Mechanical properties of Ca$_3$Co$_4$O$_9$ bulk oxides intended to be used in thermoelectric generators

Driss Kenfaui$^{a,b,*}$, Moussa Gomina$^a$, Daniel Chateignera, Jacques G. Noudema

$^a$CRISMAT, UMR 6508 ENSICAEN/CNRS, LUSAC, Université de Caen Basse-Normandie, 6 Bd Maréchal Juin, 14050 Caen Cedex 04, France
$^b$Institut Jean Lamour – CP2S, UMR 7198 CNRS – Université Lorraine, Parc de Saurupt CS 50840, F-54011 Nancy, France

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Abstract

The lamellar thermoelectric (TE) oxides Ca$_3$Co$_4$O$_9$ (Ca349) are promising candidates for energy conversion in a temperature range of 300–1200 K in air. To be well-suited for being integrated in TE devices, Ca349 bulk materials must show high mechanical reliability to withstand the assembly constrains and in-service conditions. In the aim of optimizing TE performances of these materials, specimens were elaborated by using Hot-Pressing (HP) and Spark Plasma Sintering (SPS). Indentation measurements were operated on these ceramics using both micro-hardness testing and depth-sensing nano-indentation. Fracture characteristics were assessed by 3 point bending tests. Nano-hardness ($nH$), elastic modulus ($E$), strength ($s_R$) and fracture toughness ($K_{IC}$) were shown to drastically enhance versus the pressures $P_{HP}$ and $P_{SPS}$ applied during HP and SPS treatments, respectively, which is ascribed to higher densification and, to a lesser extent, to the texture strengthening and grain boundary density decrease in the direction perpendicular to the pressing axis. The contribution to micro-hardness ($mH$) of both later factors was estimated to 30% for the hot-pressed sample under $P_{HP}=30$ MPa which depicted ($nH_{xy}=2.1\pm0.4$ GPa, $E_{xy}=56\pm4$ GPa) and ($nH_{z}=2.3\pm0.2$ GPa, $E_z=85\pm5$ GPa) in its respective planes perpendicular and parallel to the pressing axis, revealing an anisotropy of the elastic modulus. It presented $s_R=251\pm12$ MPa and $K_{IC}=2.3\pm0.4$ MPa m$^{1/2}$. Although the lower size of the intrinsic flaws was found for the HP materials, the largest mechanical characteristics were achieved by SPS under $P_{SPS}\geq50$ MPa. The elastic recovery $H/E$ of Ca349 ceramics was found among the highest ratios reported for oxides and one order of magnitude larger compared to the half-Heusler or skutterudites potential TE materials. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: C. Mechanical properties; Ca$_3$Co$_4$O$_9$ thermoelectric oxides; Spark plasma sintering; Texture; Fracture toughness

1. Introduction

Emerging ecological awareness and increasing concern for energy needs have boosted progress in materials and technology for thermoelectric (TE) energy conversion in the last two decades. TE generators are being considered for scavenging a part of enormous amount of unused waste heat, produced by automobiles and several industrial processes, to generate electric power [1]. Development projects are already underway to change the alternator in cars with a TE generator mounted on the exhaust stream, thereby enhancing fuel efficiency [1,2].

TE devices contain many material couples consisting of n-type and p-type TE elements connected electrically in series and thermally in parallel. A TE generator uses heat flow across a temperature gradient to power an electric load through an external circuit. The temperature difference provides a voltage from the Seebeck effect [3] while the heat flow drives the electrical current, which therefore determines the power output [1]. The efficiency of a TE device generally improves by increasing the TE material figure of merit $ZT=S^2T/\rho\kappa$ ($T$: temperature, $S$: Seebeck coefficient, $\rho$: electrical resistivity, and $\kappa$: thermal conductivity) [4]. A great deal of research has been then mostly focused on the transport properties in order to

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maximize ZT [1,5–11]. Figure of merit (ZT > 1) values making TE devices competitive have been achieved for several TE components, but there are still very little reports on their mechanical and thermal properties, although such information is essential for the sustainability of TE generators envisaged to be potentially used in harsh environments such as the internal combustion engines of cars. Indeed, these devices will be subjected to mechanical loading and vibration and extreme thermal cycling and shock in consequence of in-service conditions.

