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Anionogenic mixed valency in $K_xBa_{1-x}O_{2-\delta}$: Supporting information

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The frequencies ν of the Raman-active O-O stretching modes were calculated for the sixteen possible combinations of cations that coordinate an oxygen dimer octahedrally in $K_xBa_{1-x}O_{2-\delta}$, not including coordinations of six Ba^{2+} or six K^+ . The results are listed in Table S1.

We calculated the frequencies of the Raman-active O-O stretching modes for different chemical compositions by constructing supercells with doubled c -axes corresponding to $K_{0.25}Ba_{0.75}O_2$, $K_{0.5}Ba_{0.5}O_2$ and $K_{0.75}Ba_{0.25}O_2$ ($x=0.25, 0.5$ and 0.75 respectively).

For $x=0.25$ (Fig. S1a) we obtained four modes at frequencies of 1089 cm^{-1} (corresponding to the stretching of Dimer 1 coordinated by four K^+ and two Ba^{2+}), 895 cm^{-1} (stretching of Dimer 2 coordinated by six Ba^{2+}), 891 cm^{-1} (anti-phase stretching corresponding to coupling between Dimer 2 coordinated by six Ba^{2+} and two Dimers 3 coordinated by five Ba^{2+} and one K^+), and 880 cm^{-1} (anti-phase stretching of coupled Dimers 3 coordinated by five Ba^{2+} and one K^+).

For $x=0.75$ (Fig. S1c) we also obtained four modes: 1154 cm^{-1} (stretching of Dimer 1 coordinated by six K^+), 1083 cm^{-1} (anti-phase stretching of coupled Dimers 3 coordinated by five K^+ and one Ba^{2+}), 1061 cm^{-1} (anti-phase stretching corresponding to coupling between Dimer 1 coordinated by six K^+ and two Dimers 3 coordinated by five K^+ and one Ba^{2+}), and 867 cm^{-1} (stretching mode of Dimer 2 coordinated by four Ba^{2+} and two K^+).

For $x=0.5$ (Fig. S1b), four Raman-active modes were calculated, at 1134 cm^{-1} (in-phase stretching of two equivalent Dimers 1 and 1' coordinated by five K^+ and one Ba^{2+}), 1068 cm^{-1} (anti-phase stretching of Dimers 1 and 1' coordinated by five K^+ and one Ba^{2+}), 887 cm^{-1} (in-phase stretching of two equivalent Dimers 2 and 2' coordinated by one K^+ and five Ba^{2+}), and 868 cm^{-1} (anti-phase stretching of Dimers 2 and 2' coordinated by one K^+ and five Ba^{2+}).

Table S1. Calculated frequencies ν for O-O stretching modes of isolated dimers with different coordinations

ν (cm^{-1})	ab plane	c -axis
1098	4K	Ba, K
1079	4K	2Ba
973	3K, 1Ba	2K
952	3K, 1Ba	Ba, K
938	3K, 1Ba	2Ba
938	2K ^a 2Ba ^a	2K
917	2K ^a 2Ba ^a	Ba, K
916	2K ^o 2Ba ^o	2K
901	2K ^a 2Ba ^a	2Ba
895	2K ^o 2Ba ^o	2Ba
890	2K ^o 2Ba ^o	Ba, K
886	4Ba	2K
879	4Ba	Ba, K
876	3Ba, K	2K
862	3Ba, K	Ba, K
853	3Ba, K	2Ba

The calculated frequencies are for isolated oxygen dimers that are octahedrally coordinated by different combinations of cations in the ab plane and in the c -direction, listed in order of descending frequency. Superscript ^o denotes cations located opposite to each other in the ab plane. Superscript ^a denotes cations adjacent to each other in the ab plane.

The supercells in Figs. S1a-c only allow inter-layer coupling because there is only one dimer per layer. Given

the good agreement between the calculated and experimental frequencies for the $x=0.5$ supercell in Fig. S1b, we also explored the effect of simultaneous intra-layer and inter-layer coupling by constructing a supercell for $x=0.5$ with doubled b and c -axes (Fig. S1d), in which there are two dimers per layer. Eight Raman-active modes were calculated with frequencies at:

- a) 1135 cm^{-1} (in-phase stretching of four equivalent Dimers 1, 1', 1'' and 1□ coordinated by five K^+ and one Ba^{2+} , inter-layer coupling only);
- b) 1073 cm^{-1} (anti-phase stretching of the four Dimers 1, 1', 1'' and 1□, inter-layer coupling only; Dimers 1 and 1'' in one layer become longer, while Dimers 1' and 1□ in the adjacent layer become shorter, or vice versa);
- c) 1019 cm^{-1} (anti-phase stretching of two Dimers 1 and 1'', intra-layer coupling only);
- d) 1003 cm^{-1} (anti-phase stretching of two Dimers 1' and 1□, intra-layer coupling only; the frequency should be the same as c) but there is a small discrepancy due to the phonon calculation procedure in which the system was first relaxed before the frequencies were calculated);
- e) 888 cm^{-1} (in-phase stretching of four equivalent Dimers 2, 2', 2'' and 2□ coordinated by one K^+ and five Ba^{2+} , inter-layer coupling only);
- f) 869 cm^{-1} (anti-phase stretching of the four Dimers 2, 2', 2'' and 2□, inter-layer coupling only; Dimers 2 and 2'' in one layer become longer, while Dimers 2' and 2□ in the adjacent layer become shorter, or vice versa);
- g) 855 cm^{-1} (anti-phase stretching of two Dimers 2 and 2'', intra-layer coupling only);
- h) 855 cm^{-1} (anti-phase stretching of two Dimers 2' and 2□, intra-layer coupling only).

