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1 Cool-SPS stabilization and sintering of thermally fragile, potentially 2 magnetoelectric, $\text{NH}_4\text{FeP}_2\text{O}_7$ (CJ-3:IL04)

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4 Abstract

5 Cool-SPS conditions (low temperature/high pressure) can be used to densify materials with limited
6 thermodynamical stability, due to low temperature phase transition, melting, decomposition... We
7 recently demonstrated the potential of SPS for the stabilization and densification of diversified materials
8 at very low temperatures. Here we report the sintering of a potentially magnetoelectric pyrophosphate
9 with low temperature decomposition. Characterization of its magnetic properties are presented, and
10 dielectric/magnetoelectric characterization could also be performed thanks to the high densification
11 obtained at temperatures as low as 200 °C.

12 Introduction

13 Low temperature ceramic sintering techniques have recently been developed and showed extraordinary
14 potential for accessing high density at extremely low temperatures, typically below 400 °C, including
15 Cold Sintering Process [1–7], Hydrothermal Hot Pressing [8–10] and Cool-SPS [11,12]. Beyond the
16 energy and cost reduction offered by temperature reduction [13], multiple gaps are bridged by such
17 processes. Indeed, such low processing temperatures open new possibilities such as the formation of
18 novel polymer/ceramic composite materials, with ceramic as a major phase [14–16]. This also enables the
19 formation of novel LTCC materials [17]. Other perspectives have recently been recently explored in the
20 case of Cool-SPS, highlighting additional advantages of these low temperature processing techniques.
21 One of them lies in the applied pressure necessary to realize such processes. In prior works, we observed
22 that materials stability ranges may be modified under applied mechanical pressure, enabling stabilization
23 of thermodynamically fragile phases – such as compounds facing low temperature decomposition,
24 melting or irreversible phase transition [12] – and their efficient sintering (by Cool-SPS) resulting in very
25 high density (typically above 95% of theoretical density). Another one is the opportunity to use, and also
26 sinter efficiently, hydrated precursors [12], by controlling the dehydration through optimized sintering
27 cycles [11]. One may also be able to perform *in situ* synthesis of phases that cannot be synthesized
28 quantitatively otherwise [12]. Such potentialities create an opportunity to diversify the chemicals classes
29 of materials investigated for diverse properties (physical, chemical...). Exploring these low temperature
30 processing techniques can also allow for breakthroughs such as the recent elaboration of the first
31 molecular ceramic [18]. One can thus foresee the potential of low temperature sintering methods for

32 bridging processing gaps (elaboration at low temperature), chemical gaps (enabling investigation of more
33 diversified families of compounds), or even shaping gaps (processing of molecular ceramics previously
34 unknown).

35 Indeed, we are now able to obtain dense materials from powders that were up to now considered to be
36 impossible to sinter, and thus characterized as powder, films or crystals, with the inherent processing
37 demands and characterization limitations of these shapings¹. Widening the span of sinterable materials
38 opens up interesting opportunities, especially in sulfate and phosphate compounds. They usually show
39 low temperature stability, making their processing more difficult than refractory oxides. This concerns
40 various applications such as electronic properties for batteries [19] or even mechanical ones in the process
41 of biomaterials [20]. Using Cool-SPS among these low temperature processing techniques, it was
42 possible to highlight magnetoelectric properties of MnSO_4 ceramics that could not be obtained through
43 conventional sintering [11]. When looking for magnetoelectric properties in single phase materials, it
44 becomes interesting to use low temperature sintering techniques to densify materials which crystal-
45 chemical and magnetic properties allow for a potential magnetoelectric coupling. In the present study, we
46 focus our interest on $\text{NH}_4\text{FeP}_2\text{O}_7$, once reported for its structure [21]. It completes the series of iron
47 pyrophosphates AFeP_2O_7 ($\text{A} = \text{Li, Na, K, Rb, Cs, Ag}$) [22–25], which display antiferromagnetic phase
48 transitions below room temperature thanks to super-super exchange interactions [22]. $\text{NH}_4\text{FeP}_2\text{O}_7$ is also
49 isostructural to KCrP_2O_7 , a pyrophosphate which symmetry allows for a magnetoelectric coupling [26],
50 and this is an indictment to explore similar properties in the title compound. The main challenge to test
51 such a magnetoelectric coupling is to obtain a highly densified ceramic to allow for dielectric
52 characterization and avoid spurious contributions related to poor densification. To reach this objective, we
53 propose to use Cool-SPS an efficient technique to obtain both high density and phase stabilization [12].

