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 ($\Gamma$ 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 $I^e_4$ transformation, which is responsible for the ferroelectric transition in BaTiO$_3$\textsuperscript{1}, can lead to the space groups $P4mm$, $Ammm$, or $R3m$ 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 $8.5 \times 10^{18}$ cm$^{-3}$ at 1123 K according to Heikes formula, and the calculated carrier mobility was 0.13 cm$^2$V$^{-1}$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 $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_3$ ($x \leq 0.3$). The transition around 390 K is due to both a phase transition of tetragonal to cubic and a Curie transition. The lattice thermal conductivity of $\text{BaTiO}_3$ (Figure 2(b)) also follows the trend which we expected.

Fig. S1. Temperature dependence of the electrical conductivity (a) and Seebeck coefficient (b) of $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_3-\delta$ samples

Fig. S2. Temperature dependence of the thermal conductivity $\kappa$ (a) and the lattice thermal conductivity $\kappa_L$ (b) of $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_3-\delta$ as a function of the Eu$^{2+}$ content $x$ and Ti–O distance at 323 K and 1123 K.

References