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Mechanosynthesis of multiferroic hybrid organic-inorganic $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ $\text{M} = \text{Co}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ formate-based frameworks

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1 Mechanosynthesis of multiferroic hybrid organic-inorganic $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ $\text{M} = \text{Co}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ formate-based frameworks

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Abstract

The family of compounds with formula $[\text{NH}_4][\text{M}(\text{HCOO})_3]$, with M a divalent d-metal, is characterized by porous frameworks hosting NH_4^+ cations exhibiting at low temperature a spontaneous ferroelectric polarization. The presence of magnetically active divalent metal determines the occurrence of antiferromagnetic ordering below 30 K opening the avenue for a rational formulation of a new class of multiferroic materials. We demonstrate that this intriguing class of compounds can be synthesized with a mechanochemical approach. This novel route of synthesis was applied to the series $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ with $\text{M} = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ and Ni²⁺ using as reactants ammonium formate and the corresponding di-hydrated metal formates. The milling duration of the process correlates with the thermal stability of the di-hydrated metal formates indicating that the first step of the mechanochemical process is represented by the removal of water molecules. The characterizations of the final products indicate the presence of single phase $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ compounds with an excellent degree of crystallinity.

Keywords:

Mechanosynthesis, Hybrid organic-inorganic materials, Metal-organic frameworks

Abbreviations

No keyword abbreviations are available

1 Introduction

The recent discovery of functional magnetic, electric and optical properties in Metal Organic Frameworks (MOF) featured by the ABX_3 perovskite-like structure has attracted considerable interest in the research community sparking the design and synthesis of a series of new organic-inorganic hybrid materials [1–3]. Among them, the frameworks of distorted corner-linked octahedra formed by divalent metals (Cu^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} , Zn^{2+}) and $HCOO^-$ formate ligands holds a special position [4]. In these MOFs the A site is occupied by either organic cations, like protonated amines [5], or by alkaline cations (K^+ , Na^+) [6]. The flexibility of the $HCOO^-$ group in assuming different cross-linking $B \cdot OHCO \cdot B$ *sin-sin*, *sin-anti* or *anti-anti* arrangements, is at the basis of different topological networks [7]. Beside the perovskite-like structure, a second polymorphic form characterized by hexagonal cavities along the *c* axis hosting the organic cation [6,7] was observed. The hexagonal 4^9-6^6 [7] structure, having $P6_322$ symmetry, is generally found for NH_4^+ based formates combined with several types of divalent B^{2+} ions. Below room temperature the system undergoes an order-disorder transition mainly involving the position of NH_4^+ cations; the ordered phase has a polar symmetry, defined by the $P6_3$ space group, and experimental studies [8] demonstrated the occurrence of a spontaneous ferroelectric polarization. Furthermore, when the divalent cation has unpaired d -electron, antiferromagnetic ordering has been observed at low temperature and therefore, these compounds are indicated as highly promising for the rational design of a new generation of multiferroic materials [9].

The synthesis of the ammonium metal formates (AMF) can be undertaken using different approaches, ranging from mild chemistry protocols to solvothermal or hydrothermal conditions,[10] with the latter involving ammonium formate [9] or Dimethylformamide (DMF) in methanol as source of formate, used to grow suitable single crystals for electric polarization measurements. Overall, the common synthetic route is related to the precipitation of the crystalline porous MOF from a methanol solution of formic acid, ammonia and a soluble inorganic salt of the divalent metal ion [7]. All these synthetic strategies are extensively exploited in the synthesis of various inorganic-organic hybrid materials. Among them, photovoltaic hybrid methylammonium lead halides ($MAPbI_3$), were successfully obtained by using mechanochemical methods [11], demonstrating that hybrid materials can be obtained by solid state mechanical processes. Recently different research efforts have demonstrated that this unconventional approach for the preparation of solid compounds can be successfully applied with a series of advantages with respect to the conventional solvent-based methods [12,13]. The mechanosynthesis can be achieved without the use of solvents providing an environmentally sustainable route, scalable and with limited costs [14]. Hence, we applied mechanochemistry to the synthesis of compounds with general formula $[NH_4][M(HCOO)_3]$ $M = Mn = Mn^{2+}$, Co^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} . The milling treatment was carried out by combining ammonium formate with the hydrated metal formates, yielding single phase products. The characterization carried out on the final products indicates that they possess the same structural and chemical properties reported for the same compositions obtained by conventional methods. Our findings demonstrate that, as already remarked for halides based perovskite materials [11], the mechanosynthesis can be successfully applied for the synthesis of hybrid formate-based multiferroic and ferroelectric materials.