Layered cobalt oxides Ca₃Co₄O₉ (Ca₃49) are considered to be among the most expected material candidates for the aforementioned applications because they possess fairly good TE performances, resist oxidation in air, are thermally and chemically stable at high temperature, and do not exhibit any polluting or toxic character [5,6,12,13]. Prototype TE generators, fabricated exclusively from oxides, have been reported [14–18]. Ca₃49 materials have been used as p-type TE elements made by slicing and cutting conventional sintered samples that we have recently shown to possess poor mechanical properties [19,20]. That would make them too weak to withstand in-service conditions without failure. Reinforcement of the mechanical properties of Ca₃49 materials, as well as improvement of their efficiency ZT, is hence vital before these can be seriously considered for potential applications. A clear understanding of their mechanical behavior is as well required for their reliable integration together with other materials constituting the TE device. To minimize undue stress to the device, the p-type and n-type TE elements should possess similar thermal expansion coefficients and elastic modulus. The fabrication of TE device involves the machining of several hundred (or more) individual TE elements. Such machinability as well as wear resistance of material was reported to be governed by the hardness [21–25] which is linked to other mechanical properties including compressive strength [26,27], fracture toughness [28] and Young’s modulus [29]. The mechanical characteristics are needed for TE devices design as well as for the induced stress analysis by the finite element method.

In the efforts to diminish the resistivity of the Ca₃49 bulk compound toward the development of TE elements with high thermal conversion efficiency, samples were fabricated by using Conventional Sintering (CS), Hot-Pressing (HP) and Spark Plasma Sintering (SPS) methods [21,22]. In the present work, the mechanical properties, viz. micro- and nano-hardness, Young’s modulus, strength and fracture toughness are assessed for the processed Ca₃49 materials. The dependence of these properties on the resulting microstructural features and texture strength is widely explored. The mechanical characteristics of Ca₃49 materials are compared to other oxides, skutterudites, lead-antimony-silver-telluride (LAST) and half-Heuslers, TE materials reported to be as well potential candidates for energy conversion applications.

2. Experimental procedure

2.1. Materials

Conventional solid-state synthesis of Ca₃49 powders are described in detail elsewhere [19,20,30,31]. The starting precursors CaCO₃ and Co₃O₄ were weighed in the proper stoichiometric ratios and mixed in an agate ball mill before being calcined in air at 900 °C for 24 h to decompose the carbonates, thereby purifying the Ca₃49 phase. After regrind- ing, a first series of five 3–5 mm – thick and 25 mm – diameter pellets was elaborated by uniaxial cold-pressing Ca₃49 powders under 60, 80, 95, 160 and 200 MPa followed by CS treatment at 920 °C for 24 h where no uniaxial pressure was applied. The resulting relative percent densities are 58.7%, 60%, 60.9%, 64.6% and 66.3%, respectively.

A second series of pellets initially cold-pressed under 95 MPa was further treated using HP processing as described

<table>
<thead>
<tr>
<th>Uniaxial pressure P_{HP} (MPa)</th>
<th>0</th>
<th>5</th>
<th>13</th>
<th>20</th>
<th>30</th>
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<tbody>
<tr>
<td><strong>Microstructural-textural characteristics</strong></td>
<td></td>
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<td>Sample thickness (mm)</td>
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<td>4.45</td>
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<tr>
<td>Relative percent densification (%)</td>
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<td>60</td>
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<tr>
<td>Grain length (μm)</td>
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<td>≤ 9</td>
<td>≤ 12</td>
<td>≤ 14.5</td>
<td>≤ 17</td>
</tr>
<tr>
<td>Grain thickness (μm)</td>
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<td>–</td>
<td>≤ 0.18</td>
<td>–</td>
<td>≤ 0.12</td>
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<tr>
<td>Max. of [001] poles (mrad)</td>
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<td>7.82</td>
<td>9.28</td>
<td>15.36</td>
<td>22.15</td>
</tr>
<tr>
<td><strong>Mechanical characteristics</strong></td>
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<tr>
<td>μH_{perp} (GPa)</td>
<td>0.12 ± 0.01</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>nH_{perp} (GPa)</td>
<td>0.11 ± 0.03</td>
<td>1.5 ± 0.4</td>
<td>2 ± 0.3</td>
<td>1.9 ± 0.3</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>nH_{par} (GPa)</td>
<td>–</td>
<td>1 ± 0.15</td>
<td>2.2 ± 0.2</td>
<td>2 ± 0.15</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>nH_{par}/nH_{perp}</td>
<td>–</td>
<td>0.67</td>
<td>1.07</td>
<td>1.03</td>
<td>1.11</td>
</tr>
<tr>
<td>E_{xy} (GPa)</td>
<td>10 ± 2</td>
<td>53 ± 8</td>
<td>52 ± 3</td>
<td>53 ± 4</td>
<td>56 ± 4</td>
</tr>
<tr>
<td>E_{x} (GPa)</td>
<td>–</td>
<td>53 ± 3</td>
<td>77 ± 4</td>
<td>74 ± 3</td>
<td>85 ± 5</td>
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<tr>
<td>E_{x}/E_{xy}</td>
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<td>1.01</td>
<td>1.47</td>
<td>1.39</td>
<td>1.53</td>
</tr>
<tr>
<td>σ_{f} (MPa)</td>
<td>18.4 ± 0.5</td>
<td>198 ± 8</td>
<td>234 ± 6</td>
<td>254 ± 9</td>
<td>251 ± 12</td>
</tr>
<tr>
<td>K_{t} (MPa m^{1/2})</td>
<td>0.40 ± 0.02</td>
<td>1.9 ± 0.2</td>
<td>2 ± 0.3</td>
<td>2.1 ± 0.1</td>
<td>2.3 ± 0.4</td>
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</table>
elsewhere [19,30]. The pellet was set in a home-made furnace between two 0.125 mm – thick silver sheets to prevent an undesirable reaction with the alumina bearing plates during HP treatment. The material was thereafter heated up to the dwell temperature of 920 °C maintained for 24 h under an uniaxial pressure $P_{HP}$ which was varied from 0 to 30 MPa to investigate the hot-pressing effect on the microstructure of the Ca349 ceramics. The pressure was removed before cooling to avoid material cracking. The samples thickness monotonously decreased as $P_{HP}$ was increased (Table 1). An applied pressure larger than 30 MPa led to too thin samples, impractical later for further manipulations.

