Fabrication of oxide multilayer thermoelectric generators

Fraunhofer IKTS

Ernst-Abbe-Hochschule Jena
University of Applied Sciences

B. Capraro[1], D. Schabbel[1], R. Löhnert[2], A. Bochmann[2], A. Ibrahim[2], J. Töpfer[2]
[1]Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Hermsdorf, Germany
[2]Ernst-Abbe-Hochschule Jena, University of Applied Sciences, SciTec Department, Jena, Germany

ABSTRACT

Oxide-based thermoelectric multilayer generators (TEG) are fabricated using the ceramic multilayer process with oxide thermoelectric green tapes and printed metal layers. This technology is an interesting option enabling miniaturization and allowing for easy mass fabrication of multilayer TEGs. We demonstrate the fabrication of transverse multilayer thermoelectric generators (TMLTEG) with charge transport perpendicular to the heat flow direction. These generators consist of layers of tape-cast p- or n-type thermoelectric oxides in combination with metal layers printed at a certain angle with respect to the heat flow direction to create anisotropic thermoelectric properties. Applications include autonomous sensor systems with low power consumption.
We report on the tape casting of thermoelectric oxides of $Ca_3Co_4O_9$, La_2CuO_4 and $CaMnO_3$ powders including optimization of the casting slurry composition and lamination behavior. We also report on screen-printing and testing of various precious metal paste systems as well as on the co-firing behavior of oxide tapes with metal layers. We demonstrate the layer stacking and fabrication of transverse multilayer generators (TMLTEG) using various thermoelectric oxides.

MULTILAYER TECHNOLOGY OF TMLTEG-FABRICATION

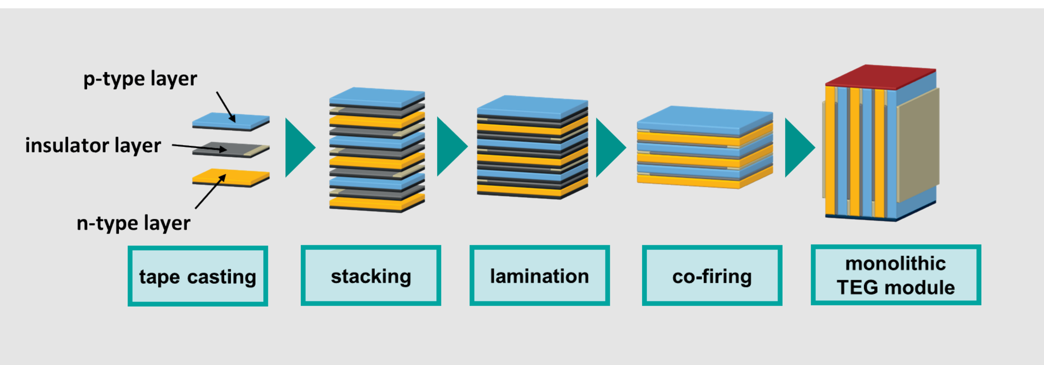

Figure 1: Standard multilayer ceramic technology for preparing MLTEG.

TRANSVERSAL THERMOELECTRIC EFFECT & MULTILAYER TECHNOLOGY

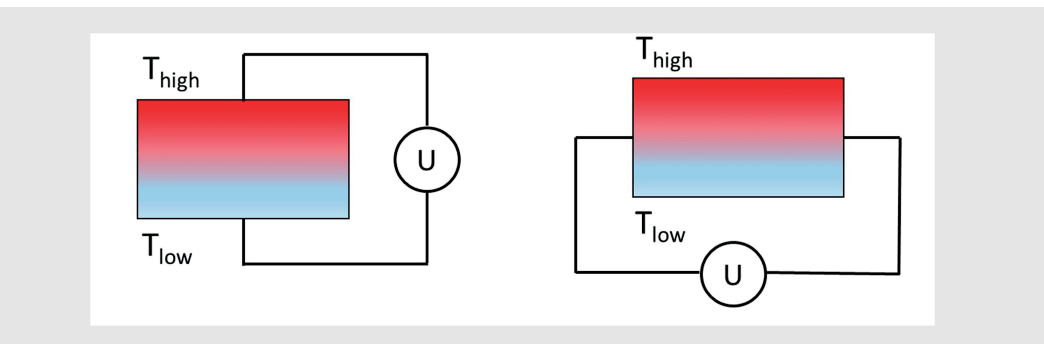

Figure 2: Longitudinal (left) and transverse thermoelectric effect (right).

