Supporting Information

Phase Transitions and Phonon Mode Dynamics of $Ba(Cu_{1/3}Nb_{2/3})O_3$ and $Sr(Cu_{1/3}Nb_{2/3})O_3$ for Understanding Thermoelectric Response

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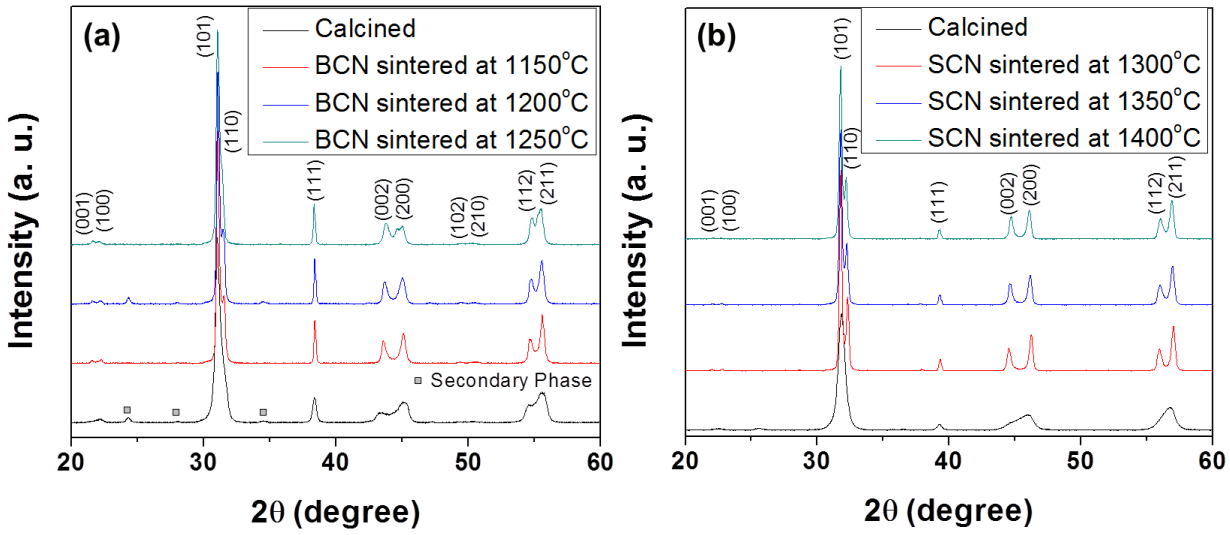
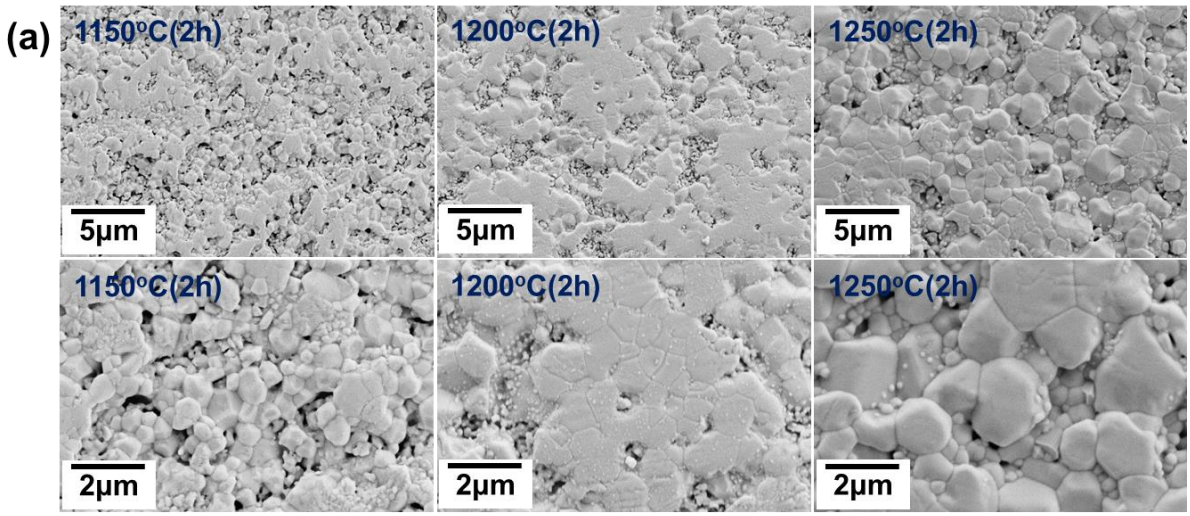


