Exploring the high-temperature thermoelectric performance of Al-doped ZnO ceramics prepared by in-situ aluminothermic reactions

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Outline:

I. Introduction

II. Experimental details

III. Preliminary results

IV. Conclusions

V. Ongoing work
I. Introduction

- The Seebeck effect

\[ \Delta V = \alpha \Delta T \]

- Thermoelectric (TE) Performance

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa} \rightarrow \text{Dimensionless Figure of Merit} \]

\[ PF = \alpha^2 \sigma \rightarrow \text{Power Factor} \]

\[ ZT \geq 1 \rightarrow \text{for practical applications} \]
I. Introduction
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❖ Wurtzite structure

❖ **Aluminothermy:** a process of producing great heat and strong chemical reduction by oxidizing finely divided aluminum with oxygen taken from another metal, this metal being thus reduced from its oxide (as molten iron is obtained from iron oxide in welding by the Thermit process)

❖ Displacement reaction between Al and ZnO [1]:

$$2Al + 3ZnO \rightarrow Al_2O_3 + 3Zn + \Delta H,$$

where the enthalpy $\Delta H_T = \Delta H_0 + \int \Delta C_p dT$ [2]

✓ n-type conduction; direct wide bandgap (~3.37 eV); low $n$ and large $\kappa$; relatively high electronegativity; high $\mu$ is expected due to strong preference towards $sp^3$ hybridization

II. Experimental details

- **Synthesis:** Solid-state reaction (targeting \( \text{Zn}_{0.995}\text{Al}_{0.005}\text{O} \) (ZAO)) and uniaxial pressing at 227 MPa

- **Samples:** \( \text{ZnO} + \begin{cases} \text{nanometric Al powder} \\ \text{micrometric Al powder} \\ \text{Al}_2\text{O}_3 \text{ powder} \end{cases} \Rightarrow \begin{cases} \text{nZAO} \\ \text{mZAO} \\ \text{ZAOO (reference)} \end{cases} \)

- **Sintering:** One step sintering in air (RT–5°C/min–1300°C, 10h–5°C/min–RT)

- **Composition, morphology and microstructure:** \( \text{XRD, SEM-EDS} \)

- **Electrical properties:** \( \sigma, \alpha, \text{PF} \) (steady state, 525 – 1175 K, 50K/30’ step, air)
III. Preliminary results

- 100% Hexagonal Wurtzite ZnO; NO ZnAl$_2$O$_4$ spinel detected
III. Preliminary results

\[ \rho_{\text{exp.}} = 5.46 \text{g/cm}^3 \ (96\% \ of \ \rho_{\text{th.}}) \]
III. Preliminary results

\[ \rho_{\text{exp.}} = 5.44 \text{g/cm}^3 (96\% \text{ of } \rho_{\text{th.}}) \]
III. Preliminary results

$\rho_{\text{exp.}} = 5.23 \text{g/cm}^3$ (92% of $\rho_{\text{th.}}$)
III. Preliminary results

*The estimated experimental error in measured values did not exceed 3-5% for $\sigma$ and 5-7% for $\alpha$. 
III. Preliminary results

Ref. 10.1039/c8ta01463a: ~300 $\mu$Wm$^{-1}$K$^{-2}$ at 900 °C, for Zn$_{0.993}$Al$_{0.007}$O samples prepared via solid state reaction.
High-density (>95%), single-phase Zn$_{0.995}$Al$_{0.005}$O (ZAO) ceramic composites have been successfully prepared from 2 different metallic Al powders, through a classical solid-state reaction involving high-temperature, in-situ aluminothermy.

The nZAO and mZAO samples show improved properties of interest (density, electrical performance), compared to the reference ZAOO samples.

The highest incorporation of Al is achieved for the nanometric Al powders.

The highest PF recorded for mZAO (700 $\mu$Wm$^{-1}$K$^{-2}$) is among the best found in literature, for similar TE compositions.

In-situ aluminothermy provides locally-strong redox conditions which facilitate sintering and allows for an efficient tuning of the microstructural design and the high-temperature TE properties of these novel ZnO-based materials.
V. Ongoing work

- Thermal diffusivity $D$ and specific heat capacity $C_p$ studies performed in similar conditions as for the electrical measurements ($\kappa = D \rho C_p; \kappa_{ph} = \kappa - \sigma LT$)

- Rietveld refinement and UV-Vis Diffuse Reflectance Spectroscopy (DRS) for determination of unit cell parameters and optical band-gap energy $E_g$, respectively

- Charge carrier concentration and/or mobility calculations

- Experimentation with multiple annealing steps and shorter sintering schemes (with $T > 1000$ °C), for a further evaluation/design/tuning of the redox-promoted, in-situ aluminothermy approach

- Stability experiments (time dependences of electrical coefficients) in various conditions of temperature and atmosphere
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### (Some) Applications of Thermoelectricity:

<table>
<thead>
<tr>
<th>Power (Watts)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>10k</td>
<td>Large scale waste heat recovery, e.g., transportation vehicles</td>
</tr>
<tr>
<td>1k</td>
<td>Microelectronics, e.g., CPU cooling</td>
</tr>
<tr>
<td>100</td>
<td>Consumer applications, e.g., Wine coolers</td>
</tr>
<tr>
<td>10</td>
<td>Space power and cooling, e.g., Voyager</td>
</tr>
<tr>
<td>1m</td>
<td>Remote wireless sensors, e.g., networks</td>
</tr>
<tr>
<td>100μ</td>
<td>Biomedical devices, e.g., pacemakers</td>
</tr>
<tr>
<td>1μ</td>
<td>Low-power applications, e.g., wrist watches</td>
</tr>
</tbody>
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