The kinetics observed during the mechanosynthesis reactions provides new insights in the role played by humidity in defining the reactivity of the reagents. This is in agreement with earlier studies suggesting that the successful synthesis of hybrid metal formates in solvent based protocols, is deeply connected to the hygroscopic nature of the starting materials.

2 Materials and methods

Polycrystalline ammonium formates were successfully synthesized by mechanochemical approach following the general synthetic scheme:



The starting reagents were hydrated metal formates and ammonium formate (Anhydrous, free-flowing, 97%, Sigma Aldrich). In case of Mn^{2+} and Cu^{2+} we used commercial reagents (Manganese(II) formate hydrate from Sigma Aldrich, Cu(II) formate hydrate from Sigma Aldrich 97%) whilst, for the remaining compounds the starting hydrate metal formates precursors were synthesized in laboratory (details are summarized in [Supplementary Information](#)).

Prior milling sessions, the reagents were pre-treated at 353 K in an oven for at least 45 min. Then, a stoichiometric amount of the powders was treated with a vertical vibration mill (FRITSCH Mini-Mill PULVERISETTE 23, steel jar). The starting powders were placed in a steel jar with a single 10 mm steel ball; the vibration was maintained at 40 Hz for several steps of 5/10 min. The product phases were checked using powder x-ray diffraction (PXRD) with a Thermo X'TRA diffractometer working with a $\text{Cu K}\alpha$ radiation and equipped with a Si(Li) solid state detector suited to suppress the $\text{Cu K}\beta$ radiation. High resolution x-ray diffraction measurements were performed with a STOE Stadi P (equipped with $\text{Mo-K}\alpha_1$ source, Ge111 monochromator produced by STOE & CIE, detector MYTHEN2 1 K produced by Dectris, in a 0.2 mm diameter capillary). The powders were placed in a capillary of 0.3 mm of diameter to avoid preferred orientations. Rietveld refinements were performed with the help of the Jana2006 software [15].

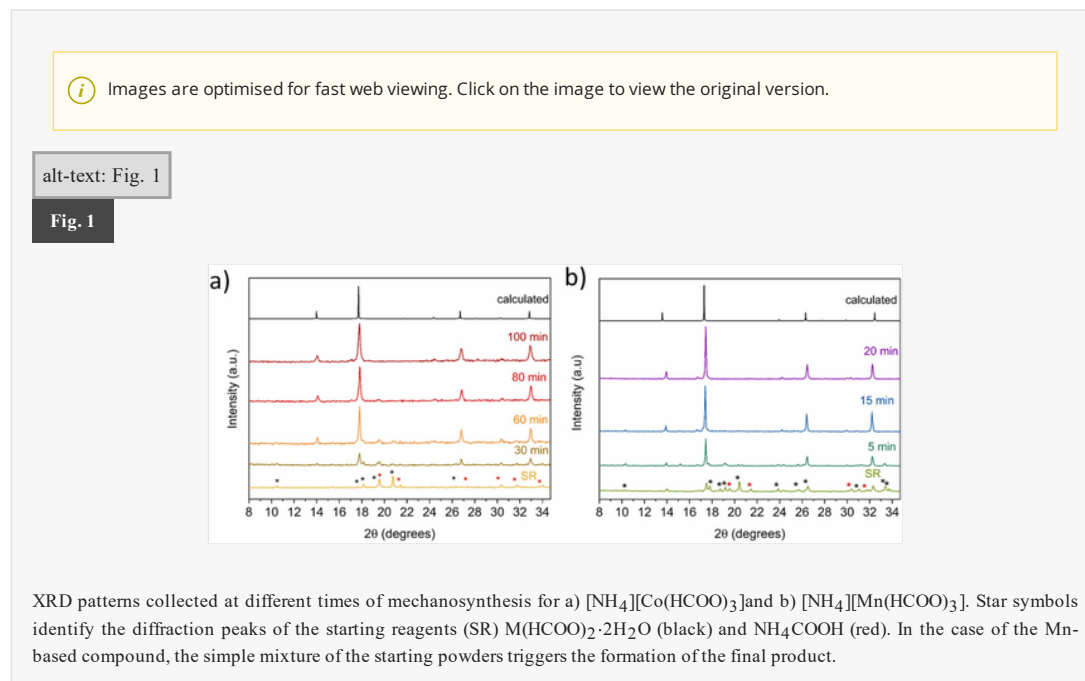
Scanning electron micrographs were collected by a Field-Emission Gun Scanning Electron Microscope (Zeiss Auriga FEG-SEM), equipped with an In-Lens detector, at 10 kV accelerating voltage. Samples analysed in SEM were previously coated with a thin $2\text{-}3\text{-}3\text{ nm}$ Au layer by means of a low-energy sputtering system (Edwards Scancoat Six), in order to remove electrostatic charge accumulation on the surface during electron-beam illumination.