Figure S1. XRD patterns of (a) $Ba(Cu_{1/3}Nb_{2/3})O_3$ (BCN) and (b) $Sr(Cu_{1/3}Nb_{2/3})O_3$ (SCN) ceramics calcined and sintered at various temperatures for 2 h.



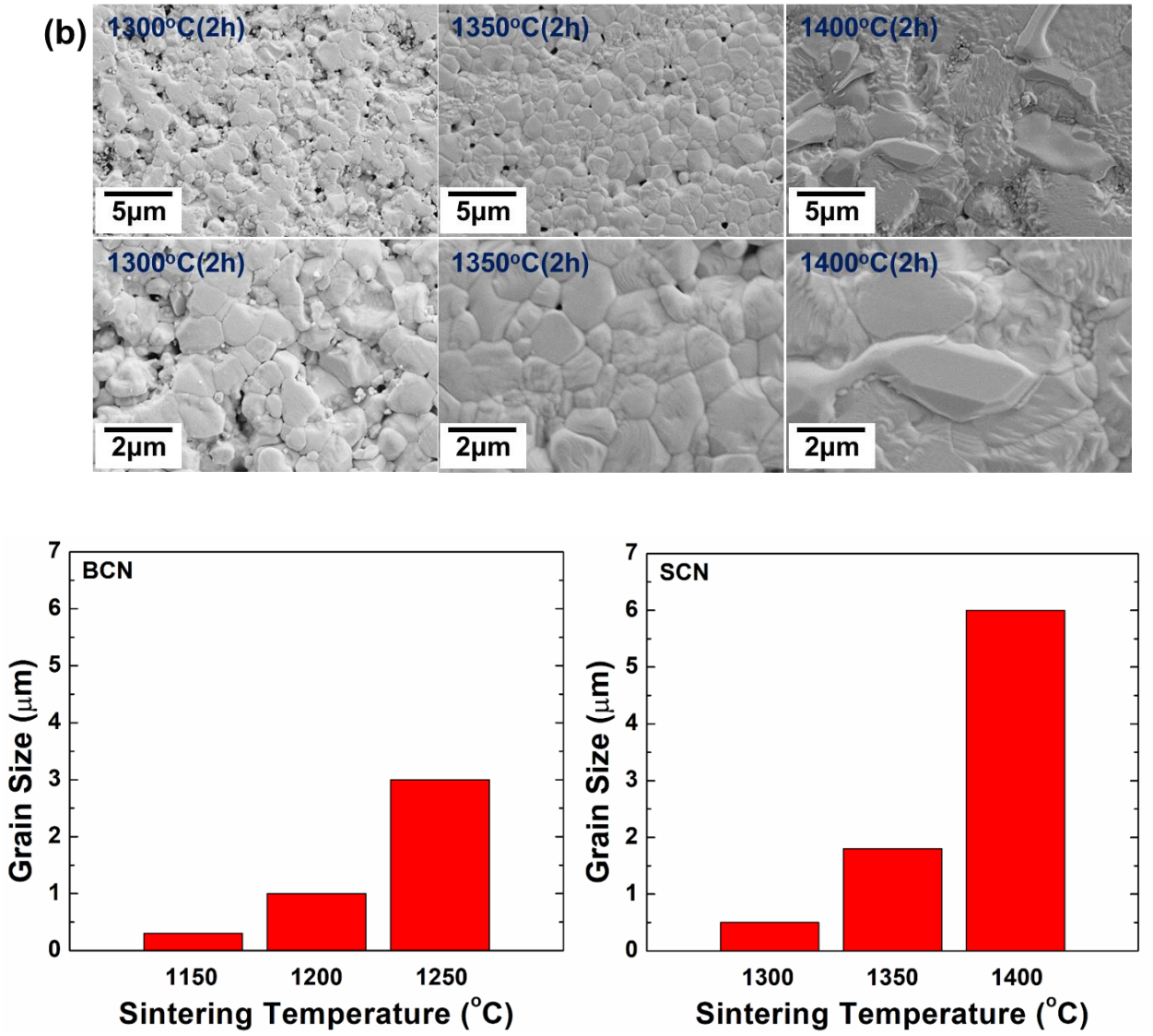


Figure S2. FESEM images of (a) $Ba(Cu_{1/3}Nb_{2/3})O_3$ (BCN) and (b) $Sr(Cu_{1/3}Nb_{2/3})O_3$ (SCN) ceramics sintered at various temperatures for 2 