Otherwise, a third series of Ca349 samples was prepared using Spark Plasma Sintering (SPS). The powders were treated in vacuum ($10^{-7}$ bar) in the SPS apparatus (Model: HP D 25/1, Fine Ceramics Technologies (FCT), Germany). For each sample, 3 g of Ca349 powders were loaded in graphite die with an inner diameter of 20 mm. A pulsed electric current (2500 A, 4 V) was injected through the die to heat the material up to the dwell temperature of 900 °C while maintaining it under an uniaxial pressure $P_{SPS}$ for 2 min. To investigate the microstructure evolution of the bulk Ca349 materials, $P_{SPS}$ was varied from 0 to 100 MPa. After SPS treatment, the as-prepared samples (thickness ~2 mm) were moderately heated at 600 °C for 2 h before being polished to remove the graphite foil used during SPS sintering.

A pellet, obtained upon cold-pressing under 95 MPa followed by CS sintering at 920 °C for 24 h without uniaxial pressure, is taken as reference sample for second and third series.

2.2. Microstructural and textural characterizations

The relative percent density of the bulk Ca349 materials was computed by comparing the samples density measured via the Archimedes method (KERN & Sohn GmbH, Baligen, Germany) to the theoretical one reported for the Ca349 phase [13]. The microstructure was investigated using a Carl Zeiss (Supra 55, Oberkochen, Germany) Scanning Electron Microscope (SEM). The chemical composition and texture were investigated using a Nano Indenter XP to evaluate the elastic contact stiffness [37].

Instrumented depth-sensing nano-indentation tests were carried out on the samples using a Nano Indenter® XP (MTS Systems Corporation, Eden Prairie, MN, USA). This system produces indentation loadings sensitive to ±1 μN and yields depth-sensing measurements within ±0.01 nm. For each test, a batch of nine imprints, ordered in a 3 × 3 array, were introduced using a Berkovich tip diamond indenter on the polished surfaces with a 50 μm mesh to avoid the interaction between the deformed areas. The maximum penetration depth was set at 2000 nm. After unloading, the recorded load–displacement data were used to compute nano-hardness and elastic modulus. The nano-hardness $nH$ is computed such that

$$nH = \frac{P_{max}}{A}$$

where $P_{max}$ refers to the load at the maximum penetration depth $h$, while $A$ is the projected contact area between the indenter and the sample at $P_{max}$.

The elastic modulus, $E$, is determined using the formula

$$E = \frac{1}{E_i} - \frac{(1 - \nu^2)}{E_i}$$

where $E_i$ is the elastic modulus of the indenter while $\nu$ and $\nu_i$ are the respective Poisson's ratios of the sample and indenter. $E_i$ refers to the reduced modulus defined as

$$E_r = \frac{\sqrt{\pi} S_h}{2\beta \sqrt{A}}$$

$\beta$ is a factor depending on the geometry of the indenter with $\beta = 1.0615$ for a Berkovich tip [38], and $S_h = \frac{d^2 H}{d^2 P}$ refers to the elastic stiffness of the specimen-indenter contact [39].

In the nano-indentation tests on Ca349 materials, we used the continuous stiffness measurements (CSM) option of the Nano Indenter1 XP to evaluate the elastic contact stiffness $S_h$ all along the loading path of the load-penetration curve.

2.3. Mechanical characterizations

2.3.1. Micro-hardness testing and depth-sensing nano-indentation

Using a Zwick mechanical testing device, a course of Vickers indentation (micro-indentation) tests were performed in ambient air on polished surfaces of the samples to assess the micro-hardness, $\mu H$, of the Ca349 ceramics. The loading time was set at 15 s and the micro-hardness, $\mu H$, calculated from the applied load, $P$, and the diagonal lengths $a_1$ and $a_2$ of the indentation imprint according to the following formula [37]:

$$\mu H = \frac{2(\sin 136°/2)P}{(a_1 a_2)}$$

$\mu H$ figures are computed from the orientation distributions (OD) of crystallites, refined using the E-WIMV formalism [35] after extraction of the peak intensities during the Rietveld cycles.