Thermal analysis measurements were carried out using Perkin Elmer TGA 8000 instruments. TGA was performed under N_2 atmosphere from 298 to 700 K with a rate of 10 K/min .

Raman measurements were obtained using a Horiba LabRAM HR Evolution confocal spectrometer (focal 800 mm), using a configuration with a holographic grating (1800 lines/mm), a set of Bragg ultra-low frequency filters for the rejection of the Rayleigh scattering and a liquid nitrogen-cooled CCD detector. The system is equipped with four different lasers (532, 632.8, 785 and 1064 nm); the 632.8 nm line of a He-Ne laser was used for excitation. Neutral density filters were used to keep the laser power on the sample under 1 mW . An Ultra-Long Working Distance (ULWD) 50X objective was used for excitation and signal collection. The spectrometer is equipped with XYZ motorized stage and autofocus. The autocalibration procedure was performed before each measurement session. Spatial resolution was about $2\text{-}\mu\text{m}$, and the spectral resolution was 0.5 cm^{-1} . The investigated spectral range was from 10 to 4000 cm^{-1} . Typical collection time of the spectra ranged from 30 to 60 s for each acquisition, with 2 repetitions.

3 Results and Discussion

Fig. 1 shows the evolution of the mechanochemical reaction versus time for two selected $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ compositions with $\text{M}^{2+}=\text{Co}$ and Mn . The PXRD pattern collected after the first 5 min of reaction reveals the immediate suppression of the diffraction peaks of HCOONH_4 . As the reaction proceeds the diffraction peaks of the remaining reagent progressively decreases leading to the complete conversion to the final product (see Fig. S1 in the Supplementary Information).




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The successful mechanochemical synthesis of the different AMF compounds is closely related to the relative content of adsorbed water in the reactants. We noticed that being both the starting reagents hygroscopic, the mechanical treatment without pre-heating in oven (at 353 K) the starting reagents did not provide the successful synthesis of the AMF and residual amounts of starting reagents are still present even after prolonged sessions of mechanochemical synthesis. This is

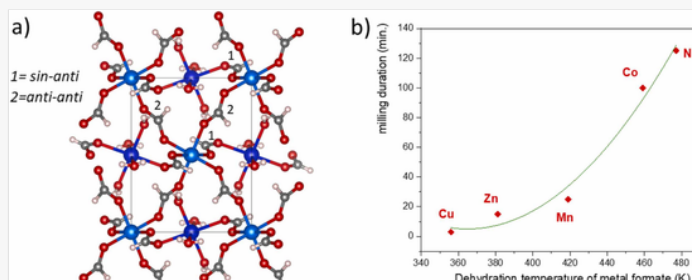
partially explained by the lack of the 1:1 molar ratio necessary to assure the correct stoichiometry. Nevertheless, the pre-heating process reduces the mechano-synthesis reaction time for all the compositions explored. The role of the absorbed water in defining the conditions in terms of energy and time required for the solid state synthesis via milling of hybrid organic-inorganic materials was addressed by D. Tsvetkov et al. [16]. The authors reported that during the grinding for the formation of CsPbI_3 a certain percent of adsorbed water constitute a favourable condition for the interaction of the starting materials CsI and PbI_2 . In that case, the yield incremented as a function of the degree of humidity. In general, liquid assisted grinding (LAG) is required when the mobility of some components, related with the diffusion coefficients of the ionic species (i.e. Cs^+ shows high solubility in water) in solution, is a fundamental prerequisite for the expected mechanical synthesis. Conversely, the synthesis of the formate compounds is strongly hindered by the presence of adsorbed water and heat treatment aimed to dry the HCOONH_4 and $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ powders is required to obtain a high yield in a reasonable milling duration.