54 **Experimental section**

55 $\text{NH}_4\text{FeP}_2\text{O}_7$ synthesis is performed through solid state reaction of a green pellet constituted of both
56 $(\text{NH}_4)_2\text{HPO}_4$ (Sigma Aldrich 98%) and $\alpha\text{-Fe}_2\text{O}_3$. The latter is obtained from the heat treatment of
57 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich 98%) at 500 °C overnight, as commercial $\alpha\text{-Fe}_2\text{O}_3$ presents a poor
58 reactivity and its use results in an important amount of non-reacted $\alpha\text{-Fe}_2\text{O}_3$. The two powders are mixed
59 in an agate mortar and pelletized, then they are fired in a furnace at 210 °C for 24h. Sealed nitrogen

¹ *The processing of films requires compatible methods and substrates, the growth of single crystals require specific methods and time, both can require multiple-step processing. Characterization methods requiring electrical contact, dense samples (i.e. dielectric measurements...) are generally impossible for powders. The characterization of films frequently require specific methods for data collection, analysis and interpretation. The characterization of crystal can be limited by their inherent anisotropy (except for the cubic crystal system) and growth habit (acicular growth, platelets...) and may require complex preparation steps (oriented cutting, polishing...).*

60 environment, as well as nitrogen flux, were used to perform the synthesis, but resulted in a high content of
61 remaining iron oxide, and sometimes promoted the formation of other phosphates as secondary phases.
62 Using a sealed primary vacuum atmosphere allowed to obtain the higher ratio of $\text{NH}_4\text{FeP}_2\text{O}_7$ over α -
63 Fe_2O_3 . When a stoichiometric ratio of $(\text{NH}_4)_2\text{HPO}_4$ and iron oxide is used, there is an important part of
64 remaining iron oxide, due to the volatilization of ammonium phosphate. Adding an excess of $(\text{NH}_4)_2\text{HPO}_4$
65 allows to compensate this volatilization, up to a point where other phases appear. The best compromise
66 was found to be a 20 wt.% excess of $(\text{NH}_4)_2\text{HPO}_4$, although traces of α - Fe_2O_3 are still visible on the XRD
67 pattern of the as-synthesized product. After synthesis, the powder was placed in a SPS sintering die made
68 of WC and surrounded by Ta foils to avoid any cross contamination between the die and the powder.

69 Dense ceramics were prepared with Spark plasma sintering (Dr. Sinter Lab spark plasma sintering system,
70 Model SPS-511S/SPS-515S) in WC:Co 10 mm die using 0.5 g of powder for each sintering attempt.
71 Thermocouple is used to monitor temperature, in contact with the inner part of the die. 12 ON/2 OFF
72 pulse sequence is applied for all samples. Densification was continuously monitored by the displacement
73 of a punch rod. A 30 °C/min heating ramp was used for all different sintering experiments, while
74 temperature was varied from 200 °C to 300 °C. Pressure was set to 300 MPa and sintering time to 10 min
75 for all samples. Sintering attempts were performed under primary vacuum of about 10 Pa. Powder and
76 pellet diffraction were performed with a Phillips X'Pert MPD X-ray diffractometer with the Bragg–
77 Brentano geometry using Cu $K\alpha_1/K\alpha_2$ radiation ($10^\circ < 2\theta < 80^\circ$ range, step of 0.017°). The ceramics'
78 relative densities were evaluated by geometrical measurements considering a theoretical density of 2.75
79 g/cm^3 for $\text{NH}_4\text{FeP}_2\text{O}_7$ [21]. The pellets' microstructures were observed on fracture surfaces, with a
80 scanning electron microscope (JEOL 840 SEM). TGA measurements were performed with a Setaram
81 tag2400 apparatus. Magnetic measurements were performed with a MPMS-7-XL (S.Q.U.I.D)
82 magnetometer (Quantum Design) on ceramics. Zero-field cooled and field cooled data were collected
83 with an applied field of 1 kOe and with increasing temperature from 2K to 300K. Silver electrodes were
84 deposited on both surfaces of the pellets and silver wires were subsequently used for sake of electrical
85 connection. Once prepared for dielectric measurements, the ceramics were placed in a Quantum Design
86 Physical Properties Measurement System (PPMS) from which a 9 T magnetic field can be applied. The
87 dielectric measurements were carried out in the frequency range of $10^2 - 10^6$ kHz (the amplitude of the
88 applied ac electric field being 1V) using an HP4194a impedance bridge, at heating and cooling rates
89 between 0,2 and 1 K/min. Measurements of capacitance and dielectric losses were first performed by
90 scanning temperature with and without application of a magnetic field of 9T. In a second step, the
91 magnetic field was swept from -9T to 9T at 2K to evaluate the magnetoelectric behavior of the samples.