The Ca349 supercell definition [36] was used during these refinements and a sample reference frame chosen in order that the direction of pressures ($P_{HP}$ and $P_{SPS}$) application corresponds to the centre of our pole figures.
2.3.2. Flexural tests

The fracture stress \( \sigma_R \) was determined for the Ca349 materials in ambient air using 3 point bending tests. The maximum tensile stress on the bottom surface of the specimen is calculated from the specimen thickness, the bending moment and the moment of inertia of the cross section. The fracture stress \( \sigma_R \) is therefore given by

\[
\sigma_R = \frac{3 F_R L}{2 BW^2}
\]

for a parallelepiped specimen, where \( F_R \) is the fracture load, \( L \) the span, \( B \) and \( W \) are the specimen width and height, respectively.

Bars for flexural tests were cut from the samples with almost the same \( W \sim 2 \text{ mm thickness, } B \sim 3 \text{ mm width and } L=12 \text{ mm span to enable a comparison among strength values. The load was applied in the direction parallel to the pressing axis during the processing.}

Fracture toughness measurements were performed on single-edge notched bend (SENB) specimens with relative notch length of \( a_0/W \sim 0.33 \) introduced using a 50 \( \mu \text{m} \) thick saw. The fracture toughness is hence computed according to the following formula:

\[
K_{IC} = Y \sigma_R \sqrt{a_0}
\]

\( Y \) is a polynomial function of the \( a_0/W \) ratio that takes into account the finite size of the specimen. This factor depends on the geometry of the specimen and the loading configuration. For a SENB specimen, \( Y \) values are tabulated versus \( a_0/W \) and \( L/W \) ratios. Here, the predominant fracture mode is the one corresponding to a crack opening under a normal tensile stress perpendicular to the notch plane, commonly known as mode I.

3. Results and discussion

3.1. Hardness and elastic modulus

3.1.1. \( \text{Ca}_3\text{Co}_4\text{O}_9 \) processed by CS and HP

Fig. 1 depicts the evolution of the micro-hardness \( \mu H_{xy} \) of isotropic Ca349 ceramics of the first series as a function of the achieved densification. The mean \( \mu H_{xy} \) reported for each sample is an average over the 10 imprints on \((x,y)\) planes of the samples (Fig. 2) introduced by applying a load of 2 N parallel to the cold-pressing axis. A linear increase of the \( \mu H_{xy} \) values versus the relative density is observed up to around 66\%, our instrumental limit for the cold-pressing equipment. Denser isotropic Ca349 ceramics are hardly achievable without inducing a texture because of the layered character of the crystal structure [13] which results in lamellar grains [19,20,30,31]. The micro-hardness \( \mu H_{xy} \) of highly densified (96\%) Ca349 ceramics with randomly oriented grains was then estimated at 0.9 GPa by extrapolation of the values associated to the five aforementioned specimens (Fig. 1).

Micro-hardness measurements were carried out as well on strongly textured and 96%-densified Ca349 samples (Table 1) processed using HP under 30 MPa. The imprints on \((x,y)\) plane of the sample (Fig. 2) were obtained by applying a load of 5 N parallel to the direction of pressure \( P_{HP} \) application. The corresponding \( \mu H_{xy} \) value raises from 0.12 \( \pm \) 0.01 GPa for the reference sample to 1.3 \( \pm \) 0.1 GPa for the textured one, highlighting a hardening of more than one order of magnitude predominantly ascribed to the densification and, to a lesser extent, to the texture strengthening and the grain length increase (Table 1) inducing a reduction in the \((x,y)\) plane grain boundary density (GBD). Indeed, while the reference sample evidences a strongly porous microstructure (60\% of the theoretical density) with small grains loosely assembled and randomly distributed (Fig. 3a) in keeping with the weak texture strength (Fig. 3b), the sample processed by HP under 30 MPa appears more homogenous and presents much denser microstructure with largely grown platelets compactly stacked up along the pressing axis and highly oriented (Fig. 3e). The maximum of the \{001\} poles is around 22 mrd (Fig. 3f), the strongest texture recorded hitherto on Ca349 materials.

The crystallographic orientation and GBD decrease contributions to the micro-hardness is quantified to about 31\% by comparing the \( \mu H_{xy} \) value of the textured material to the estimated hardness of the isotropic ceramics at the same relative density (96\%).

Nano-hardness, \( nH \), and Young’s modulus, \( E \), were determined for Ca349 samples via nano-indentation tests. In order to check eventual anisotropy influence on these mechanical properties in the samples textured by HP, imprints were
introduced on (x,y) and (x,z)/(y,z) planes of the sample (Fig. 2) by applying the load parallel (nHxy and Exy) and perpendicular (nHz and Ez) to the direction of pressure PHP application, respectively.

