Synthesis and Thermoelectric Properties of $Ce_yRu_{4-x}Ir_xSb_{12}$ Filled Skutterudite Compounds

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Outline

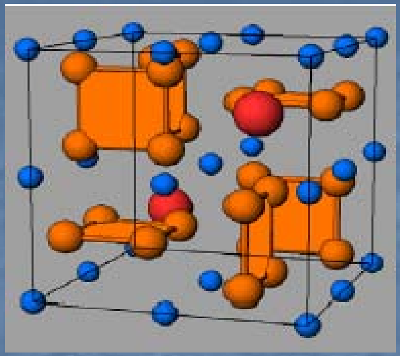
- Motivation
- Synthesis
- Physical Properties
- Thermal Transport Properties
- Further Exploration

Motivation

- Radioisotope Thermoelectric Generators (RTGs) have offered reliable, long-lived electrical power on many important NASA deep space missions.
- Past RTGs used PbTe/TAGS and SiGe.
- Skutterudite based unicouples have been under development at JPL since 1997.
  - Materials to date are limited to 975 K hot junction operation
  - p-$Ce_1Fe_3Ru_1Sb_{12}$; n-CoSb3
- Drive to improve thermoelectric efficiency and specific power of RTG's up to a hot-junction temperature of 1275 K.

Current Materials

JPL has developed skutterudite thermoelectric unicouples utilizing p-$Ce_1Fe_3Ru_1Sb_{12}$ and n-$CoSb_3$ which are capable of operating up to a ~ 975 K hot-junction temperature.



Skutterudite Crystal Structure

Skutterudite unicouple

Substitute Ru and Ir for Fe in an effort to develop more refractory skutterudite compounds and push hot-junction temperature to 1275 K

Element	Melting Point (K)
Fe	1808
Ru	2583
Ir	2683

New Composition : $Ce_yRu_{4-x}Ir_xSb_{12}$

$Ce_yRu_{4-x}Ir_xSb_{12}$ Synthesis

- The Ce filling fraction was selected and calculated according to the Ce filling fraction phase diagram established for $Ce_yFe_{4-x}Co_xSb_{12}$ compositions.
  - $Ce_{0.95}Ru_{3.5}Ir_{0.5}Sb_{12.0}$
  - $Ce_{0.9}Ru_{3.25}Ir_{0.75}Sb_{12.0}$
  - $Ce_{0.9}Ru_{3.0}Ir_{1.0}Sb_{12.0}$
- Ce pieces, Sb shots, Ru and Ir powders combined in BN crucible and placed in quartz ampoule. Evacuated to 10^{-5} Torr and sealed.
- Heated to 1475 K for at least 12 hours, water quenched, annealed at 1275 K for 48 hours.
- Milled under Ar for 10 minutes and powder pressed in graphite die at 975 K for 90 minutes.

$Ce_yRu_{4-x}Ir_xSb_{12}$ - Composition

Composition and Geometric Density, d, of p-type Skutterudite Materials

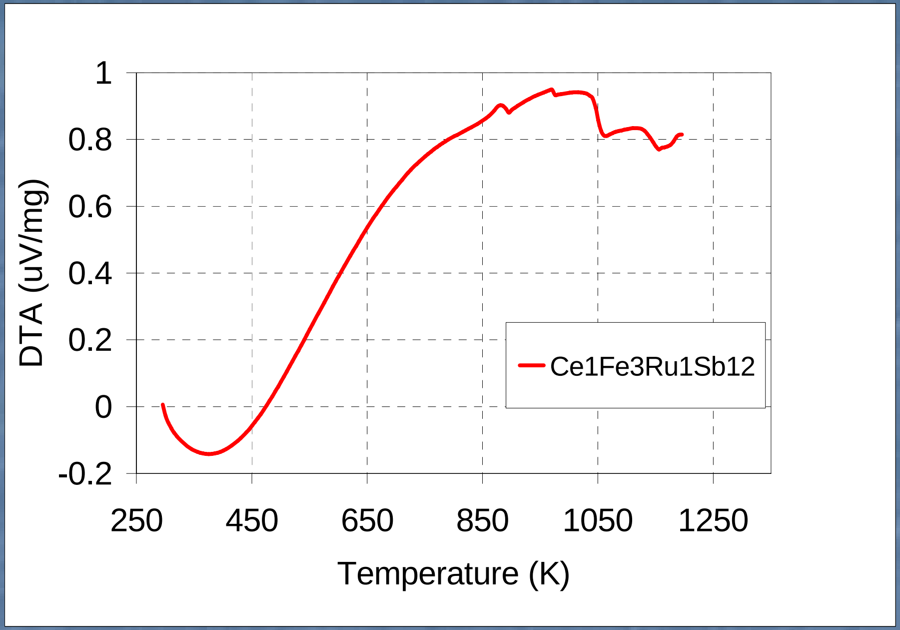
Composition	d (g/cm³)
$Ce_{0.95}Ru_{3.5}Ir_{0.5}Sb_{12.0}$ (NSKP21)	8.41
$Ce_{0.9}Ru_{3.25}Ir_{0.75}Sb_{12.0}$ (NSKP29)	8.46
$Ce_{0.9}Ru_{3.0}Ir_{1.0}Sb_{12.0}$ (NSKP23)	8.15