92 **Results and discussion**

93 XRD data confirm the structural model proposed in the literature [21], and points the difficulty to fully
94 separate as-synthesized $\text{NH}_4\text{FeP}_2\text{O}_7$ phase from $\alpha\text{-Fe}_2\text{O}_3$ (see figure 1a and b). Whatever the temperature
95 conditions tested for synthesis, $\alpha\text{-Fe}_2\text{O}_3$ traces remain present after synthesis of the powder. At
96 temperatures higher than 210 °C, decomposition of the target pyrophosphate occurs, and other phosphates
97 are formed. On the opposite, synthesis performed below 210 °C show a limited reactivity, leading to an
98 important amount of remaining $\alpha\text{-Fe}_2\text{O}_3$. Therefore, synthesis temperature was set to 210 °C, and 220 °C
99 is considered as decomposition temperature under vacuum, and is reported on figure 1 c) as a dashed red
100 line. Despite the presence of hematite in the powder, XRD profile refinements (see table 1) confirm that
101 lattice parameters of $\text{NH}_4\text{FeP}_2\text{O}_7$ phase are consistent with literature data [21]. After the powder was
102 synthesized, it was placed in a WC die to be sintered in Cool-SPS conditions. Sintering temperature
103 ranging from 200 to 300 °C were used to prepare ceramics. Interestingly, it is observed that the
104 contribution of $\alpha\text{-Fe}_2\text{O}_3$ traces to XRD patterns is apparently suppressed, as its very presence after
105 sintering can be doubted for ceramics prepared at 250°C and above (figure 1 a and b). An hypothesis for
106 that observation deals with the presence of 20 wt.% of ammonium hydrogen phosphate during synthesis,
107 which may remain unreacted, possibly in amorphous form. We know from XRD on as-synthesized
108 powder that $\alpha\text{-Fe}_2\text{O}_3$ remains in excess. Therefore, Cool-SPS treatment on the as-synthesized powder, in
109 which some precursors remain, likely promotes their reactivity while sintering is performed, ultimately
110 resulting in the formation of pure, crystalized $\text{NH}_4\text{FeP}_2\text{O}_7$ when Cool-SPS is performed at 300°C. This
111 makes the present processing route a reactive sintering, which probably contributes to the high density
112 obtained, despite the very low temperature used, down to 200 °C, even below the synthesis temperature.
113 From table 1, we can confirm the preservation of $\text{NH}_4\text{FeP}_2\text{O}_7$ lattice parameters, thus phase purity. Table
114 1 also displays densities of pellets sintered at temperatures ranging from 200 to 300 °C. All of them show
115 a density above 94 %, even reaching 98 % for a 300 °C sintering treatment. Thanks to Cool-SPS
116 efficiency, short sintering time (10 min only) and very low sintering temperatures are sufficient to obtain
117 highly dense ceramic materials. These observations confirm the possibility of using SPS in such low
118 temperature conditions, to extend the stability range of some compound, and to rely on reactive sintering
119 in Cool-SPS conditions.

120 Moreover, considering thermal analysis performed on the initial powder (figure 1c), decomposition in air
121 occurs in three steps ranging from 170 to 600 °C. The important information to consider in the present
122 case is the starting decomposition temperature, 170 °C. This corresponds to 130 °C below the sintering
123 temperature. However, we know from investigating its synthesis conditions that $\text{NH}_4\text{FeP}_2\text{O}_7$ is more
124 stable under vacuum than in air. Decomposition temperature has previously been determined as 220 °C
125 under vacuum. Considering now the highest sintering temperature used to obtain a 98% dense sample,

126 this represents 80 °C above the decomposition temperature under vacuum. It suggests a modified thermal
127 stability range in Cool-SPS conditions compared to atmospheric pressure conditions, which has already
128 been pointed out for other materials [12]. As the refined lattice parameters of the ceramics (table 1),
129 obtained from profile refinements (figure 1 a), show very good consistency with the literature and from
130 one sample to the other, it is clear that Cool-SPS processing above decomposition temperature preserves
131 (and indeed increase) the phase purity from as-synthesized powder to 300 °C sintered ceramic of
132 $\text{NH}_4\text{FeP}_2\text{O}_7$. This confirms the preservation of the phase 80 °C above its decomposition temperature in
133 vacuum and allows using the obtained samples for further physical characterizations.