h. The histogram refers to the grain sizes in both the samples.

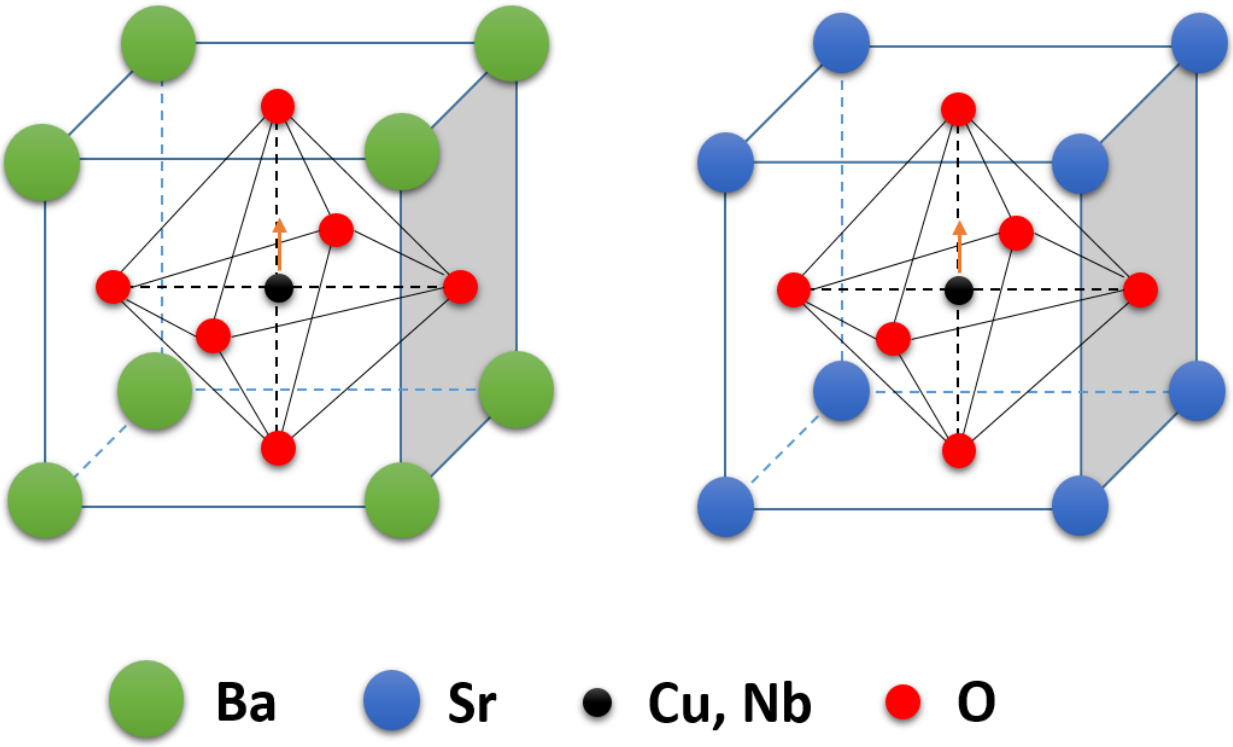


Figure S3. Schematic view of the crystalline structure of $A(Cu_{1/3}Nb_{2/3})O_3$ (A=Ba, Sr) and partial substitution of Ba/Sr on A sites in the perovskite structure. The displacement of A sites and 1:2-repeated Cu and Nb cation sites are omitted for clarity.