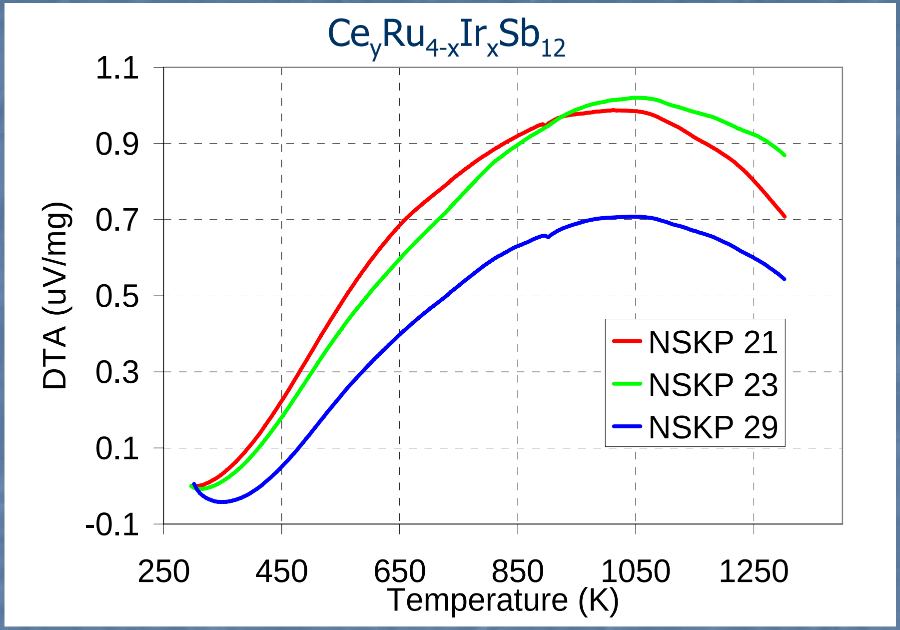
Samples' geometric densities are 95-98% of the calculated theoretical values

Microprobe analysis revealed that the samples were ≥97% phase pure.

Impurities were primarily $RuSb_2$ and $CeSb_2$

Differential Thermal Analysis





No decomposition was observed for $Ce_yRu_{4-x}Ir_xSb_{12}$ up to 1275 K.

Decomposition onset temperature for p-type $Ce_1Fe_3Ru_1Sb_{12}$ was ~ 1040 K.

Sublimation

- Sublimation is potentially one of the main degradation mechanisms of thermoelectric unicouples for power generation, therefore a low sublimation rate is desirable for thermoelectric materials.
- Beginning of life sublimation rates are decreased by an order of magnitude with $Ce_yRu_{4-x}Ir_xSb_{12}$ compared to low-temperature p-type $Ce_1Fe_3Ru_1Sb_{12}$.
- With an adequate insulating material (e.g aerogel), the sublimation rate could be decreased to an acceptable level (~10^{-7} g/cm^2/hr) for long-term operation.

Sublimation rates (g/cm^2/hr) for p-type skutterudite materials at several temperatures.

Sample	973 K	1073 K	1173 K
$Ce_1Fe_3Ru_1Sb_{12}$	1.04×10^{-3}	-	
$Ce_{0.95}Ru_{3.5}Ir_{0.5}Sb_{12}$	5.45×10^{-4}	1.52×10^{-3}	8.00×10^{-3}
$Ce_{0.9}Ru_{3.25}Ir_{0.75}Sb_{12}$	3.09×10^{-4}	1.64×10^{-3}	9.27×10^{-3}
$Ce_{0.9}Ru_{3.0}Ir_{1.0}Sb_{12}$	1.83×10^{-4}	9.13×10^{-4}	8.08×10^{-3}