The average nHxy, nHz, Exy and Ez values of the Ca349 samples treated by HP under various pressures PHP up to 30 MPa are regrouped in Table 1. The nano-hardness drastically improves with PHP. Indeed, nHxy raises from 0.11 ± 0.03 for the reference sample to 1.5 ± 0.4 GPa under an effect of a moderate pressure PHP as high as 5 MPa. In this PHP range, the Ca349 ceramics are markedly densified from 60% to 90.5% whereas the texture strength only goes from 3.48 to 7.82 mrd, emphasizing that nHxy increase mainly derives from the densification in accordance with the micro-hardness. The texture as well as the reduction in (x,y) plane GBD (Table 1) secondarily contributed to the nHxy enhancement.

Beyond 5 MPa, the samples display similar nHxy values to within ± one standard deviation in data although the texture strength and the grains length notably increase (Table 1), endorsing hence the primacy of the densification effect on nHxy. nHxy reaches 2.1 ± 0.4 GPa for the hot-pressed material under 30 MPa, corresponding to 19 fold the reference sample. Here, it is worth noting that this hardness value is 3.7 and 2.1 fold the hardest compounds Ba0.075Sr0.025Yb0.1Co4Sb12 and Zr0.5Hf0.5Ni0.6Pd0.4Sn0.99Sb0.01 reported so far for the hot-pressed skutterudite [40] and half-Heusler [41,42] TE materials, respectively.

The nano-hardness nH was found to be higher than nHxy for PHP higher than 13 MPa, due to more significant texture strengthening (beyond 9 mrd) as can be observed in Fig. 3c–f. nHZ attains 2.3 ± 0.2 GPa for a pressure PHP of 30 MPa, which is 21 fold the reference sample. Under such pressure, the Ca349 ceramics display a hardness anisotropy Hz/Hxy = 1.11, which can be overlooked owing to the nHxy and nHZ values similarity to within ± one standard deviation in data.

On the other hand, while the isotropic material (reference sample) presents μHxy and nHxy of around 0.11 GPa, the nHxy value of the sample textured by HP under 30 MPa shows an increase of 38% compared to the μHxy one, which is probably tied to the more localized character of nano-indentation measurements. Bearing in mind the larger grain length (17 μm) for the textured sample, this result suggests that nHxy values are closer to those of the grains, whereas those of μHxy correspond to the macroscopic values taking into account the grain boundaries and porosity effects. A discrepancy between micro- and nano-hardness was also reported by Yang et al. [43] on Ti(CxN1−x), Zr(CxN1−x) and Hf(CxN1−x) compounds.

The elastic modulus, E, depends as well on the applied pressure PHP. Ez raises from 10 ± 2 to 53 ± 8 GPa as PHP is increased from 0 to 5 MPa, due to the same factors noted for nHxy.

Fig. 3. SEM micrographs of the microstructure, and [020], [001] and [100] pole figures obtained for (a and b) the Ca349 conventionally sintered (CS) sample (reference) and the hot-pressed ones under pressures PHP of (c and d) 13 and (e and f) 30 MPa. Insets evidence the thickness of the platelets achieved under these pressures and how the latters are aligned and stacked up along the hot-pressing axis.
$E_{xy}$ reaches $56 \pm 4$ GPa for the materials processed under 30 MPa, i.e. 5 times larger compared to the reference sample. This value is comparable to the Young’s modulus reported on AgSbPb$_{18}$Te$_{20}$ LAST compound, but, about 2 fold the values recorded on Ag$_{0.5}$SbPb$_{18}$Te$_{20}$ and Ag$_{0.7}$SbPb$_{18}$Te$_{20}$ ones treated by HP as well [44]. However, it remains more than 2 and 4 fold lower compared to the largest stiffness reported on the hot-pressed Co$_{0.9}$Fe$_{3.5}$Co$_{0.5}$Sb$_{12}$ (also on Co$_{0.95}$Pd$_{0.05}$Te$_{0.05}$Sb$_{12}$) and Zr$_{0.5}$Hf$_{0.5}$Co$_{0.9}$Sb$_{0.9}$Sn$_{0.1}$ compounds for the skutterudite [45] and half-Heusler [41,42] TE families, respectively. It is relevant to note that the reported compounds cited here possess larger bulk density ($> 98\%$).

$E_z$ displays a steeper increase than $E_{xy}$ tied to the texture strengthening (Fig. 3e and f), and attains $85 \pm 7$ GPa for the sample hot-pressed under $PHP = 30$ MPa. The stiffness anisotropy $E_z/E_{xy}$ appears more pronounced than for the hardness and increases with $PHP$ up to 1.53 for the latter.