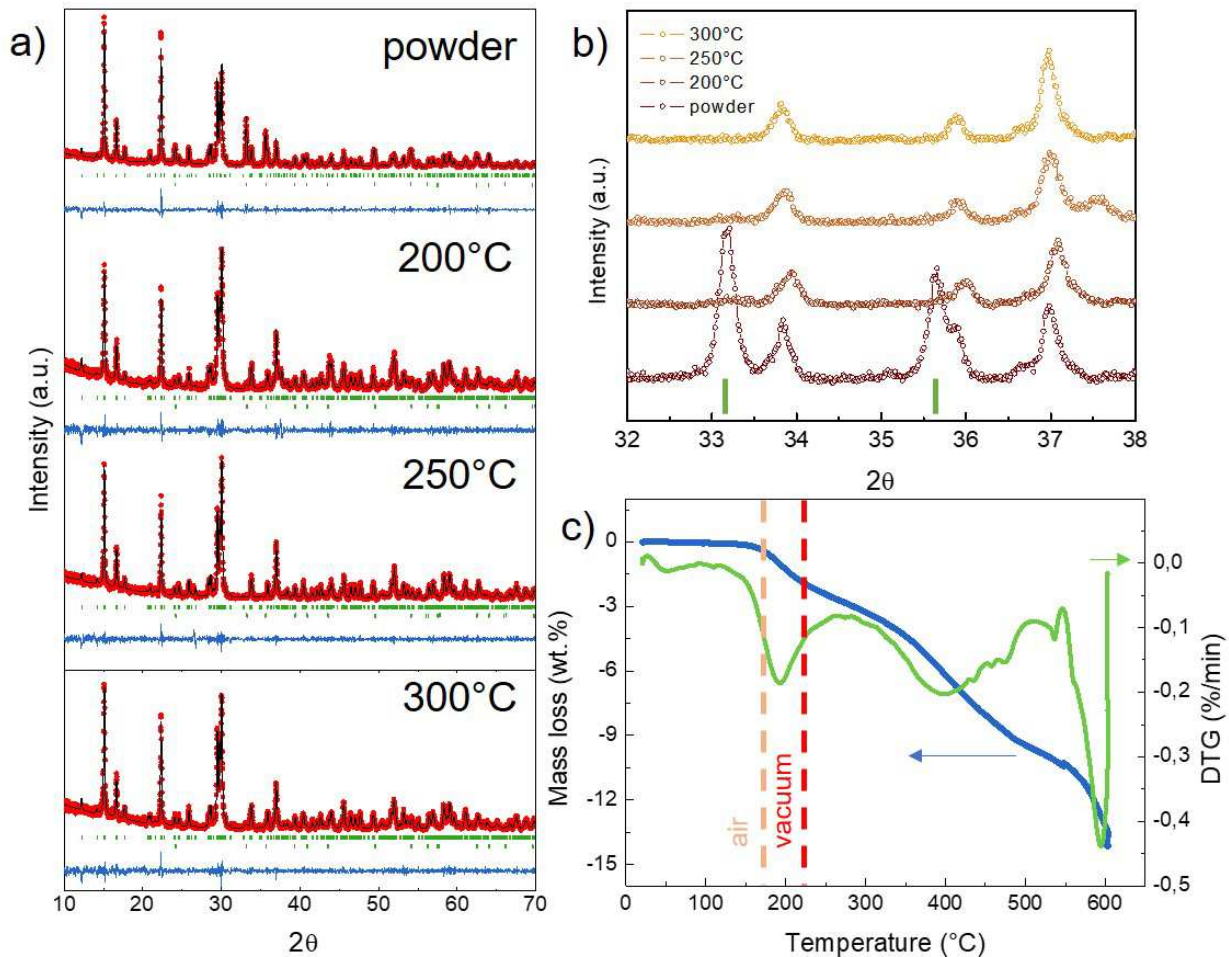
134 SEM images were taken on fractured pellets to observe their microstructure. According to these
135 observation (figure 2), no open porosity is observed, and the high densifications geometrically measured
136 are confirmed. Considering the quality of the pure and dense ceramics prepared, physical characterization
137 can be performed on the sintered samples. In the following, all characterizations presented correspond to
138 300 °C sintered pellet, which is both the most dense and most pure specimen at our disposal. Since no
139 magnetic characterization of $\text{NH}_4\text{FeP}_2\text{O}_7$ has been reported previously, the present work is an opportunity
140 to complete the data concerning the AFeP_2O_7 series ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Ag}$). Figure 3 displays zero
141 field cool magnetic measurement revealing a maximum of magnetization of 0.17 emu.g^{-1} at 21 K, and
142 thus a transition to an antiferromagnetic phase below that point. The Curie-Weiss fit perfectly describes
143 the sample magnetic behaviour at high temperature in the paramagnetic state, with $C = 1.19 \text{ emu.K.mol}^{-1}$
144 and $\theta = -32.9 \text{ K}$, confirming the antiferromagnetic nature of magnetic interactions in $\text{NH}_4\text{FeP}_2\text{O}_7$. These
145 observations are consistent with literature data on AFeP_2O_7 ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Cs}, \text{Ag}$) [22–25], which are
146 recalled in table 2 along with the contribution from this work. Most representatives of this series show
147 antiferromagnetic transitions at low temperatures, and all of them present negative value of θ , indicative
148 of antiferromagnetic interactions. Our data places the ammonium representative as the one displaying the
149 weakest magnetic interactions in the series from this viewpoint, and also show that the magnetic
150 behaviour in this series can not be rationalized on the basis of a simple crystal-chemical parameter such as
151 ionic radius. Since high density pellets can be obtained after sintering, it is now possible to perform
152 reliable dielectric measurements. Figure 4a presents the dielectric measurements performed on pellet
153 sintered at 300 °C, which were found reproducible from several ceramics prepared in the same conditions.
154 According to the small value of the permittivity and the low level of losses (below 0.01), we can tell that
155 the quality of grain boundaries is very good, as defect-related contributions from grain boundaries would
156 otherwise clearly dominate the dielectric response of the sample. A relaxation is observed in the losses
157 from 150 to 100 K, which is associated with a slight decrease in the real part of permittivity. However, the
158 mechanism associated with this dielectric anomaly has not been identified yet, and the small amplitude of
159 permittivity evolution prevents deeper analyses to identify it. As $\text{NH}_4\text{FeP}_2\text{O}_7$ crystal symmetry allows for