The role of water, in ruling the evolution of the mechano-synthesis, is particularly evident considering that the decomposition temperature of the hydrated metal formates correlates with the time necessary for the complete mechano-synthesis in all the investigated AMF compounds. As illustrated in Fig. 2a) the milling time required for the complete reaction span from few minutes for Cu^{2+} to 125 min for Ni^{2+} with an exponential dependence with the dehydration temperature of $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ precursor [17,18]. Particularly, for the Cu-based compound, the milling frequency must be reduced from 40 Hz to 20 Hz in order to avoid the melting of the mixture and the consequent failure of the synthesis process. Thus, the rate-limiting step, likely ruling the kinetics of the reaction, is related to the removal of the crystallized water molecules in the hydrated metal formates. It is worth to stress that all the $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ compounds used are isostructural. Typically, the orthorhombic crystal structure of hydrated metal formates possesses two independent sites for the M^{2+} ions showing the classical octahedral coordination [19]. In the first site, the metal ion shows close interactions with oxygen from six formate groups whereas in the second one the coordination is completed with the oxygen of four water molecules. The metal sites surrounded by only formate ligands are linked by *anti-anti* arrays whereas the units involving the water molecules show *sin-anti* arrangement as evidenced in Fig. 2b). The dehydration process promoted by the mechano-synthesis induces the substitution of the water molecules in the coordination sphere of the M^{2+} ions with the formate ions provided by HCOONH_4 . The increased number of ligands available to connect the different metal sites contributes to the anionic framework formation characterized by channels accommodating the NH_4^+ cations. The construction of hexagonal cavities of the AMF constituted with *anti-anti* bridging of the formates groups requires the global rearrangement of the metal formate network with the breaking of selected M^{2+} -O interactions. Hence, the critical step is represented by the endothermic transformation of the hydrated metal formates and the thermal stability of such reactants determines the milling duration. In this context the presence of absorbed water obviously inhibits the dehydration process of the metal formates. Interestingly, the relation between the mechano-synthesis time and the metal specie corresponds to the Irving-Williams series [20]. This classical sequence represents the trend of the M^{2+} metals in relations to crystal field theory and provide a plausible explanation for the different thermal stability of the hydrated metal formates. As pointed out in several mechano-synthesis studies [21] the increase of the vibration frequency corresponds to a sensible decrease of the milling time. Nevertheless, in formate based compounds, the increment of the vibration frequency does not allow for a fine control of the energy required to promote the mechano-synthesis avoiding the melting of the reactive powders. This is particularly evident for the formation of $[\text{NH}_4][\text{Cu}(\text{HCOO})_3]$, being $\text{Cu}(\text{HCOO})_2$ very sensitive to the experimental conditions. The role of humidity and crystallization water in deciding the successful mechano-synthesis of hybrid materials has received increasing attention [22].

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Fig. 2



a) Perspective view of the orthorhombic structure of $\text{M}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ compounds. Dark and bright blue spheres indicate the two symmetrically independent metal sites showing a different environment. The dark blue site is linked with four water molecules and is connected with other sites with *sin-anti* mode of formate ligand. b) Milling duration versus metal formate de-hydration temperature for the synthesis of $[\text{NH}_4][\text{M}(\text{HCOO})_3]$.