- current und heat flow perpendicular to each other
- anisotropic thermoelectric properties required
- single crystals, thin films, or artificial anisotropy
- rotated stack of alternating metal/oxide layers
- 2 materials only

$$Z_{long}^{max}\bar{T} = \frac{(S_{ox}-S_{met})^2}{\left(\sqrt{L_{ox}}+\sqrt{L_{met}}\right)^2} \qquad Z_{tr}^{max}\bar{T} = \frac{(S_{ox}-S_{met})^2}{\left(\sqrt{L_{ox}}+\sqrt{L_{met}(1+Z_{long}\bar{T})}\right)^2}$$

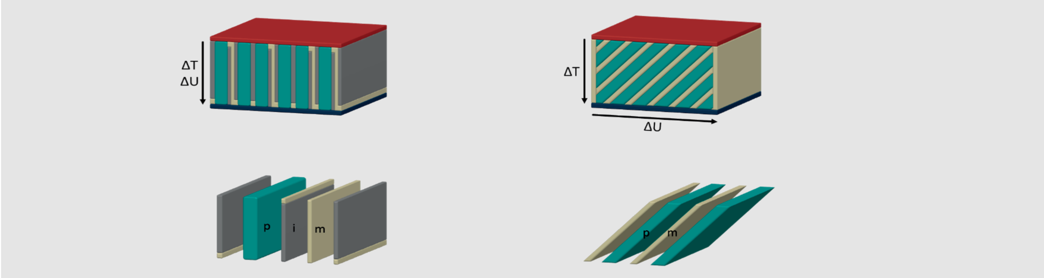

Figure 3: Figure of merit, longitudinal (left) and transverse (right).

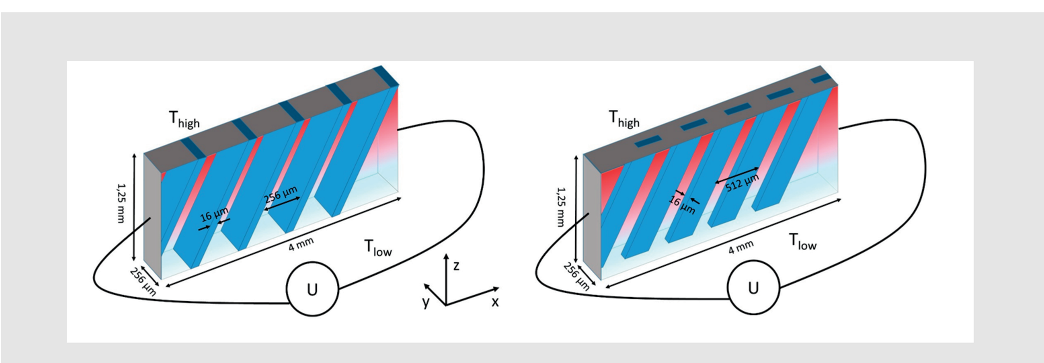

Figure 4: Transverse multilayer thermoelectric generator TMLTEG.

- rotate metal layers by 90° → printable metal strips
- Cofiring of printed metal layers on TE oxide green tapes

FABRICATION STEPS ON TRANSVERSE MLTEG

- tape casting of thermoelectric ceramic
- screen-printing of metal strips
- stacking & lamination
- co-firing of the laminated stack
- typical thickness:
  oxide 50 ... 300 µm
  metal 10 … 15 µm

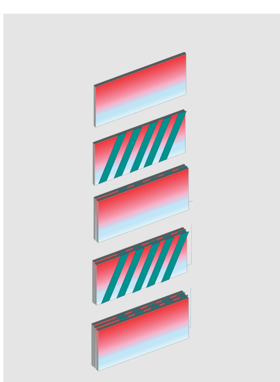

Figure 5: Transverse MLTEG.

TAPE CASTING

- tape development along the process chain of tape casting technology

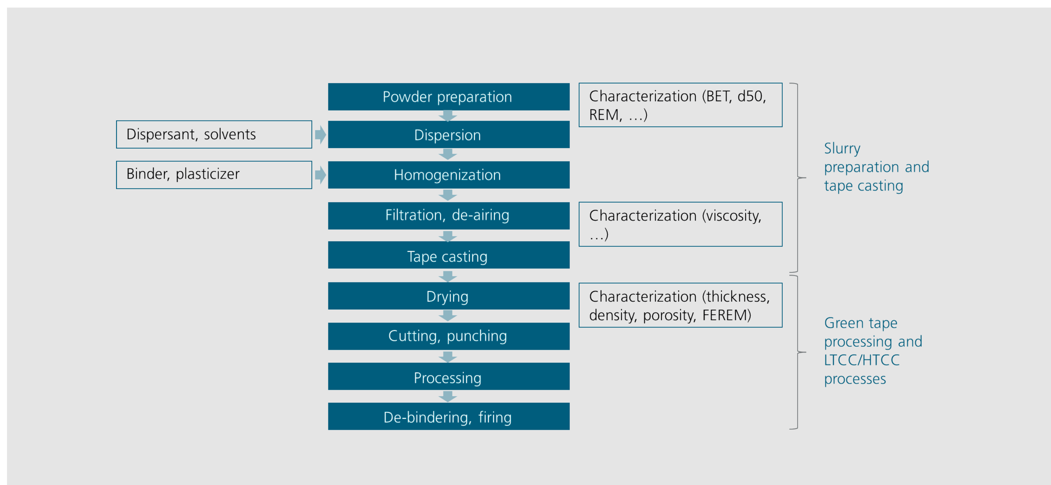

Figure 6: Process chain tape casting.