160 a magnetoelectric coupling [26] it is worth trying to investigate it through magnetic field dependent
161 dielectric measurements. On figure 4b is displayed the dependence of dielectric permittivity to applied
162 magnetic field, at 300 kHz and 2 K for the same sample. As can be observed from the plot, a dependence
163 is measured, mostly between ± 3 to ± 6 T, which remains of rather small amplitude, preventing us from
164 performing additional characterization (such as magnetic field dependent polarization) and concluding on
165 its nature. Anyway, this points out the possible presence of a magnetoelectric in the phase, which requires
166 further investigations to be confirmed.

167 **Conclusion**

168 It was possible to synthesize $\text{NH}_4\text{FeP}_2\text{O}_7$ powder from solid state route, by firing diammonium hydrogen
169 phosphate and iron oxide at 210°C under primary vacuum. However hematite $\alpha\text{-Fe}_2\text{O}_3$ remains present
170 after synthesis, while XRD confirms the stabilization of the target phase, with lattice parameters similar to
171 those reported in the literature [21]. Among the key features of the present work is the behavior of this
172 material during its processing by Cool-SPS. Although no literature data deal with the densification of this
173 material, it was possible to obtain a highly dense material using temperature as low as 200°C and
174 sintering time as short as 10 min. This illustrates the potential of low temperature sintering techniques,
175 such as Cool-SPS, for the elaboration of highly densified ceramics. As $\text{NH}_4\text{FeP}_2\text{O}_7$ decomposes in air
176 around 170°C and in vacuum around 220°C , this also illustrates the possibility, pointed previously [12],
177 to densify some thermodynamically fragile materials beyond their thermal stability range, and expand the
178 range of possible characterizations to that allowed by ceramics, which are otherwise mostly limited to
179 studies performed on powder or single-crystals. Moreover, in the present case, although the targeted
180 phase could not be obtained as a pure powder after synthesis, Cool-SPS processing essentially removed
181 the $\alpha\text{-Fe}_2\text{O}_3$ excess, most probably thanks to reactive sintering. Finally, obtaining such phase-pure, high-
182 density pellets allowed to perform physical characterizations. Magnetic measurements revealed an
183 antiferromagnetic phase transition at 21 K, consistent with literature data on other members of AFeP_2O_7
184 ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Cs}, \text{Ag}$) family showing similar properties. Dielectric properties could be measured on
185 dense pellet, confirming the quality of grain boundaries and exhibiting a dielectric anomaly in the range
186 100-150 K. In parallel, magnetic dependence of permittivity exhibits a clue for magnetoelectric coupling
187 in $\text{NH}_4\text{FeP}_2\text{O}_7$, which needs to be further investigated.