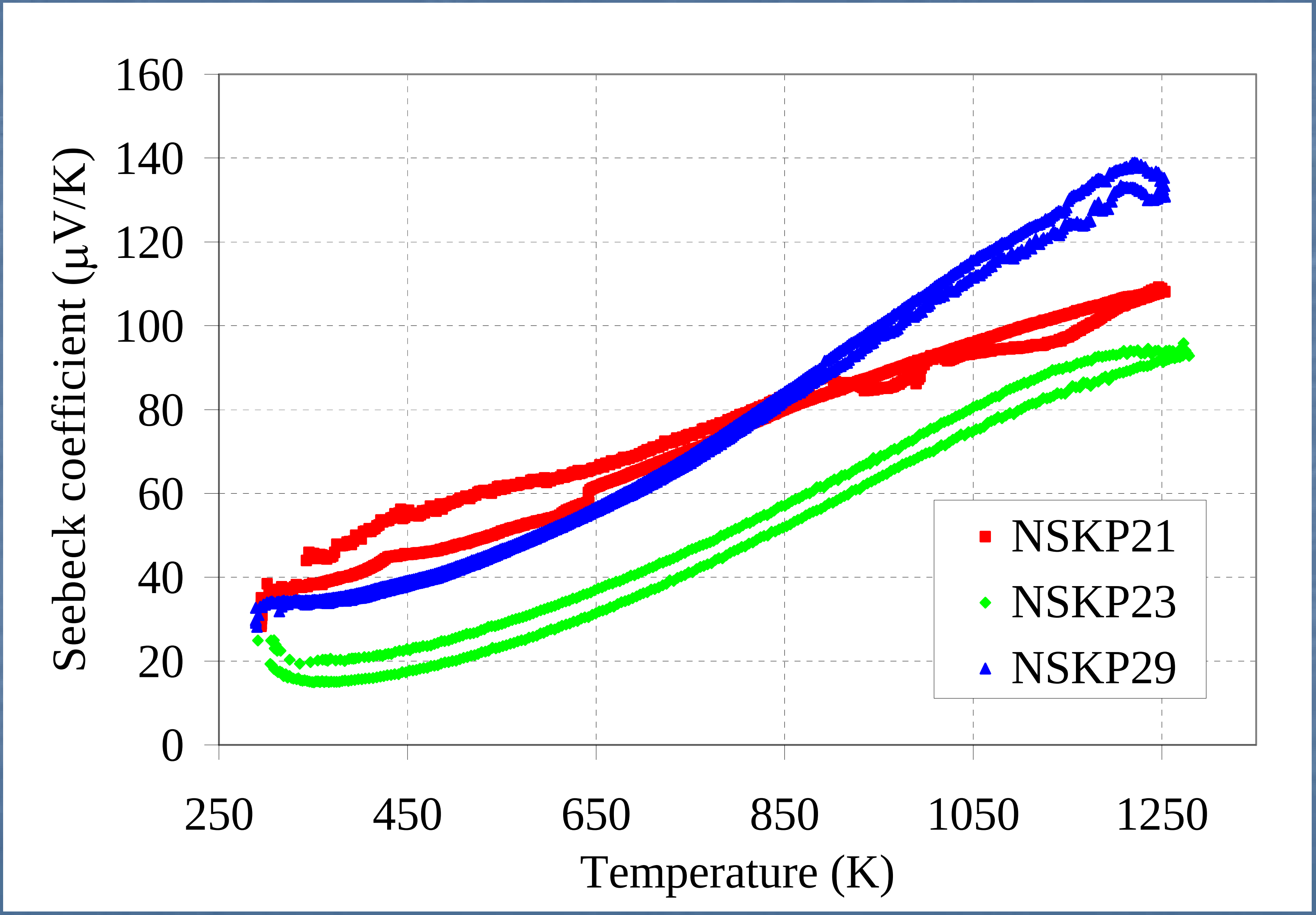
Thermal Transport Properties

Room temperature measurements show that electrical resistivity increases with increasing Ir concentration, while the Seebeck coefficient and thermal conductivity both decrease

