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Supplementary Information - Defect chemistry and electrical properties of $BiFeO_3$

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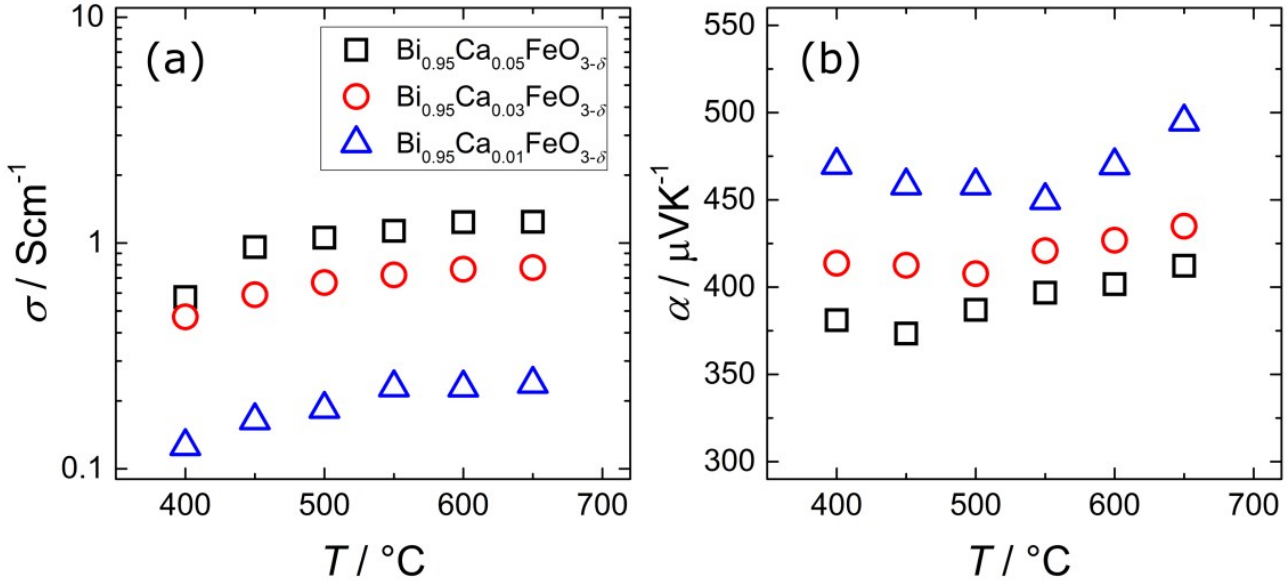

Figure 1S. Temperature dependence of electrical conductivity σ **(a)** and Seebeck coefficient α **(b)** of $Bi_{1-x}Ca_xFeO_{3-\delta}$ measured in pure O_2.

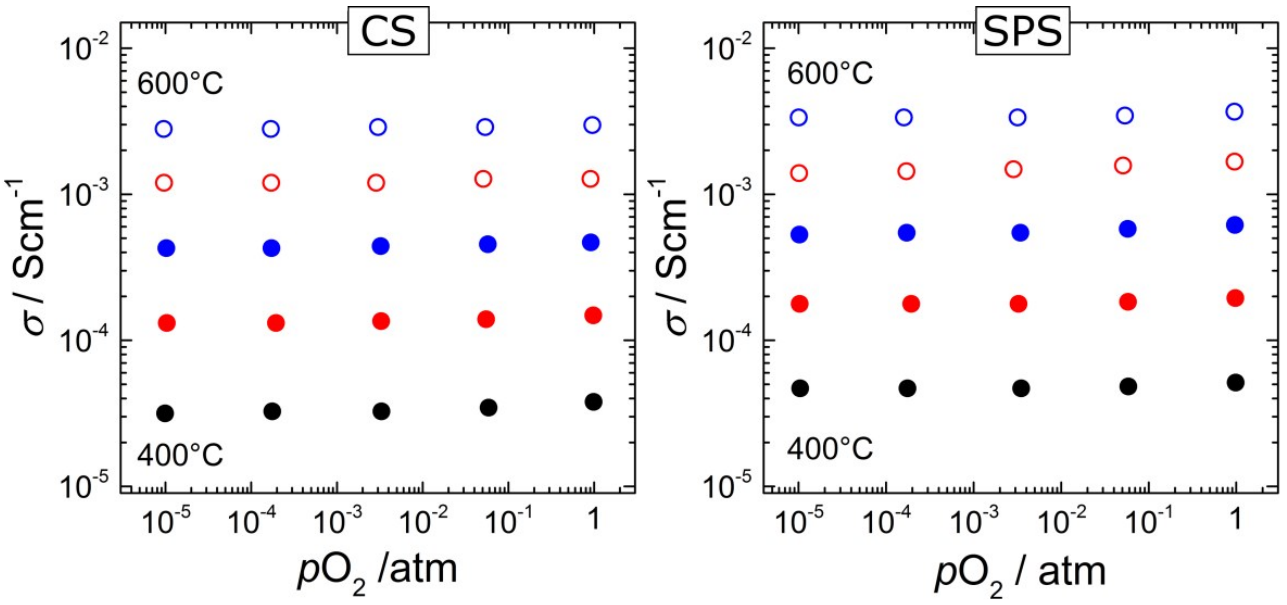

Figure 2S. Conductivity against oxygen partial pressure at different temperatures for $BiFeO_3$ ceramics prepared by mechanosynthesis and sintered either conventionally (CS) or by spark plasma sintering (SPS), Ref [24]