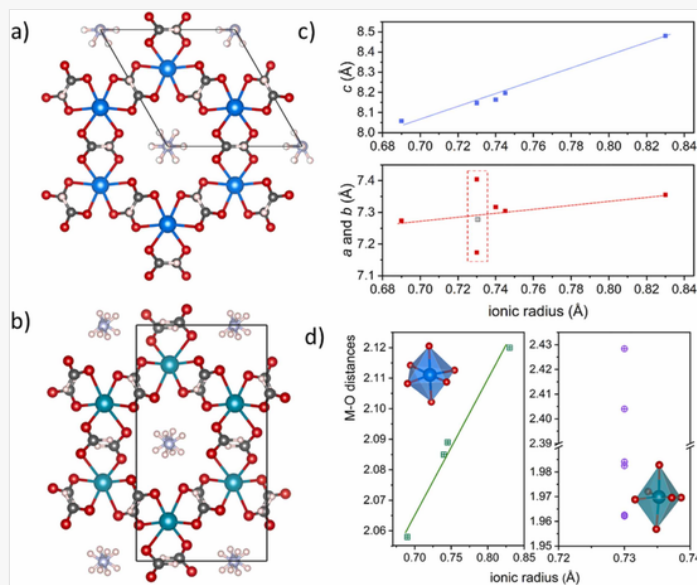
Dehydration processes promoted by mechanochemistry are described as a useful step to the readily establishment of multidimensional coordination polymers through polymerization of small molecular units [23]. By adopting mechanochemical methods, the hydration or dehydration of hybrid materials can be rationally conceived through the control of the degree of humidity.

The different AMFs synthesized by the novel mechanochemistry process were thoroughly characterized by structural, thermal and microstructural analyses. For each composition obtained by mechanical milling PXRD measurements indicated the presence of the hexagonal hybrid MOF as single phase except for the Cu^{2+} variant. In the latter case we obtained the expected orthorhombic phase [24]. The crystal structure of this compound is characterized by a distorted lattice displaying pseudo-hexagonal cavities where NH_4^+ are distributed. This distorted framework is originated by the strong Jahn-Teller distortion of the Cu^{2+} . Fig. 3(a) and (b) report the crystal structures corresponding to $\text{M}^{2+}=\text{Mn}$, Ni, Co, Zn and $\text{M}^{2+}=\text{Cu}$ respectively. The crystal data for the polycrystalline product of the mechanochemistry was obtained by Rietveld refinements (see Figs. S2–S3 in Supplementary Information). Table S1 resumes the cell constants refined for all obtained compounds and graphically represented in Fig. 3(c). The lattice constants of the hexagonal crystal structures, whose values are in agreement with those previously published, increase as the ionic radii of the divalent metal increases (we used the values for each divalent M^{2+} ion appeared in the Shannon tables [25] and summarized in Table S2 in Supplementary Information). To compare the unit cell constants of the Cu^{2+} compound with the rest of AMFs we transformed the unit cell by applying the conversion matrix indicated in Table S3. The new lattice has a pseudo-hexagonal monoclinic symmetry showing $\gamma \sim 118^\circ$. The panel shown in Fig. 3(d) illustrates the M-O bond lengths of regular octahedral environment for hexagonal structures. The distorted coordination the Cu^{2+} is characterized by four basal Cu-O bond lengths of ~ 1.98 Å and two apical bonds lengths of ~ 2.4 Å.

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Fig. 3




a) View along the c axis of the hexagonal structure of $[\text{NH}_4]\text{M}(\text{HCOO})_3$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}, \text{Zn}$ and Ni). b) View along the c axis of the orthorhombic structure of $[\text{NH}_4][\text{Cu}(\text{HCOO})_3]$. c) Unit cell constants obtained from the Rietveld refinements plotted against the ionic radii of each M^{2+} ion (the series is Ni, Cu, Zn, Co and Mn); the dotted lines highlight the unit cell parameters of the distorted Cu-based crystal structure transformed by applying the matrix reported in the Sup. Info, the grey symbol indicates the average value. d) M-O distances for the hexagonal (left) and orthorhombic (right) symmetry versus ionic radii of the divalent M^{2+} ions. The size of the symbols exceeds the e.d.s of the cell parameters.