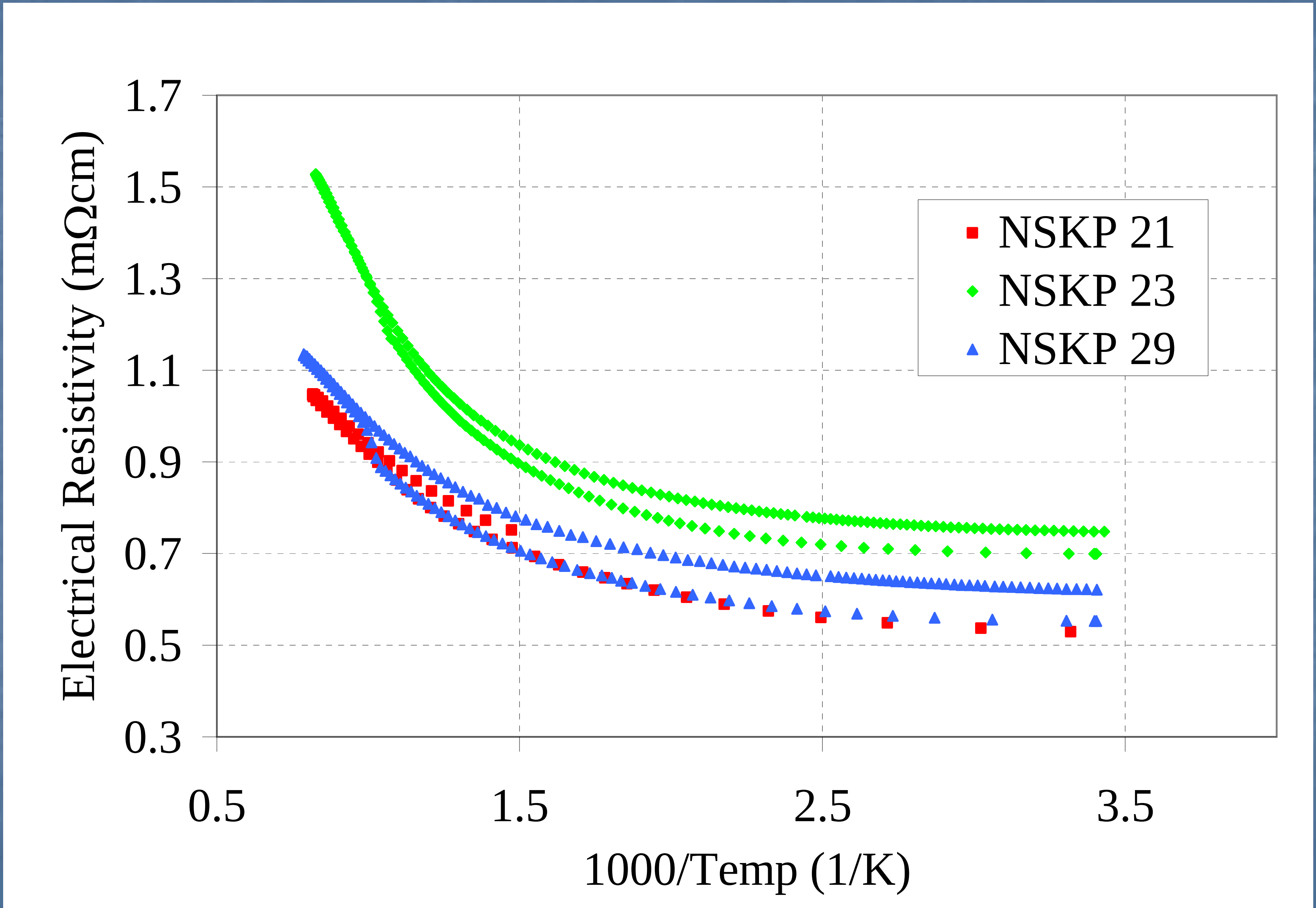
Thermal transport properties of $Ce_yRu_{4-x}Ir_xSb_{12}$ materials at 300 K. (S, Seebeck coefficient; ρ, electrical resistivity; κ, thermal conductivity)

Sample ID	S (μV/K)	ρ (mΩcm)	κ (mW/cmK)
$Ce_1Fe_3Ru_1Sb_{12}$	61.0	0.54	25
$Ce_{0.95}Ru_{3.5}Ir_{0.5}Sb_{12}$	40.0	0.46	33.4
$Ce_{0.9}Ru_{3.25}Ir_{0.75}Sb_{12}$	28.7	0.55	32.6
$Ce_{0.9}Ru_{3.0}Ir_{1.0}Sb_{12}$	14.0	0.70	27.9