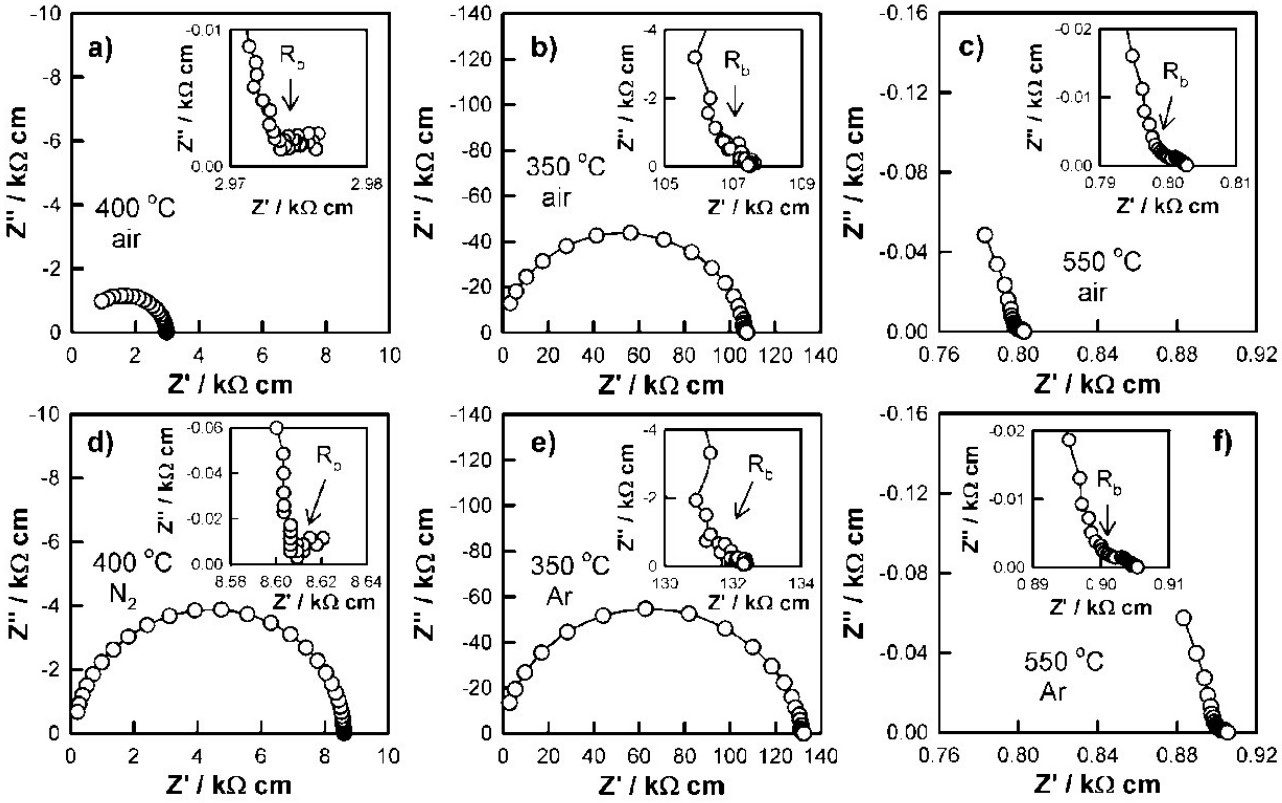

Figure 3S. Impedance data of nominally undoped BFO at different temperatures and atmospheres.

Figure 3S shows impedance data for undoped $BiFeO_3$ measured under various atmospheres. A single, almost ideal, semicircular arc, whose low-frequency intercept gives the total resistance of the sample, is observed in the impedance complex plane plots, Z" *vs* Z', and represents the bulk response of the sample, R_b. The associated capacitances are in the range ~10 to ~50 pF cm^{-1} and increase on increasing the temperature. In addition, above 500°C, a small low-frequency arc or "tail" with an associated resistance < 10 is observed and it may be associated to a Schottky barrier between the sample–electrode interface. Importantly, the low frequency impedance data terminate with the low frequency intercept of the arc on the Z′ axis (insets) independently of the measuring atmosphere and, therefore, there is no evidence of an additional, inclined Warburg spike attributed to charge transfer impedances at the sample−electrode−air interface. Thus, the charge carriers appear to be electronic in nature rather than ionic.

Details on the optimization procedure

The defect chemical model proposed here, allows to calculate the total conductivity and Seebeck coefficient for a given set Λ of the five parameters included. Since both coefficients are dependent on the same free parameters, standard curve-fitting algorithms implemented in many software tools cannot be used here. In order to calculate the dashed lines in Figs. 1 and 5, we therefore used a custom-made script described in the following. We define a deviation function, which, for a given parameter set Λ sums up the relative deviation of both conductivity and Seebeck coefficient:

$$f(\Lambda) = \sum_{p(O_2)} \frac{(\sigma_{Exp} - \sigma_{Calc}(\Lambda))^2}{(\sigma_{Exp} + \sigma_{Calc}(\Lambda))^2} + \sum_{p(O_2)} \frac{(\alpha_{Exp} - \alpha_{Calc}(\Lambda))^2}{(\alpha_{Exp} + \alpha_{Calc}(\Lambda))^2}$$

Here, the indices Exp and Calc refer to the experimental and modelled values, and the summation is performed over all measured oxygen partial pressures. This function is evaluated for a large number ~10^7 of different parameter sets Λ with each parameter within Λ spanning a large range of reasonable values. Starting from the parameter set, which resulted in the lowest deviation, we then minimize f further by subsequently varying one parameter at a time.