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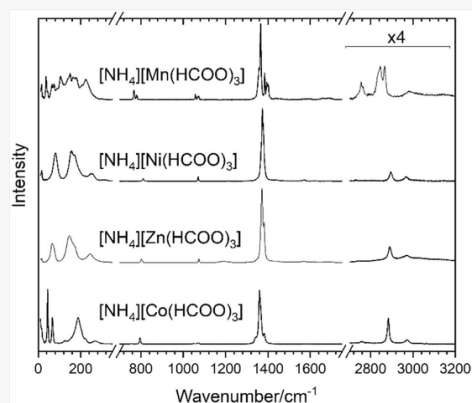
In Fig. 4 the Raman spectra of selected isostructural compositions (with Mn, Co, Ni and Zn) are shown. The overall spectra is that expected for hybrid organic-inorganic formate-based frameworks [26–29]. The Co containing sample has not a correspondence in literature; its spectra is intermediate between the previous ones, with a number of peaks similar

to Ni and Zn samples, but with small bandwidth, as the Mn sample. The sharpness of the Raman peaks can be a sign of a better order or a higher harmonicity of the lattice. The position and attribution of the Raman bands for the four samples is reported in Table S4 in Supporting Information. The attribution was made in agreement with the literature [26–29]: some of the bands are readily assigned as their position corresponds to the wavenumbers typical of formate and ammonium ions [28,30]. In particular, we can observe the most intense peaks in the region $1300\text{--}1400\text{ cm}^{-1}$, due to the C-O symmetric stretching mode (ν_2) of formate ions. The presence of multiple peaks in this region is due to the lowering of the formate ions symmetry, from C_{2v} to C_2 . In some cases, a further splitting can be caused by the presence of non-equivalent formate units in the structure, as has been observed for Mg-frameworks [28] and in the Mn-framework shown in this work. Other typical formate vibrations are visible in the regions $750\text{--}810\text{ cm}^{-1}$ (COO symmetric deformation, ν_3), $1050\text{--}1070\text{ cm}^{-1}$ (ν_6), $1570\text{--}1595\text{ cm}^{-1}$ (C-O anti-symmetric stretching, ν_4). In the high wavenumber region, $2600\text{--}3200\text{ cm}^{-1}$, the strongest peak is attributed to the C-H stretching (ν_1) of formate ions. The wavenumber of this mode increases with the lowering of C-H distance [28] and this is well reflected by the increase of the ionic radius of the metal ions ($\text{Mn}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$). The same trend is shown by the O-C-O bending mode (ν_3), even in presence of splitting. In the high wavenumber region, different weaker vibrations due to the N-H symmetric and antisymmetric stretching modes (ν_1 and ν_3) of ammonium ions are visible.

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Fig. 4



Raman spectra of the AFM obtained by mechano-synthesis. The high-wavenumbers part is magnified X4.

The ammonium N-H symmetric and antisymmetric bending modes are observed in the ranges $1430\text{--}1450\text{ cm}^{-1}$ (ν_3) and $1600\text{--}1700\text{ cm}^{-1}$ (ν_2). The splitting of the ν_2 modes indicates the lowering of the NH_4^+ symmetry to D_3 due to the crystal field. The ammonium ion vibrational modes are generally very weak in the Raman spectra, and indeed some of them are barely visible or not detected (especially in the Co containing sample). In the low wavenumber region, between 15 and 330 cm^{-1} , a large number of overlapping bands is observed. The latter region is typical of translations and librations of the ions (metals, formate and ammonium). Librations have the largest Raman signals, and are expected in the $130\text{--}220\text{ cm}^{-1}$ (HCOO^-) and $300\text{--}480\text{ cm}^{-1}$ (NH_4^+) regions. The translations of the divalent metal ions usually have very low Raman signals, often not visible. The Raman analysis of the Mn-based compound shows a complex sequence of bands, compared to the corresponding spectra of isostructural hexagonal MOF's, and differs significantly from the one published in Ref. [26]. To elucidate the origin of the Raman spectrum of $[\text{NH}_4][\text{Mn}(\text{HCOO})_3]$ further structural characterizations are necessary. Indeed, the mechano-treatment might impart local structural distortions not detected by the powder diffraction experiments. So far, the presence of amorphous phases originated by the milling process cannot be excluded.