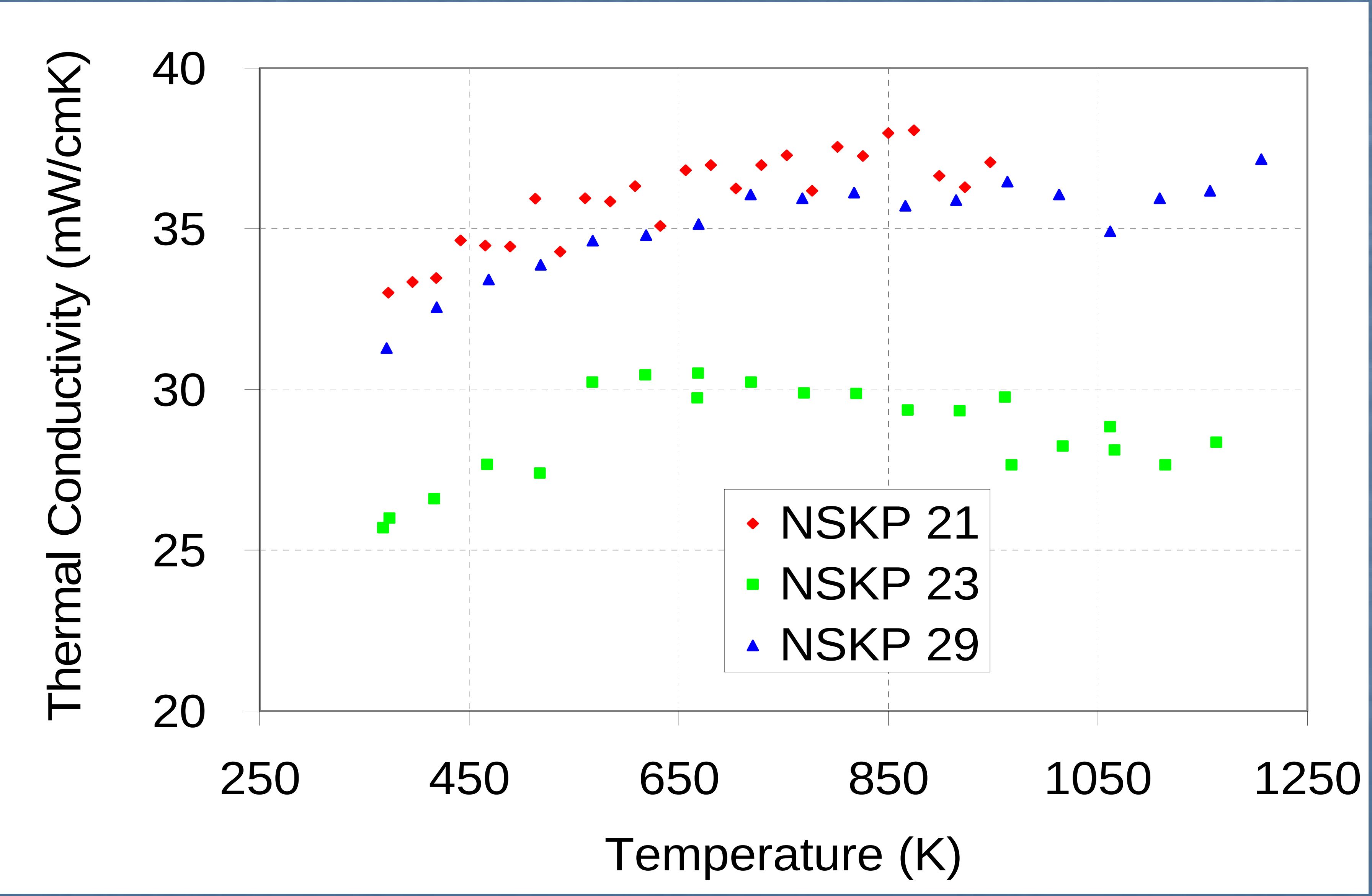
Seebeck Coefficient



Electrical Resistivity



Thermal Conductivity



Summary of Results

- The best ZT value was obtained for the $Ce_{0.9}Ru_{3.25}Ir_{0.75}Sb_{12.0}$ composition with a value of ~ 0.7 at 1275 K.
- The thermal conductivity for the $Ce_yRu_{4-x}Ir_xSb_{12}$ compositions are inherently low up to 1275 K.
- Further improvements in ZT values can likely be achieved by further increasing the Seebeck coefficient at high-temperatures.
  - The Ce filling fraction needs to be further established for the $Ce_yRu_{4-x}Ir_xSb_{12}$ system to allow for the preparation of single-phase samples as the Ir concentration is increased.

Conclusions

- $Ce_yRu_{4-x}Ir_xSb_{12}$ is thermally stable up to 1275 K, an improvement over previous p-type skutterudite material ($Ce_1Fe_3Ru_1Sb_{12}$).
- May be suitable for long term operation in an advanced RTG environment when segmented with low temperature p-type material and an appropriate insulating material (e.g. aerogel)

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