3.1.2. Ca$_3$Co$_4$O$_9$ processed by SPS

Fig. 4 depicts SEM micrographs of fractured surfaces of the samples consolidated by SPS under pressures, $P_{SPS}$ of 30, 50 and 75 MPa. For $P_{SPS} =30$ MPa (Fig. 4a), the sample exhibits much stronger bulk density (98.3%) compared to the reference sample (Fig. 3a), and the grains show roughly platelet-like shape with a tendency to be oriented and stacked perpendicularly to the pressing direction. However, limited porous zones comprising smaller and more isotropic grains persist, which is suggestive of an uncompleted material sintering. Under $P_{SPS} =50$ MPa (Fig. 4b), the sample is almost fully densified (99.6%) with no porous zone.

Table 2 shows neither a significant reinforcement of the texture nor an increase of the mean grain size with the $P_{SPS}$ pressure as can be seen from Fig. 4a–c as well. Such limitation probably stems from the increasing lateral pressure applied by the die walls on the sample during the uniaxial $P_{SPS}$ pressing. Since the sample is constrained within the die, the material deformation is hindered and the grain rotation blocked when the porosity is ejected. Under $P_{SPS} =75$ MPa, the sample (Fig. 4c) depicts porous zones imputable to the larger lateral pressure causing an antagonist effect to $P_{SPS}$ one, thereby decreasing the bulk density to 98.5%. Full densification (99.2%) was achieved again under 100 MPa.

Since the Ca$_3$49 samples processed by SPS depicted a weak texture, the nano-indentation was performed only in the direction parallel to the pressing axis to introduce the imprints on $(x,y)$ plane of the samples. The average $nH_{xy}$ and $E_{xy}$ values considerably improve with $P_{SPS}$ (Table 2). Increasing $P_{SPS}$ from 0 to 30 MPa led $nH_{xy}$ and $E_{xy}$ to enhance from 0.11±0.03 to 2.3±0.1 GPa and from 10±2 to 74±3 GPa, respectively, due essentially to the density strengthening from 60% to 98.3%. Looking at the values of the maximum of the (001) poles, the texture seems to induce almost no effect. $nH_{xy}$ and $E_{xy}$ reveal a tiny increase afterward, elucidating the porosity in Ca$_3$49 samples are basically wiped out at low $P_{SPS}$ range and major of densification is achieved under $P_{SPS}$ not higher than 30 MPa; material densification becoming more and more difficult for higher $P_{SPS}$ values. The densest sample (processed under 100 MPa) depicts $nH_{xy}$ value of $3.2 \pm 0.4$ GPa which is 26 fold the reference sample hardness and the largest achieved so far on Ca$_3$49 materials. This value is also more than 5 times that of the spark plasma sintered CoSb$_3$ and LaFe$_2$Sb$_{12}$ reported to be the hardest compounds of the skutterudite material family [47], and about 4 fold the TE material Bi$_2$Te$_3$ elaborated by SPS, already used in commercial TE modules [46]. Regarding the reported oxides treated by SPS, the largest value obtained for Ca$_3$49 materials is higher than that of BaCeO$_3$ and SrCeO$_3$ alkaline-earth perovskite oxides, similar to that of BaMoO$_3$ and lower than that of BaZrO$_3$, BaUO$_3$, BaSnO$_3$, BaHfO$_3$, SrMoO$_3$, SrZrO$_3$, SrZrO$_3$, SrZrO$_3$.
SrTiO$_3$, SrHfO$_3$ and SrRuO$_3$ ones [48–50] although the Ca$_3$O$_3$ sample displays larger bulk density compared to the latter. The hardest alkaline-earth perovskite oxide SrRuO$_3$ possesses hardness almost 4 fold the value of the hardest Ca$_3$O$_3$ sample.

$E_{xy}$ ranges from 82 ± 6 to 86 ± 5 GPa for $P_{SPS}$ larger or equal to 50 MPa and is then comparable to the one measured for the sample hot-pressed under 30 MPa, indicating that further densification brought by SPS compensates for the texture produced by HP. However, these values remain lower than those reported for the spark plasma sintered alkaline-earth perovskite oxides [48–50], skutterudite compounds [47], or half-Heusler alloys [51].

