To investigate the possibility of the pressure-induced valence change in bismuth-bearing cuprates, we performed high-pressure X-ray absorption measurements on the hole-doped superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$ up to 48.2 GPa, where the sample moves in an insulating-like state [7]. It is found that no dramatic valence change is observed in the pressure range of superconducting-insulating transition (Fig.S7).

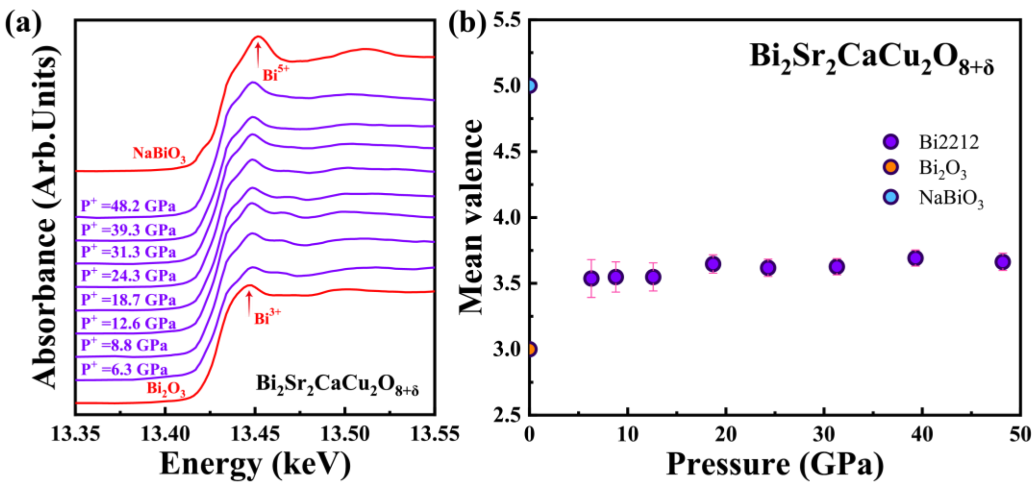

Fig. S7 (a) X-ray absorption spectra of the $Bi_2Sr_2CaCuO_{8+\delta}$ superconductor measured at different pressures. The red data are the ambient-pressure spectra of the reference material Bi_2O_3 and $NaBiO_3$. (b) Mean valence (ν) of Bi ions in $Bi_2Sr_2CaCuO_{8+\delta}$ as a function of pressure. The orange and blue solid stand for the main valence of Bi_2O_3 and $NaBiO_3$.

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