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Supplementary Information

Cool-SPS an opportunity for low temperature sintering of fragile materials

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Powders used for sintering have been characterized by XRD in order to confirm the presence of the target phases and the absence of remaining impurities. TGA measurements were also performed on the powders to determine their decomposition temperature in air. Figure S1 displays results of both TGA and XRD (including a profile matching refinement) on each precursor. In the two specific cases of hydrated precursors $MnSO_4 \cdot H_2O$ and $Na_2Cu(CO_3)_2 \cdot 3H_2O$, TGA and XRD have been performed on the hydrated phases used for SPS, while the target phases are anhydrous $MnSO_4$ and $Na_2Cu(CO_3)_2$ respectively.

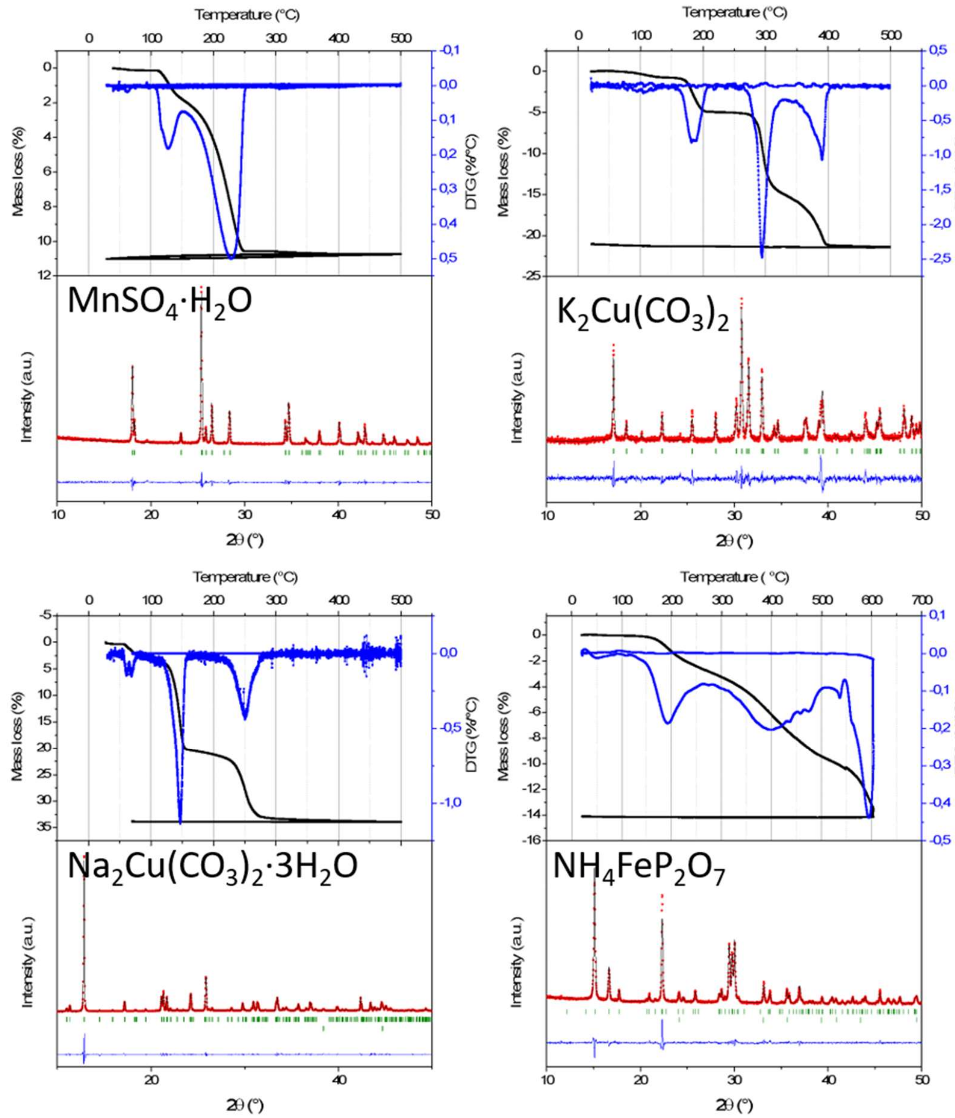

Figure S1: TGA and XRD measurements performed on precursor powders used for sintering