Comparing the frequencies obtained above with the experimental Raman peaks, we notice that intra-layer coupling modes c) and d) do not appear experimentally, whereas all the inter-layer coupling modes a), b), e) and f) are observed. We cannot determine whether intra-layer coupling modes g) and h) are experimentally observed because they would coincide with the broad $\sim 840\text{ cm}^{-1}$ peak attributed to inter-layer coupling. However, we can conclude from the absence of modes c) and d) that intra-layer coupling in $\text{K}_x\text{Ba}_{1-x}\text{O}_2$ is negligible. The reason for this is probably the significant difference in dimer-dimer distances. For inter-layer coupling the dimers are separated by $\sim 3.40\text{ \AA}$, whereas the corresponding distance for intra-layer coupling is $\sim 3.86\text{ \AA}$.

We also carried out phonon calculations on antiferromagnetic KO_2 and paramagnetic BaO_2 (using the experimental body-centered tetragonal structures for both) in order to check the validity of our calculations on $\text{K}_x\text{Ba}_{1-x}\text{O}_2$. For KO_2 we obtained an in-phase stretching mode at 1177 cm^{-1} (Raman active) and an anti-phase stretching mode at 1010 cm^{-1} (Raman forbidden – see main text). Experimentally, only one mode is observed, in the range $1141\text{--}1143\text{ cm}^{-1}$.^{1,2} For BaO_2 we calculated an in-phase stretching mode at 906 cm^{-1} (Raman active) and an anti-phase mode at 901 cm^{-1} (Raman forbidden), which compares with a single experimentally observed mode in the range $843\text{--}851\text{ cm}^{-1}$.³

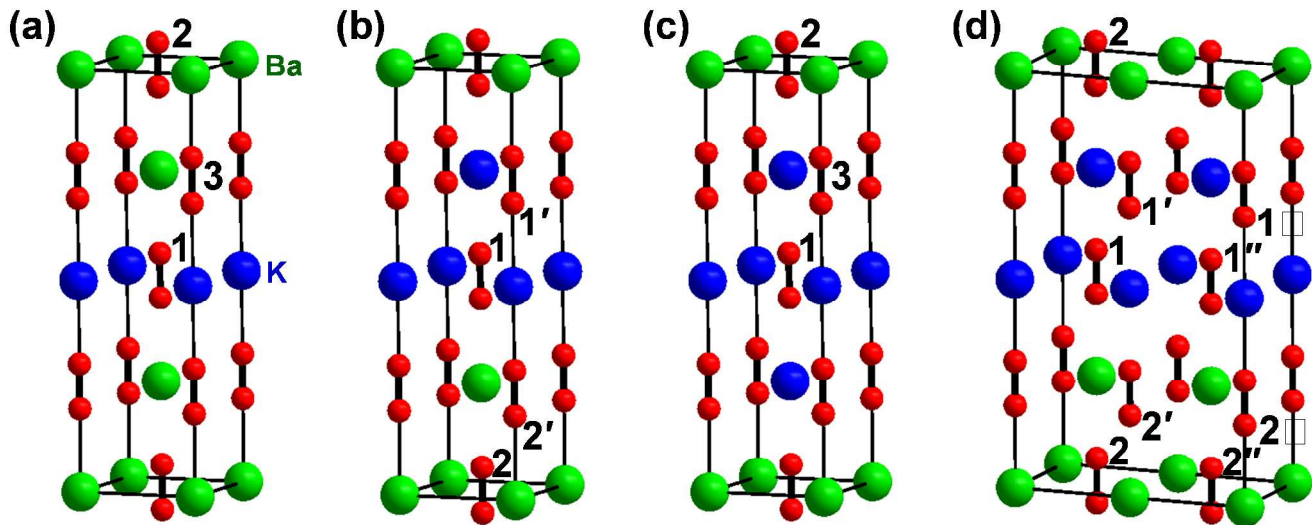


Figure S1. Supercells constructed for phonon calculations on (a) $\text{K}_{0.25}\text{Ba}_{0.75}\text{O}_2$, (b) $\text{K}_{0.5}\text{Ba}_{0.5}\text{O}_2$, (c) $\text{K}_{0.75}\text{Ba}_{0.25}\text{O}_2$ and (d) $\text{K}_{0.5}\text{Ba}_{0.5}\text{O}_2$ (doubled b and c -axes). The labels 1, 2 and 3 refer to oxygen dimers discussed in the text.

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