- preparation of casting slurry was carried out with thermoelectric oxides of $Ca_3Co_4O_9$ (CCO), Sr-doped La_2CuO_4 (LSCO) and $CaMnO_3$ (CMO) powders
- determination of optimal dispersant for the powders
  - powders were dispersed in methylethylketone/ethanol using the dispersant Malialim[TM] AKM053 by Akzo Nobel
  - best results with 1.5 % by mass Malialim[TM]
- investigations into influence of chain length of PVB (poly vinyl butyral) - binders on properties of the slurry and green tapes
  - slurries were prepared using Malialim and S261A (alkyl benzyl phthalate) by Ferro as plasticizer
  - combination of long and short chain binders Butvar PVB B79 and B76 by Eastman chem. shows best results
  - content of binder and plasticizer was determined as a function of BET surface area of thermoelectric powder
- tape casting experiments
  - tape caster "KWH" with a doctor blade
  - casting velocity: 0.4 m/min
  - casting width: 140…160 mm
  - blade gap: 0.3…1 mm
  - length of drying channel: 12.8 m

Figure 7: Tape caster "KWH", View from the front end into the drying channel

- tape characterization
  - measurement of green density and thickness
  - thermal analysis (TG, DTA, DSC)

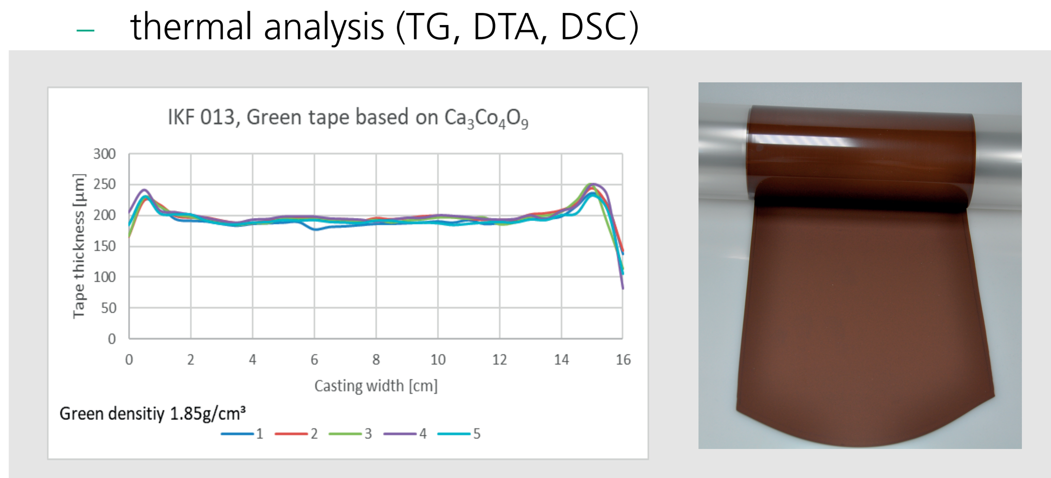

Figure 8: Tape thickness of IKF013 (left), green tape IKF 013 (right).

GREEN TAPE PROCESSING

- printing of the stripe structure on green sheets measuring 50x20 mm²
- Heraeus TC7303 paste (Ag conductor paste for LTCC)
- drying of the printed layer at air
- stacking the printed layers
- lamination at 80 °C, 3000 ps
- cofiring