XRD profile refinement of the $MnSO_4 \cdot H_2O$ precursor shows no secondary phase and confirms phase purity. Refined parameters (a = 7.7676(1) Å ; b = 7.6649(1) Å ; c = 7.1232(1) Å ; β = 115.8462(7)°, space group A2/a) correspond to literature data (Y. le Fur, J. Coing-Boyat, and G. Bassi, "Structure des sulfates monohydrates, monocliniques, des metaux de transition, MSO4 (H2O) (M = Mn, Fe, Co, Ni et Zn)," Comptes Rendus Hebd. des Seances l'Academie des Sci. Ser. C, Sci. Chim., vol. 262, pp. 632–635, 1966). TGA performed on $MnSO_4 \cdot H_2O$ shows two mass losses of 2% and 9% ranging respectively from 110 to 150 °C and from 150 °C to 250 °C. These two mass losses correspond to water release from the precursor and lead to total dehydration of the powder. No further mass loss is detected up to 500 °C, which is consistent with the decomposition temperature of $MnSO_4$ being 780 °C[35]. Final mass loss of 11 % observed at 250 °C corresponds to a single H_2O molecule per $MnSO_4$ unit, which confirms the composition of $MnSO_4 \cdot H_2O$ of the precursor. Thus, to obtain a powder consisting in pure and anhydrous $MnSO_4$, a thermal treatment at 250 °C is needed.

The phase $Na_2Cu(CO_3)_2 \cdot 3H_2O$ is confirmed by XDR profile refinement and the absence of additional peaks asserts its purity. Refined cell parameters are a = 9.6933(1) Å ; b = 6.0953(1) Å ; c = 13.7895(1) Å ; β = 91.9155(6)° in $P2_1/n$ space group, and are consistent with cell parameters refined from single crystal data, available in the literature (A. Escuer, F. a Mautner, E. Peñalba, and R. Vicente, "Crystal Structure and Magnetic Behavior of Two New Dinuclear Carbonato-Bridged Copper(II) Compounds. Superexchange Pathways for the Different Coordination Modes of the Carbonato Bridge in Polynuclear Copper(II) Compounds," Inorg. Chem., vol. 37, no. Ii, pp. 4190–4196, 1998). In the case of $Na_2Cu(CO_3)_2 \cdot 3H_2O$ TGA measurement mainly shows three mass losses. The first one ranges from 50 to 75 °C and corresponds to a mass loss of 2.5 %, while the second one, which the most important mass loss with 18 %, ranges from 120 to 160 °C. The third and final mass loss corresponds to 12.5 % and ranges from 220 to 275 °C. In situ XRD (not shown) revealed that this third mass loss corresponds to the decomposition of the phase in both CuO_2 and Na_2CO_3 phases. The two previous mass losses amount to 20.5 %, which is consistent with 3 H_2O molecules per $Na_2Cu(CO_3)_2$ formula unit. TGA analysis suggests that a thermal treatment in the range 160-220 °C should yield the anhydrous phase $Na_2Cu(CO_3)_2$.

$K_2Cu(CO_3)_2$ was directly obtained in pure and anhydrous form thanks to the synthesis method used. XRD pattern refinement shows a good crystallization of the phase without any secondary phase detected. Lattice parameters were refined as a = 11.4281(2) Å; b = 17.6533(1) Å; c = 6.1532(1) Å in the orthorhombic Fdd2 space group. These parameters correspond to the ones refined on single crystal (A. Farrand, A. Gregson, B. Skelton, and A. White, "Crystal structure of the ferromagnetic polymer potassium Bis(carbonato)cuprate(II)," Aust. J. Chem., vol. 33, pp. 431–434, 1980)," Dalton Transactions. 2010). TGA measurement on $K_2Cu(CO_3)_2$ shows three mass losses. The first one occurs between 160 and 210 °C, represents a 5 %wt. loss, and corresponds to the loss of residual water from synthesis. Decomposition occurs in two steps visible through the two mass losses ranging from 270 to 320 °C and from 350 to 400 °C, and thus decomposition temperature is determined as 270 °C.