SCN / BCN powders - Second Harmonic Generation (SHG)

Second Harmonic Generation (SHG) measurements were undertaken using a pulsed Nd:YAG laser (1064nm). The powders were mounted in between two cover slips surrounded by a plastic washer, with a thickness of 1 mm. The fundamental was recorded by splitting the beam and using a photodiode. The SHG signal was measured using a photomultiplier tube with filters to prevent the fundamental from being detected – no signal was detected in the photomultiplier tube if no sample was present in the beampath. The laser was pulsed at 1 Hz and up to 500 repeat iterations

were collected and averaged mathematically. A $K_{0.5}Na_{0.5}NbO_3$ (KNN) reference sample was used to calibrate the system to have a strong SHG signal.

Figure S4 shows the results of the SHG patterns. The KNN shows a clear signal at the same laser power settings and conditions. The SCN and BCN powders do not show any evidence of a second harmonic signal above the background in an average over 500 iterations. However, this result does not imply that the material must be centrosymmetric, as it is only the signal that confirms it must be non-centrosymmetric. The samples may either a) be centrosymmetric b) have a very weak non-linear optical response so that the peak is below the detectable threshold, or c) be strongly absorbing in either the infrared or green wavelengths.

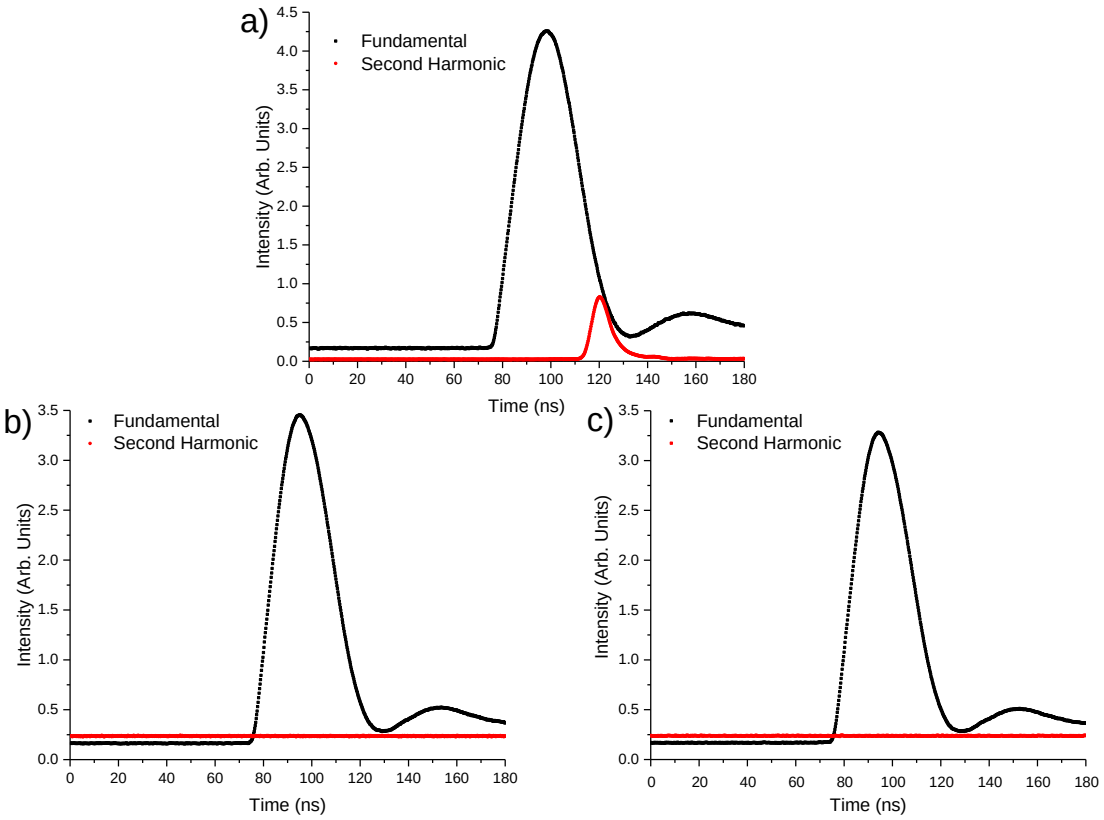
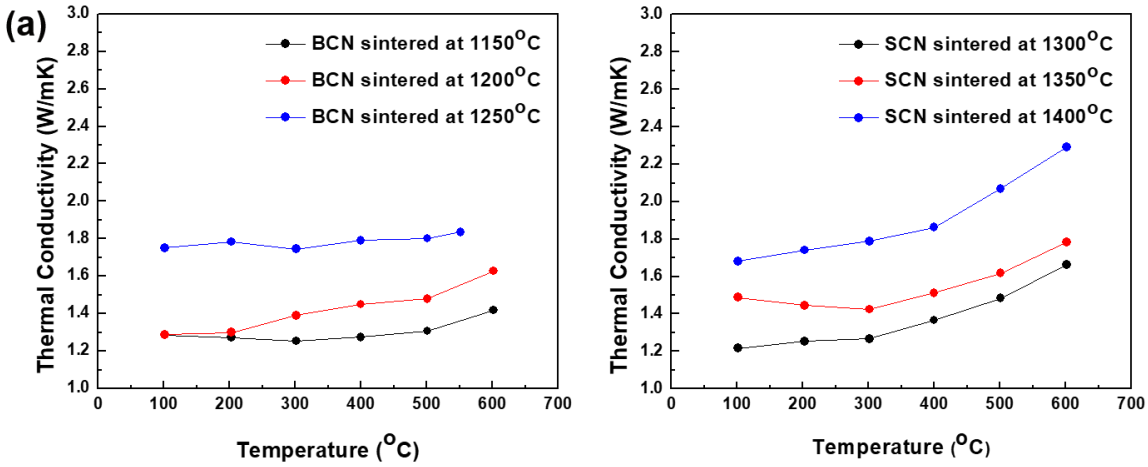
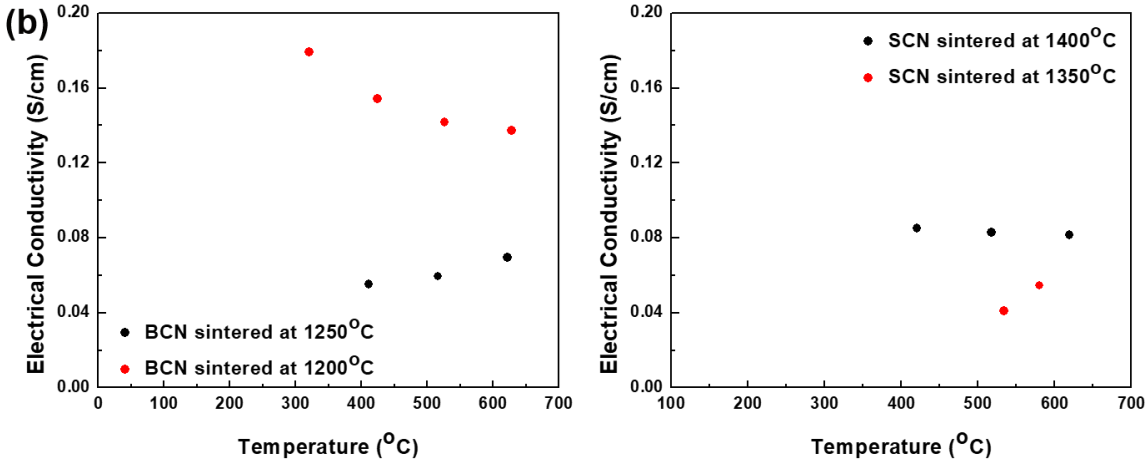
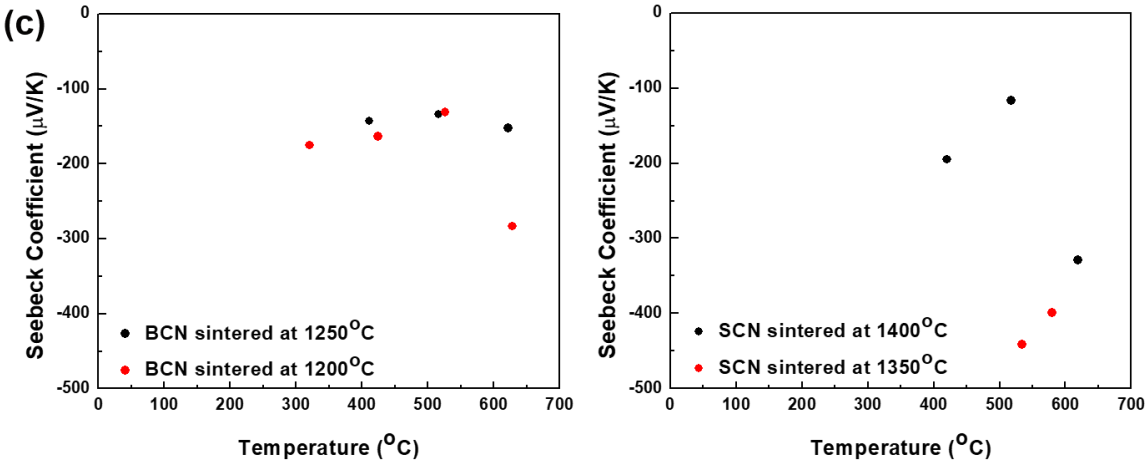


