Supporting Information

Roles of Na doping in BiCuSeO oxyselenides

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Experimental Details

Samples with the chemical composition $Bi_{1-x}Na_xCuSeO$ (x=0, 0.005, 0.01, 0.015, 0.02) were synthesized by a two-step solid state reaction route. All raw materials including Na_2Se are purchased from Alfa Aesar. A stoichiometric mixture of Bi_2O_3 (4 N), Bi (3 N), Cu (3 N), Se (5 N) and Na_2Se(3 N) powders was mixed by hand in mortar and pressed into bars which were then sealed in silica tubes, under vacuum, and heated at 573 K for 15 h. The obtained materials were crushed into powders, and then cold pressed into bars and heated again at 973 K for another 15 h in sealed silica tubes. After that, obtained columns were ground into powders, the obtained powders were densified by a spark plasma sintering system (Sumimoto SPS1050, Japan) under an axial compressive stress of 50 MPa in vacuum at 973 K for 6 min, resulting in a disk-shaped sample of Ø 15 × 10 mm. The obtained SPS processed pellets were cut along the radial direction of the disk sample into bars with dimensions of about 12 mm × 3 mm × 3 mm that were used for simultaneous measurement of the Seebeck coefficient and the electrical conductivity using an Ulvac Riko ZEM-3 instrument (ZEM-3, ULVAC-RIKO, Japan) under a helium atmosphere from room temperature to 923 K. The thermal conductivity was calculated from $\kappa=DC_p\rho$, where the thermal diffusivity (D) was measured using the laser flash diffusivity method in a Netzsch LFA427 (NETZSCH, LFA427, Germany), the thermal diffusivity data were analyzed using a Cowan model with pulse correction and heating and cooling cycles gave reproducible values for each sample. The specific heat capacity (Cp) was determined by differential scanning calorimetry (NETZSCH DSC 404C Germany). The density (ρ) was determined by using the dimensions and mass of the sample, which was then reconfirmed using the Archimedes method. The Hall coefficients, R_H, of the samples were measured at room temperature using a Hall effect measurement system (SWIN,

Hall8800, Taiwan China), and a magnetic field of 0.5T was applied. The carrier concentration (n_H) was calculated by $nH=1/eR_H$, where e is the electronic charge. The carrier mobility (μ) was calculated by $\mu=\sigma R_H$, where σ is the electrical resistivity.

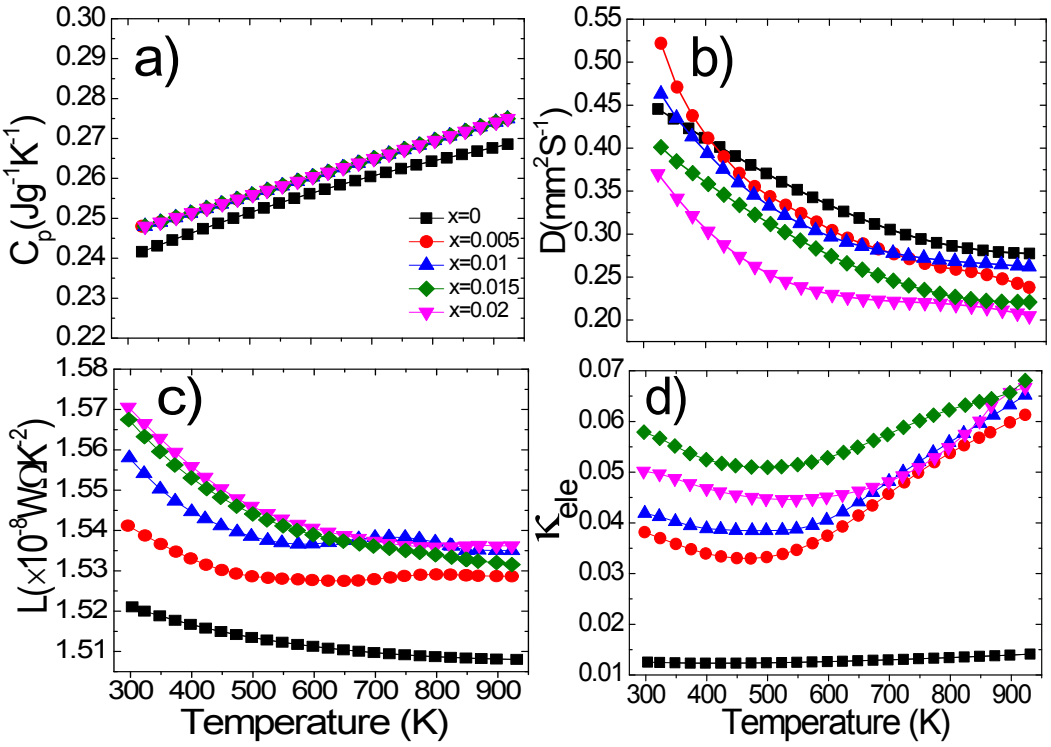

Figure S1: Thermoelectric properties as a function of temperature for $Bi_{1-x}Na_xCuSeO$ samples: (a) Heat capacity; (b) Thermal diffusivity; (c) Lorenz number; d) Electronic thermal conductivity