XRD pattern of $NH_4FeP_2O_7$ shows a good crystallization, with the presence of remaining Fe_2O_3 after synthesis that could not be avoided. Anyway, $NH_4FeP_2O_7$ is the main phase and has lattice parameters a = 7.5107(1) Å ; b = 10.0008(1) Å ; c = 8.2697(1) Å and β = 105.7985(2)° in monoclinic $P2_1/c$ space group, in good agreement with literature (B. F. Alfonso, J. A. Blanco, M. T. Fernández-Díaz, C. Trobajo, S. A. Khainakov, and J. R. García, "On the crystal structure and thermal decomposition of ammonium-iron(iii) bis(hydrogenphosphate)," Dalton Transactions. 2010). For this pyrophosphate, TGA measurement has been performed up to 600 °C, and revealed a continuous mass loss starting at 170 °C and extending continuously up to 600 °C. A first mass loss ranging from 170 to 270 °C can be identified in the DTG, during which decomposition of the phase already occurs. Therefore, this signal is used to determine the decomposition temperature in air as 170 °C.

Table S2: Refined parameters of sintered pellets and the corresponding powder precursors or literature values when hydrated phase precursor is used

Table 1: Refined cell parameters for both powders and pellets of various compositions, $MnSO_4$ and $Na_2Cu(CO_3)_2$ are compared to literature values since no powder with the same composition can be used as reference

Material		a (Å)	b (Å)	c (Å)	β (°)
$K_2Cu(CO_3)_2$	*Pellet*	11.4337(4)	17.6604(4)	6.1571(3)	90
	Powder	11.4281(2)	17.6533(1)	6.1532(1)	90
$NH_4FeP_2O_7$	*Pellet*	7.5200(2)	10.0071(2)	8.2807(2)	105.896(2)
	Powder	7.5107(3)	10.0008(1)	8.2697(1)	105.7985(2)
$MnSO_4$*	*Pellet*	6.8551(3)	8.0467(3)	5.2642(2)	90
	Literature[33]	*6.848*	*8.048*	*5.267*	*90*
$Na_2Cu(CO_3)_2$*	*Pellet*	5.6482(1)	8.1779(2)	6.1729(1)	116.260(1)
	Literature[34]	*5.64(2)*	*8.19(2)*	*6.18(2)*	*116.2(2)*