Figure S4. SHG from a) KNN reference sample b) SCN powder c) BCN powder. Neither the SCN nor BCN powders show a detectable second harmonic signal over 500 iterations.


(a)
Thermal Conductivity (W/mK)
Temperature (°C)
BCN sintered at 1150°C
BCN sintered at 1200°C
BCN sintered at 1250°C
SCN sintered at 1300°C
SCN sintered at 1350°C
SCN sintered at 1400°C


(b)
Electrical Conductivity (S/cm)
Temperature (°C)
BCN sintered at 1250°C
BCN sintered at 1200°C
SCN sintered at 1400°C
SCN sintered at 1350°C


(c)
Seebeck Coefficient (μV/K)
Temperature (°C)
BCN sintered at 1250°C
BCN sintered at 1200°C
SCN sintered at 1400°C
SCN sintered at 1350°C

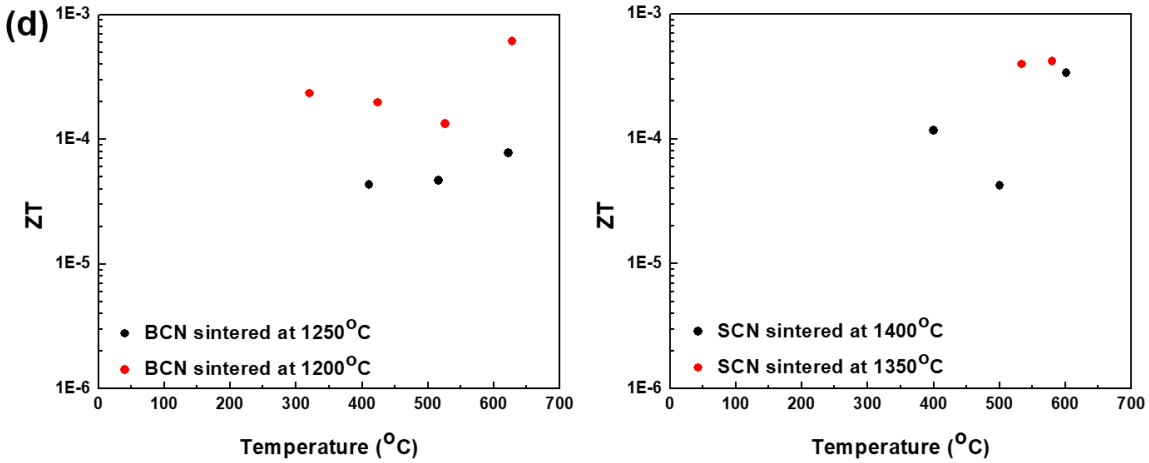


Figure S5. The (a) thermal conductivity, (b) electrical conductivity, (c) Seebeck coefficient, and (d) *ZT* of $Ba(Cu_{1/3}Nb_{2/3})O_3$ (BCN) and $Sr(Cu_{1/3}Nb_{2/3})O_3$ (SCN) ceramics sintered at various temperatures for 2 h.