The elastic recovery of materials has been shown to be reflected by the hardness to elastic modulus ratio $H/E$, a non-dimensional parameter commonly used for comparison of materials [39,41]. Fig. 5 compares to each other the elastic recoveries for Ca$_3$O$_3$ ceramics elaborated by using CS, HP and SPS, and to those of other bulk TE oxides and some TE material families reported to be potentially useful for energy conversion applications. First, one emphasizes that the oxides possess much larger elastic recovery compared to most other materials. The ($H/E$)$_{xy}$ ratio of Ca$_3$O$_3$ oxides processed by HP increases with $P_{HP}$ and ranges from 0.0284 to 0.0373. A similar trend is also noted for the ($H/E$)$_{xz}$ ratio which is lower and spans from 0.0188 to 0.0271 in the explored $P_{HP}$ range, reflecting an elastic recovery anisotropy in the textured Ca$_3$O$_3$ oxides. The ($H/E$)$_{xy}$ ratios achieved on Ca$_3$O$_3$ oxides treated by SPS and HP are similar and more than 3 fold the reference sample value. Furthermore, they are one order of magnitude higher than $H/E$ ratios obtained for half-Heusler alloys [41,42] or Na$_{1.5}$Co$_2$-$x$Ag$_x$O$_4$ oxides [53], prepared by HP and CS, respectively. They illustrate likewise almost similar $H/E$ superiority when being compared to the skutterudites [40,47]. The $H/E$ ratio is reported to vary from 0.0094 to 0.0299 for LAST compounds (Ag$_a$Pb$_b$Sb$_c$Te$_d$ with 0.006 $\leq a \leq 0.043$, 0.417 $\leq b \leq 0.480$, 0.011 $\leq c \leq 0.50$ and 0.496 $\leq d \leq 0.517$) [55,56] depending on their compositions, which is inferior or equal to those of our consolidated Ca$_3$O$_3$.

The hot-pressed and spark plasma sintered Ca$_3$O$_3$ oxides display larger elastic recovery than the perovskite oxides depicted in Fig. 5 whatever the processing method, except SrMoO$_3$ and BaUo$_3$ which show similar ($H/E$)$_{xy}$ and higher ($H/E$)$_{xz}$ ratios, respectively. We note as well that there are copper oxides (Sm$_2$CuO$_4$, Gd$_2$CuO$_4$, Nd$_2$CuO$_4$) [54] possessing similar $H/E$ values, and the highest reported $H/E$ ratios are for the oxides Ca$_{0.95}$Sm$_{0.05}$MnO$_3$ ($H/E$=0.0539) [52] and SrRuO$_2$ ($H/E$=0.0789) [48] treated by SPS and CS, respectively.

Table 2

<table>
<thead>
<tr>
<th>Uniaxial pressure, $P_{SPS}$ (MPa)</th>
<th>0</th>
<th>30</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microstructural–textural characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative percent densification (%)</td>
<td>60</td>
<td>90.3</td>
<td>99.6</td>
<td>98.5</td>
<td>99.2</td>
</tr>
<tr>
<td>Grain length (μm)</td>
<td>≤ 5</td>
<td>≤ 7</td>
<td>≤ 8</td>
<td>≤ 7</td>
<td>≤ 8</td>
</tr>
<tr>
<td>Max. of the {001} poles (mrd)</td>
<td>3.48</td>
<td>3.74</td>
<td>3.94</td>
<td>4.05</td>
<td>3.49</td>
</tr>
<tr>
<td><strong>Mechanical characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$nH_{xy}$ (GPa)</td>
<td>0.11±0.03</td>
<td>2.34±0.14</td>
<td>2.7±0.3</td>
<td>3.1±0.4</td>
<td>3.2±0.5</td>
</tr>
<tr>
<td>$E_{xy}$ (GPa)</td>
<td>10±2</td>
<td>74±3</td>
<td>82±6</td>
<td>87±5</td>
<td>86±5</td>
</tr>
<tr>
<td>$\sigma_y$ (MPa)</td>
<td>18.4±0.5</td>
<td>252±9</td>
<td>282±7.7</td>
<td>250±14</td>
<td>284±8</td>
</tr>
<tr>
<td>$K_I$ (MPa m$^{1/2}$)</td>
<td>0.40±0.02</td>
<td>2.80±0.09</td>
<td>2.92±0.05</td>
<td>2.82±0.1</td>
<td>2.77±0.09</td>
</tr>
</tbody>
</table>

Fig. 5. $H/E$ ratios for conventional sintered (CS), hot-pressed (HP) and spark plasma sintered (SPS) Ca$_3$O$_3$ materials compared to those reported for other oxide, skutterudite and half-Heusler materials.
A similar enhancement in $\sigma_R$ was noted for the samples treated by SPS under an equivalent pressure. The materials prepared under higher $P_{SPS}$ of 50 MPa were found to possess strength as high as $282 \pm 8$ MPa, i.e. 15 times the reference material. To our knowledge, this is the largest strength obtained so far on Ca349 bulk materials.

Increasing $P_{SPS}$ to 75 MPa causes the strength to drop by 11%, which is well correlated to the presence of weakly dense zones noted on the corresponding microstructure (Fig. 4c). In contrast, these strength shortfalls were not observed when $P_{SPS}$ was further increased to 100 MPa, which is consistent with the density level noted on the corresponding specimen (Table 2).