The TGA analysis, depicted in Fig. S5 (see Supporting Information), shows for all the compounds a subtle decrement of weight around 373 K that is attributed to the removal of the adsorbed water [8,31,32]. We noticed, in all the composition explored, two main weight losses. The first decomposition step is related to the formation of the metal formate $\text{M}(\text{HCOO})_2$ [7,8] from the AMF structure, whereas the second steps is related to the decomposition into the final metal oxides. TGA analysis for the AMF compound with Cu provides a singular thermal decomposition with a drop of weight corresponding to 50% of the initial mass. This could indicate a different decomposition path with respect the rest of AMFs analysed. To elucidate this unusual behaviour we will set a series of XRD experiments on $[\text{NH}_4][\text{Cu}(\text{HCOO})_3]$ at high temperature.

The AMF phases present a good degree of crystallinity as indicated by the PXRD measurements performed both in reflection and transmission geometries. To ascertain the impact of milling duration on the crystal morphology, SEM

micrographs (see Figs. S6 and S7 in Supplementary Information) were collected on $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$ and $[\text{NH}_4][\text{Co}(\text{HCOO})_3]$ obtained after 15 and ~~100~~100 min of milling treatments respectively. We note that, under vacuum and electron beam, the crystalline phases tend to modify their habits seemingly indicating the occurrence of degradation processes. It is therefore worth to highlight that MOF are very sensitive to low pressure conditions sometimes inducing collapse of the porous frameworks [33]. As it is evidenced in Fig. S6 the Zn-based compound is characterized by aggregated rounded particles with dimensions spreading from few microns to tens of nanometres. Conversely, $[\text{NH}_4][\text{Co}(\text{HCOO})_3]$ is composed by squared crystals with regular shapes and a larger polydispersity. Since the vibrational energy was unvaried and the milling was interrupted after 55 min for each session it is reasonable to suppose that the different morphology is related to the different behaviour of the metal formates in reacting under mechanical impulse. Further studies aimed to characterize the mechanical synthesis by in-situ XRD or micro-Raman experiments could unravel the conversion mechanism of the metal formates.

4 Conclusions

We demonstrated that the mechanosynthesis of multiferroic hybrid formates is possible with a facile and rapid process of milling starting from the ammonium and hydrated metal formates. The systematic study of the best experimental conditions indicated that the reactants adsorbed water can negatively influence the successful synthesis of the complex formate frameworks. Indeed, the mechanosynthesis of different AMF compositions evidenced the interesting correlation between the milling time and the de-hydration temperature of the different hydrated metal formates. As indicated by diffraction and SEM measurements, the AFM obtained by milling display good crystallinity and the absence of lattice stains at least within the resolution of our diffraction experiments. The solvent-free method could open up the fabrication of new formate-based frameworks circumventing the limits related to the solubility of some metal salts and the unfavourable competition of the solvents in occupying the cavities of such porous materials. Therefore, the mechanosynthesis of the AMF can be considered as a straightforward synthetic strategy pointing out the opportunity to design novel formate-based complex perovskite-like hybrids encompassing electric and magnetic properties.

CRedit authorship contribution statement

Francesco Cugini: Methodology. **Massimo Solzi:** Methodology. **Mauro Gemmi:** Data curation. **Lara Righi:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.


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Appendix A Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jallcom.2021.163288](https://doi.org/10.1016/j.jallcom.2021.163288).

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Highlights

- Mechanochemical synthesis as a new route to synthesize $[\text{NH}_4][\text{M}(\text{HCOO})_3]$ compounds
- Dehydration process of metal formate as the first step of the synthesis
- XRD and Raman spectroscopy indicate a single phase product for all the compositions explored

Appendix A Supplementary material

 [Multimedia Component 1](#)

Queries and Answers

Q1

Query: Please confirm that given names and surnames have been identified correctly and are presented in the desired order, and please carefully verify the spelling of all authors.

Answer: I checked the names of authors. They are all correct.

Q2

Query: Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact m.radhakrishnan@elsevier.com immediately prior to returning your corrections.

Answer: Your guess is correct. This article is not associated to some special issue/collection.

Q3

Query: Please type the full funder name and country, plus grant IDs in the text, if available. Correctly acknowledging the primary funders and grant IDs of your research is important to ensure compliance with funder policies. Have we correctly interpreted the following funding source and country name you cited in your article: "Italian Ministry for Education, University and Research, Italy"?

Answer: Yes