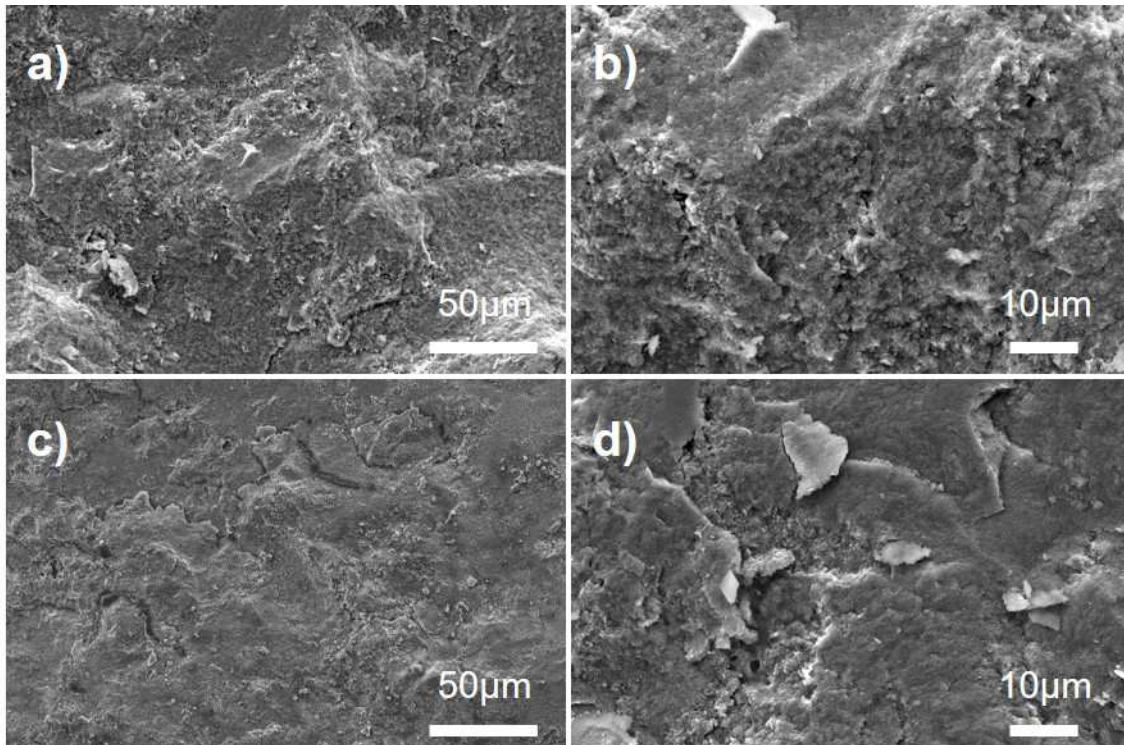
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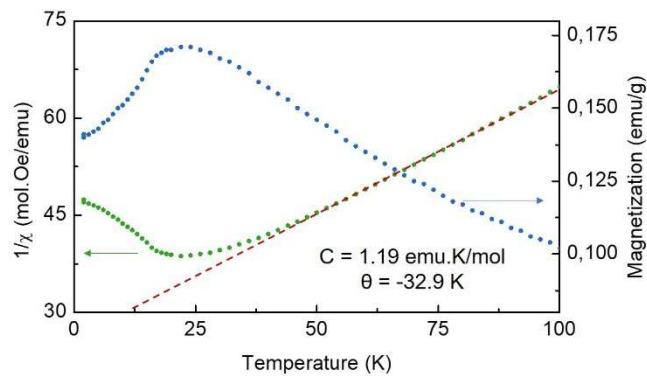
190 *Figure 1: a) XRD patterns collected on synthesized powder and sintered pellets at various temperatures ; b) zoom in the region of*
 191 *32° ≤ 2θ ≤ 38, with a green mark representing Bragg positions for Fe₂O₃ hematite phase (other contributions are due to the title*
 192 *compound) ; c) TGA in air at constant heating rate of 5 °C/min from room temperature to 600 °C on NH₄FeP₂O₇ powder after*
 193 *synthesis (blue line correspond to TG data and green line to dTG), dashed orange line represents the starting decomposition*
 194 *temperature in air extracted from TGA(170 °C) while red dashed line represents the stability temperature observed in primary*
 195 *vacuum, obtained from synthesis (220 °C)*

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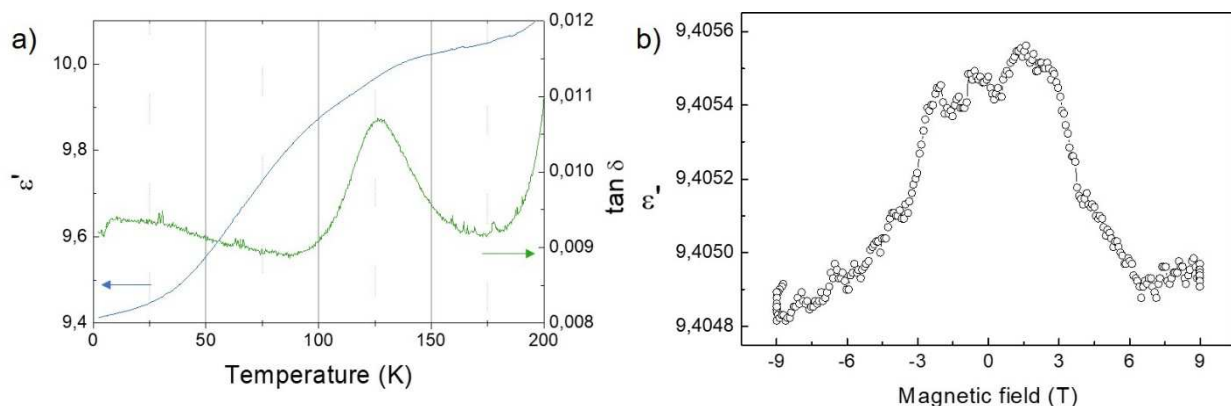
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Figure 2: SEM images of fractured samples sintered at (a-b) 200 °C and (c-d) 300 °C



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Figure 3: Zero field cool measurement on pellet sintered at 300 °C - 300 MPa - 10 min, green dots correspond to inverse of magnetic susceptibility and blue dots to sample magnetization ; red dashed line corresponds to Curie-Weiss fit