Importantly, although the Young’s modulus, $E$, was not impaired by these defected areas, SPS processing in its classical configuration with pressure larger than 50 MPa proves to be harmful toward some critical mechanical characteristics of Ca349 bulk materials. Likewise, samples elaborated in such processing conditions revealed a worsening of the TE properties [22]. Nonetheless, we have recently reported an amended SPS configuration, referred to as edge-free spark plasma sintering or spark plasma texturing (SPT), enabling a free deformation of the grains perpendicular to the pressing axis, thereby preventing defected areas and, concomitantly, inducing a rapid material texturization [58].

Fig. 6b shows the texture effect on the 3 point bending loading curve of a SENB specimen, processed by HP under 30 MPa, tested in flat-wise orientation. Beyond the maximum load, the crack propagates in a more or less controlled manner reflecting the successive ruptures of stacked platelets.

The HP processing was found to be highly effective for enhancing the resistance of Ca349 ceramics to crack propagation from a major flaw. Compared to the isotropic ceramic (reference), the fracture toughness $K_{IC}$ recorded a significant increase factor of 4.7 upon HP under $P_{HP}=5$ MPa. This factor monotonously increased with $P_{HP}$ to reach 5.7 for $P_{HP}$ of 30 MPa, which is derived from the material densification, texture strengthening and diminishing in the $(x,y)$ plane GBD.

The SPS processing fosters superior resistance to crack propagation in Ca349 ceramics. Indeed, a higher improvement (more than 7 times) was obtained in $K_{IC}$ under pressure $P_{SPS}$ of 30 MPa, and is ascribed to the fully material densification. $K_{IC}$ topped at $2.92 \pm 0.05$ MPa m$^{1/2}$ for $P_{SPS}$ of 50 MPa, the material with the highest bulk density. As with the strength $\sigma_R$, $K_{IC}$ slightly drops for larger $P_{SPS}$ values, in keeping with the microstructure features (Fig. 4c). SEM observations showed that failure proceeds by intergranular cracking.

With the aim to evaluate the size of the intrinsic flaws in the samples processed by CS, HP and SPS, we made use of Eq. 6. Assuming that the intrinsic flaws are small, the strength $\sigma_R$ measured on smooth Ca349 ceramics was used and the shape factor $Y$ was set equal to $\sqrt{\pi}$. Fig. 7 shows the evolution of the intrinsic flaw size versus the applied pressure $P_{SPS}$. While the isotropic sample depicts the largest intrinsic flaws (150 µm) which are likely the pores resulting from the weak densification (60% of the theoretical density), the flaw size considerably drops as the uniaxial pressure $P_{SPS}$ is applied. Furthermore, the intrinsic flaw size does not seem to depend on the pressure.
(same for \(P_{HP}\) shown in the inset). Despite higher densification is achieved by SPS processing, HP treatment results in smaller intrinsic flaws, probably linked to the higher grain orientation by this process (Fig. 3e) while in SPS the disorientation between grains is much more pronounced (Fig. 4). For the same applied pressure of 30 MPa, HP processing leads to lower fracture toughness (2.30 MPa m\(^{1/2}\)) than SPS (2.80 MPa m\(^{1/2}\)). That may be ascribed to the higher GBD in the \((x,z)/(y,z)\) planes (the grains are thinner) in the materials treated by HP (Table 1). We note an increase in flaws size for \(P_{SPS}\) of 75 MPa in accordance with the microstructure observation (Fig. 4c), and for \(P_{HP}\) of 30 MPa probably due to the cracking of the thinner grains.

4. Conclusions

Micro-hardness (\(\mu H\)), nano-hardness (\(nH\)), elastic modulus (\(E\)), strength (\(\sigma_R\)) and fracture toughness (\(K_R\)) were assisted for Ca\(_3\)Co\(_4\)O\(_9\) (Ca349) bulk oxides initially processed by using Hot-Pressing (HP) and Spark Plasma Sintering (SPS) toward the optimization of their thermoelectric (TE) properties. These mechanical characteristics were shown to be drastically fostered under the effects of both processes. They are the largest for Ca349 materials fully densified by SPS under \(P_{SPS} \geq 50\) MPa with \(nH_{CS} = 3.2 \pm 0.5\) GPa, \(E_{CS} = 87 \pm 5\) GPa, \(\sigma_R = 284 \pm 8\) MPa, and \(K_R = 2.82 \pm 0.4\) MPa m\(^{1/2}\), corresponding to more than 29, 8, 15 and 6 fold the conventional sintered (CS) ceramics often used in TE devices. Although Ca349 ceramics treated by HP were found to depict lower mechanical characteristics, they remain however drastically more reliable compared to the CS ones. We note that the hot-pressed Ca349 materials were reported to possess the best TE performances as well, which makes them most suitable for being used in TE devices. The elastic recovery \(HIE\) of Ca349 materials processed by HP and SPS can reach 0.04, which is more than one order of magnitude larger compared to the half-Heusler or skutterudites promising candidates for TE applications.

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References