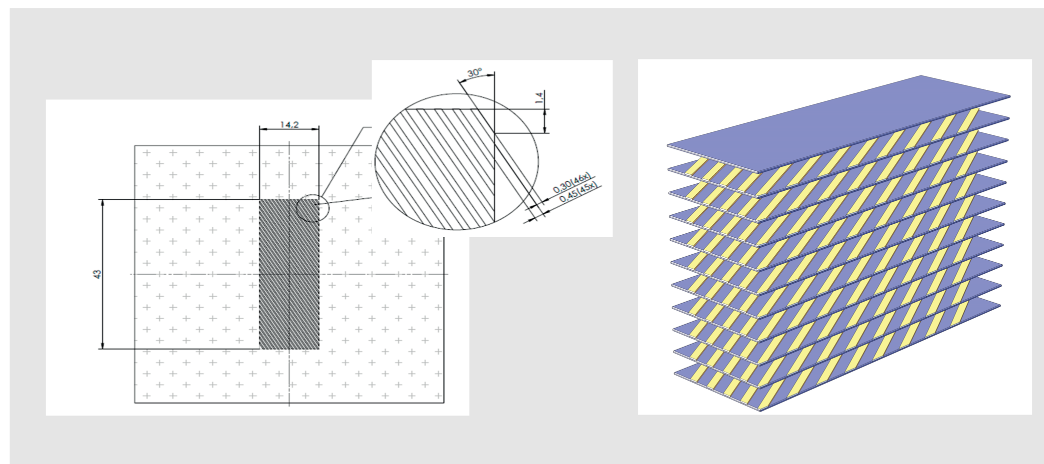

Figure 9: Sieve structure (left), scheme of the stack structure (right).

TMLTEG CHARACTERIZATION

- SEM-image
- x-ray tomography scans
- Electrical measurement

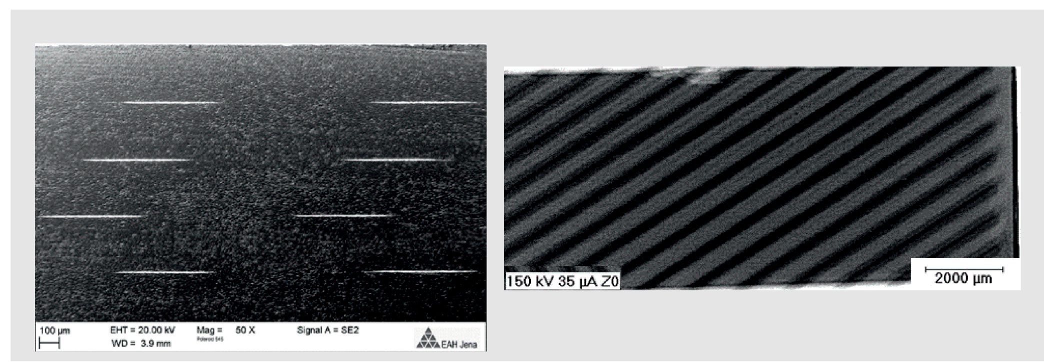

Figure 10: SEM image (left), X-ray tomography scan TMLTEG`s (right) for $CaMnO_3$ and AgPd 1000 °C.

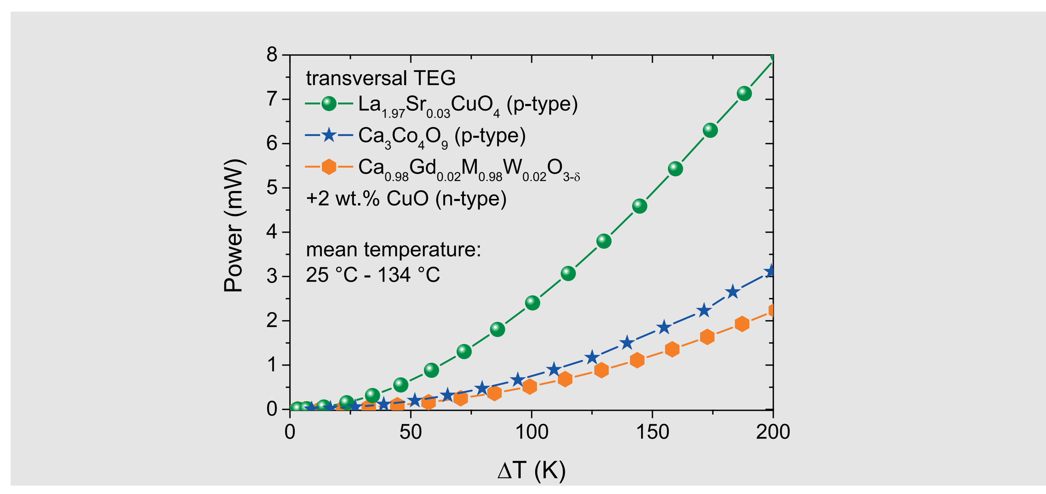

Figure 11: Power vs. temperature difference for $Ca_3Co_4O_9$, doped La_2CuO_4, $CaMnO_3$ with Ag/Pd metallization, co-firing 6 h 920-1000 °C.

SUMMARY

- successful fabrication of transverse multilayer thermoelectric generators
  - cofiring of 2 materials: thermoelectric oxide & metal
  - simple geometry: metal stripes on oxide layers
  - fabrication with ceramic multilayer technology
  - co-firing as monolithic device

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Contact: Beate Capraro
Fraunhofer Institute for Ceramic Technologies and Systems IKTS
Ceramic Tapes
Michael-Faraday-Str. 1, 07629 Hermsdorf, Germany
Phone +49 36601 9301 1022
beate.capraro@ikts.fraunhofer.de

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