Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Tailoring the structure and thermoelectric properties of $BaTiO_3$ via Eu^{2+} substitution

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Polar modes comprise all the symmetry-breaking atomic displacements causing ferroelectric transitions, normally cation off-centerings with respect to their coordination cage, which relate to the centre (Γ point) of the Brillouin zone; to non-polar modes, or zone-boundary modes (R point), belong, for example, the rotational modes that cause the antiferrodistortive transition in both $EuTiO_3$ and $SrTiO_3$. The Γ_4^- transformation, which is responsible for the ferroelectric transition in $BaTiO_3$[1], can lead to the space groups *P*4*mm*, *Amm*2, or *R*3*m* depending on the direction of the order parameter, i.e. the off-centering of Ti or Ba/Eu. This means that an electric dipole could form, respectively, in the directions <100>, <110>, or <111> with respect to the parent cubic structure.

A pure $BaTiO_3$ sample has been prepared and the transport properties have been evaluated under the same conditions as the substituted ones. Regarding the very large electrical resistivity of $BaTiO_3$ at room temperature, it was not possible to measure the electrical transport properties below 473 K with our ZEM measurement system. The electrical conductivity of $BaTiO_3$ was around 16 S/m at 1123 K, which is extremely lower than that of our Eu^{2+} substituted samples. Compared with Eu^{2+} substituted samples, $BaTiO_3$ sample possesses a much higher Seebeck coefficient in the entire investigated temperature range. The carrier concentration of $BaTiO_3$ was estimated to be 8.5×10^{18} cm^{-3} at 1123 K according to Heikes formula, and the calculated carrier mobility was 0.13 $cm^2V^{-1}s^{-1}$, which is consistent with reference data [2,3]. As shown in Figure 1(a), the thermal conductivity of $BaTiO_3$ sample

possess a similar trend as $Ba_{1-x}Eu_xTiO_3$ ($x \leq 0.3$). The transition around 390 K is due to both a phase transition of tetragonal to cubic and a Curie transition [4]. The lattice thermal conductivity of $BaTiO_3$ (Figure 2(b)) also follows the trend which we expected.

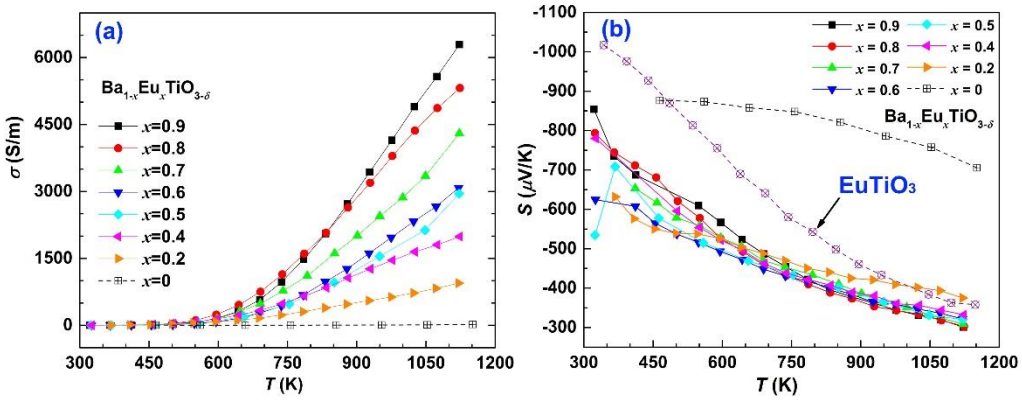

Fig.S1. Temperature dependence of the electrical conductivity (a) and Seebeck coefficient (b) of $Ba_{1-x}Eu_xTiO_{3-\delta}$ samples

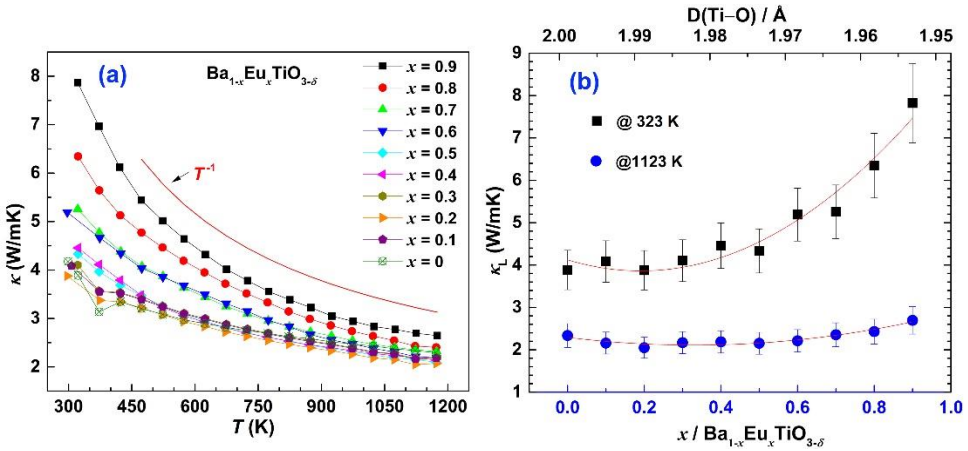

Fig.S2. Temperature dependence of the thermal conductivity κ (a) and the lattice thermal conductivity κ_L (b) of $Ba_{1-x}Eu_xTiO_{3-\delta}$ as a function of the Eu^{2+} content x and Ti–O distance at 323 K and 1123 K.

References

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