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Figure 4: a) Dielectric measurement in the range 2 – 200K, measured at 300 kHz min and b) Magnetic field dependence of permittivity at 300 kHz measured on a pellet sintered at 300 °C - 300 MPa - 10

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Table 1: Refined lattice parameters for powder and pellets sintered at various temperatures

Sample	Sintering temperature (°C)	a (Å)	b (Å)	c (Å)	β (°)	Relative density (%)
#1	200	7.5175(3)	10.0065(3)	8.2738(3)	105.895(3)	94.1(5)
#2	250	7.5180(2)	10.0055(3)	8.2780(2)	105.901(3)	95.6(5)
#3	300	7.5176(2)	10.0043(2)	8.2729(2)	105.900(3)	98.0(5)
Powder	-	7.5197(4)	10.0023(5)	8.2759(5)	105.856(6)	-
Reference [20]	-	7.5219(2)	10.0018(3)	8.2729(3)	105.887(3)	-

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Table 2: Comparison of some crystal-chemical and magnetic data for the pyrophosphate series $M^I\text{FeP}_2\text{O}_7$ ($M^I = \text{Na}, \text{K}, \text{Cs}, \text{NH}_4, \text{Ag}$).

Compound	Space group	θ (K)	R_A (Å)	Ref.
NaFeP_2O_7	$P2_1/c$	-53	1,18	[23]
AgFeP_2O_7	$P2_1/c$	-165.9	1,28	[22]
KFeP_2O_7	$P2_1/c$	-90	1,51	[23]
$\text{NH}_4\text{FeP}_2\text{O}_7$	$P2_1/c$	-32.9	1,55	This Work
CsFeP_2O_7	$P2_1/c$	-64.9	1,74	[25]

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- 214 [1] J.-P. Maria, X. Kang, R.D. Floyd, E.C. Dickey, H. Guo, J. Guo, A. Baker, S. Funahashi, C.A.
215 Randall, Cold sintering: Current status and prospects, *J. Mater. Res.* 32 (2017) 3205–3218.
- 216 [2] H. Guo, A. Baker, J. Guo, C.A. Randall, Protocol for Ultralow-Temperature Ceramic Sintering:
217 An Integration of Nanotechnology and the Cold Sintering Process, *ACS Nano.* 10(11) (2016) 10606–
218 10614.
- 219 [3] S. Funahashi, J. Guo, H. Guo, K. Wang, A.L. Baker, K. Shiratsuyu, C.A. Randall, Demonstration
220 of the Cold Sintering Process Study for the Densification and Grain Growth of ZnO Ceramics, *J. Am.*
221 *Ceram. Soc.* 100 (2017) 546–553.
- 222 [4] S.S. Berbano, J. Guo, H. Guo, M.T. Lanagan, C.A. Randall, Cold sintering process of
223 $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ solid electrolyte, *J. Am. Ceram. Soc.* 100 (2017) 2123–2135.
- 224 [5] D. Wang, D. Zhou, S. Zhang, Y. Vardaxoglou, W. Whittow, D. Cadman, I. Reaney, Cold-
225 Sintered Temperature Stable $\text{Na}_{0.5}\text{Bi}_{0.5}\text{MoO}_4\text{-Li}_2\text{MoO}_4$ Microwave Composite Ceramics, *ACS*
226 *Sustain. Chem. Eng.* 6 (2018) 2438–2444.
- 227 [6] I.J. Induja, M.T. Sebastian, Microwave dielectric properties of mineral sillimanite obtained by
228 conventional and cold sintering process, *J. Eur. Ceram. Soc.* 37 (2017) 2143–2147.
- 229 [7] H. Guo, A. Baker, J. Guo, C.A. Randall, Cold Sintering Process: A Novel Technique for Low-
230 Temperature Ceramic Processing of Ferroelectrics, *J. Am. Ceram. Soc.* 99 (2016) 3489–3507.
- 231 [8] A. Ndayishimiye, S. Buffière, M.A. Dourges, A. Largeteau, M. Prakasam, S. Mornet, O. Kaman,
232 J. Zdeněk, J. Hejtmánek, G. Goglio, Design of 0–3 type nanocomposites using hydrothermal sintering,
233 *Scr. Mater.* 148 (2018) 15–19.
- 234 [9] A. Ndayishimiye, A. Largeteau, M. Prakasam, S. Pechev, M.A. Dourges, G. Goglio, Low
235 temperature hydrothermal sintering process for the quasi-complete densification of nanometric α -quartz,
236 *Scr. Mater.* 145 (2018) 118–121.
- 237 [10] A. Ndayishimiye, A. Largeteau, S. Mornet, M. Duttine, M.-A. Dourges, D. Denux, M. Verdier,
238 M. Goune, T. Herisson de Beauvoir, C. Elissalde, G. Goglio, Hydrothermal Sintering for Densification of
239 Silica . Evidence for the Role of Water, *J. Eur. Ceram. Soc.* 38 (2018) 1860–1870.
- 240 [11] T. Herisson de Beauvoir, F. Molinari, U.-C. Chung-Seu, D. Michau, D. Denux, M. Josse,
241 Densification of MnSO_4 ceramics by Cool-SPS: evidences for a complex sintering mechanism and
242 magnetoelectric coupling, *J. Eur. Ceram. Soc.* 38 (2018) 3867–3874.
- 243 [12] T. Herisson de Beauvoir, A. Sangregorio, I. Cornu, C. Elissalde, M. Josse, Cool-SPS: an
244 opportunity for low temperature sintering of thermodynamically fragile materials, *J. Mater. Chem. C.* 6(9)
245 (2018) 2229–2233.
- 246 [13] D. Sohrabi Baba Heidary, M. Lanagan, C.A. Randall, Contrasting energy efficiency in various
247 ceramic sintering processes, *J. Eur. Ceram. Soc.* 38 (2018) 1018–1029.
- 248 [14] X. Zhao, J. Guo, K. Wang, T. Herisson De Beauvoir, B. Li, C.A. Randall, Introducing a ZnO-
249 PTFE (Polymer) Nanocomposite Varistor via the Cold Sintering Process, *Adv. Eng. Mater.* (2018)
250 1700902.

