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# Effect of the nanostructuration of skutterudite materials on their oxidation behaviours

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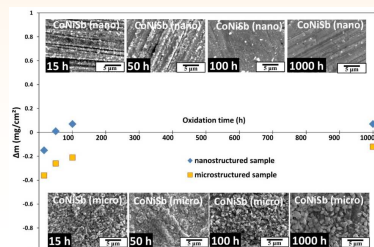
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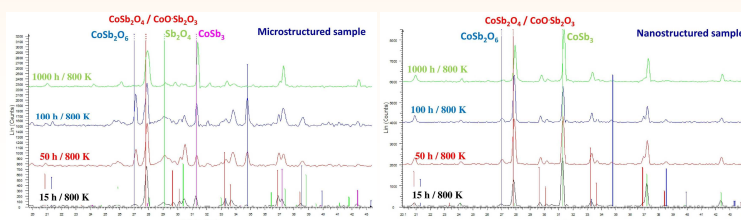
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Doped  $\text{CoSb}_3$ -based skutterudites compounds such as  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$  and  $\text{Ce}_{0.75}\text{Fe}_3\text{CoSb}_{12}$  are promising thermoelectric materials thanks to a high figure of merit ( $ZT > 1$ ). This property makes these doped  $\text{CoSb}_3$ -based skutterudites interesting materials to produce thermoelectric generators able to convert heat into electrical energy. Several recent developments have established that the nanostructuration of these materials enhance their thermoelectrical properties. However, the impact of the nanostructuration on the oxidation behavior of the skutterudites has never been studied. Indeed, their operating temperature under oxidative atmosphere (e.g. in air environment) is drastically limited because of their strong oxidation that produces oxides layers made of  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_4$ ,  $\text{CoSb}_2\text{O}_6$  or  $\text{CoSb}_2\text{O}_4$ . These reactions promote the degradation of the thermoelectric properties of the material and the decrease of the device durability. Therefore the objective of this research work is to determine the impact of the nanostructuration on the oxidation behavior of two interesting doped  $\text{CoSb}_3$ -based skutterudites,  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$  and  $\text{Ce}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ .

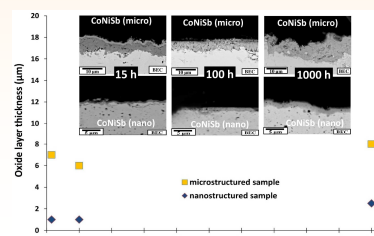
## Oxidation behaviour at 800 K of the micro- and nano-structured n-type skutterudite ( $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$ )



mass variation and surface morphology evolution as a function of the oxidation time



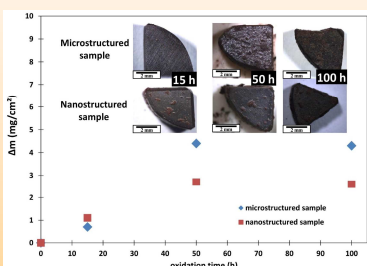
XRD patterns as a function of the oxidation time



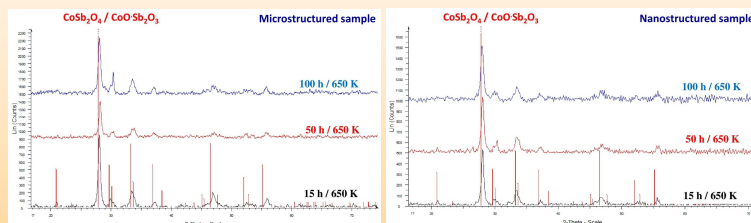
cross-sections observations and thicknesses evolution as a function of the oxidation time

- Oxidation of the **microstructured**  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$  sample:
  - surface modification and mass loss linked to some vaporization
  - constant thick oxide layer (7  $\mu\text{m}$ ) made of  $\text{CoSb}_2\text{O}_6$ ,  $\text{Sb}_2\text{O}_4$  and  $\text{CoSb}_2\text{O}_4$  /  $\text{CoO} \cdot \text{Sb}_2\text{O}_3$
- Oxidation of the **nanostructured**  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$  sample:
  - no surface modification and almost no mass variation
  - constant thin oxide layer (1  $\mu\text{m}$ ) made of  $\text{CoSb}_2\text{O}_4$  /  $\text{CoO} \cdot \text{Sb}_2\text{O}_3$  with a few amount of  $\text{CoSb}_2\text{O}_6$

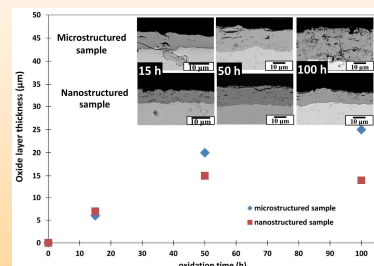
## Oxidation behaviour at 650 K of the micro- and nano-structured p-type skutterudite ( $\text{Ce}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ )



mass variation and surface morphology evolution as a function of the oxidation time



XRD patterns as a function of the oxidation time



cross-sections observations and thicknesses evolution as a function of the oxidation time

- The **micro- and nano-structured**  $\text{Ce}_{0.75}\text{Fe}_3\text{CoSb}_{12}$  samples are highly oxidized during the thermal treatment.
- The mass variations are similar for both samples, following a square root law.
- A thick oxide layer made of  $\text{CoSb}_2\text{O}_4$  /  $\text{CoO} \cdot \text{Sb}_2\text{O}_3$  is observed.

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The oxidation of the n-type skutterudite material ( $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_3$ ) is enhanced by its nanostructuration since the surface oxide layer formed remains very thin up to 1000 hours. The oxidation of the p-type material ( $\text{Ce}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ ) depicts similar behaviors whatever the structuration (micro- or nano-). The nanostructuration of these thermoelectric materials is known to improve their thermoelectric properties. Since there is no significant negative effect on their oxidation behavior, these nanostructured thermoelectric materials are good candidates for industrial uses in air atmosphere at these temperatures.