(*) obtained after sintering of powder crystallizing in a hydrated phase

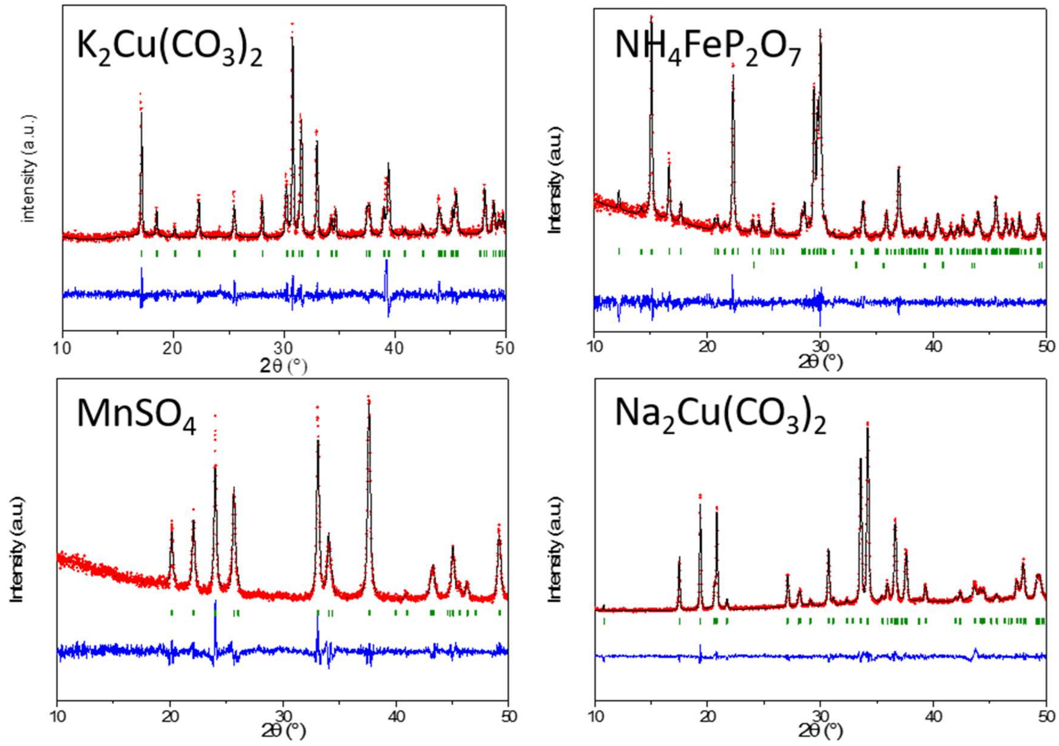

Figure S3: Refined XRD profiles for sintered pellets

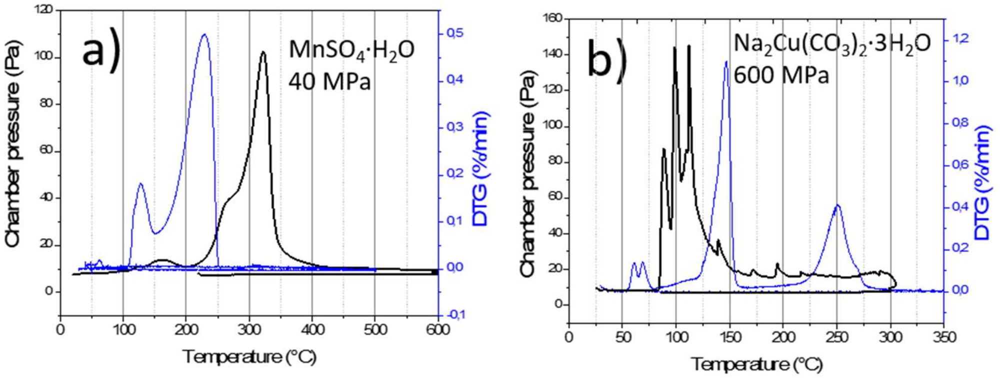

Figure S4: SPS chamber pressure while heating and DTG from Figure S1 for $MnSO_4 \cdot H_2O$ and $Na_2Cu(CO_3)_2 \cdot 3H_2O$

In the case of $MnSO_4 \cdot H_2O$, the gas release pattern has a profile similar to the DTG obtained while performing TGA under air at ambient pressure, but a temperature shift is observed. DTG shows a dehydration ranging from 110 to 250 °C whereas during SPS processing, dehydration occurs in the temperature range 210 to 350°C. The corresponding shift of 100 °C can arise from a stabilization of the hydrated form under the application of pressure. Heating up to 600 °C (under 400 MPa) shows no further gas release and the full dehydration is confirmed by the absence of hydrated phase in the XRD pattern of the resulting pellet (Figure 5).

In the case of $Na_2Cu(CO_3)_2 \cdot 3H_2O$, DTG measurement shows a total dehydration at 160 °C and a decomposition ranging from 220 to 280 °C (determined from XRD). SPS chamber pressure shows an important water release from 70 to 130 °C, followed by a slow pressure decrease up to 160 °C, with occasional spikes that could be related to the release of water vapor that was retained in the powder due to its densification. In this case, dehydration appears to be shifted towards lower temperatures by the application of a pressure of 600 MPa. It is also worth mentioning the absence of gas release corresponding to decomposition up to 300 °C, although such a decomposition is observed in TGA above 220 °C in air.