- 251 [15] J. Guo, H. Guo, D.S.B. Heidary, S. Funahashi, C.A. Randall, Semiconducting properties of cold
252 sintered V₂O₅ ceramics and Co-sintered V₂O₅-PEDOT:PSS composites, *J. Eur. Ceram. Soc.* 37 (2016)
253 1529–1534.
- 254 [16] J. Guo, S.S. Berbano, H. Guo, A.L. Baker, M.T. Lanagan, C.A. Randall, Cold Sintering Process
255 of Composites : Bridging the Processing Temperature Gap of Ceramic and Polymer Materials, *Adv.*
256 *Funct. Mater.* 26 (2016) 7115–7121.
- 257 [17] S. Funahashi, H. Guo, J. Guo, A.L. Baker, K. Wang, K. Shiratsuyu, C.A. Randall, Cold sintering
258 and co-firing of a multilayer device with thermoelectric materials, *J. Am. Ceram. Soc.* 100 (2017) 3488–
259 3496.
- 260 [18] T. Herisson de Beauvoir, V. Villemot, M. Josse, On the first molecular ceramic, obtained by
261 Cool-SPS, submitted.
- 262 [19] X. Fleury, M.H. Noh, S. Geniès, P.X. Thivel, C. Lefrou, Y. Bultel, Fast-charging of Lithium Iron
263 Phosphate battery with ohmic-drop compensation method: Ageing study, *J. Energy Storage.* 16 (2018)
264 21–36.
- 265 [20] D. Grossin, S. Rollin-Martinet, C. Estournès, F. Rossignol, E. Champion, C. Combes, C. Rey, C.
266 Geoffroy, C. Drouet, Biomimetic apatite sintered at very low temperature by spark plasma sintering:
267 Physico-chemistry and microstructure aspects, *Acta Biomater.* 6 (2010) 577–585.
- 268 [21] B.F. Alfonso, J.A. Blanco, M.T. Fernández-Díaz, C. Trobajo, S.A. Khainakov, J.R. García, On
269 the crystal structure and thermal decomposition of ammonium-iron(iii) bis(hydrogenphosphate), *Dalt.*
270 *Trans.* 39 (2010) 1791–1796.
- 271 [22] K. V. Terebilenko, A.A. Kirichok, V.N. Baumer, M. Sereduk, N.S. Slobodyanik, P. Gütlich,
272 Structure and magnetic properties of AgFeP₂O₇, *J. Solid State Chem.* 183 (2010) 1473–1476.
- 273 [23] D. Riou, N. Nguyen, R. Benloucif, B. Raveau, LiFeP₂O₇ : Structure and magnetic properties,
274 *Mater. Res. Bull.* 25 (1990) 1363–1369.
- 275 [24] T. Moya-Pizarro, R. Salmon, L. Fournes, G. Le Flem, B. Wanklyn, P. Hagenmuller, Etudes
276 cristallographique magnétique et par résonance Mössbauer de la variété de haute température du
277 pyrophosphate NaFeP₂O₇, *J. Solid State Chem.* 53 (1984) 387–397.
- 278 [25] E. Dvoncova, K.-H. Lii, Synthesis, crystal structure, and magnetic susceptibilities of CsFeP₂O₇
279 and RbFeP₂O₇, *J. Solid State Chem.* 105 (1993) 279–286.
- 280 [26] S. Gentil, D. Andreica, M. Lujan, J. Rivera, F. Kubel, H. Schmid, Synthesis, structure and
281 magnetic susceptibility of KCrP₂O₇ , a potential antiferromagnetic magnetoelectric, *Ferroelectrics.* 204
282 (1997) 35–44.
- 283