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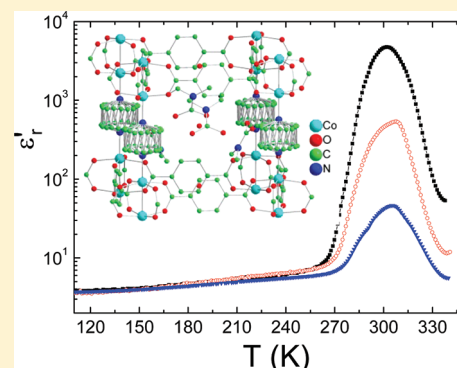
Apparent Colossal Dielectric Constants in Nanoporous Metal Organic Frameworks

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S Supporting Information

ABSTRACT: In this work, we show that the hybrid material $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [4\text{DMF} \cdot 1\text{H}_2\text{O}]$, shows an apparent colossal dielectric constant at room temperature ($\epsilon'_r \approx 5000$ at 300 K for $\nu = 100$ Hz). Nevertheless, such response does not imply colossal polarizability processes, as its dielectric constant is not purely intrinsic, but is greatly enhanced by the activation of extrinsic dielectric effects close to room temperature associated to the diffusion of numerous guest molecules through the channels. If such extrinsic contributions are eliminated or reduced, the values of the dielectric constant turn to be much smaller, as observed in the closely related $\text{Co}_2(1,4\text{-bdc-NH}_2)_2(\text{dabco}) \cdot [7/2\text{DMF} \cdot 1\text{H}_2\text{O}]$, $\text{Co}_2(1,4\text{-ndc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 2\text{H}_2\text{O}]$ and $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 1/2\text{H}_2\text{O}]$ compounds. Therefore, we warn about the imperious necessity of distinguishing between intrinsic and extrinsic effects in electrically inhomogeneous MOF materials that display a certain conductivity in order to adequately interpret their dielectric behavior.



INTRODUCTION

Hybrid materials consisting of metal atoms or clusters that are linked by polyfunctional organic ligands forming one-, two-, or three-dimensional structures that can be nanoporous, the so-called metal organic frameworks MOFs, have been extensively studied in the past decade in view of their interesting potential applications, for example, in catalysis and gas storage.¹ In addition they are receiving increasing attention as they can display a wide range of interesting functional properties² among them, and as very recently found, dielectric³ and even multiferroic properties.^{2c,4,5}

In this new search for dielectric hybrids, a very interesting possibility is the appearance of electrical order or dielectric anomalies induced by order–disorder processes of polar and/or H-bonded guest molecules allocated in cavities of host structures.³

Such a behavior has been found, for example, in alkylammonium transition metal formates such as $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$ ($\text{M}^{2+} = \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}$, etc.).^{5,6} These are dense MOFs with perovskite structure, where a cooperative ordering^{5,6a} or freezing^{6b} of the guest species leads to a remarkable dielectric transition in the range 160–185 K depending on the specific metal.^{5,6}

Very interestingly, some MOFs that contain interconnected nanopores (tunnels) where movable polar molecules are loosely bound have also been reported to show interesting dielectric behavior.^{7–10} Nevertheless an important limitation is that their very porous structure facilitates the evaporation or loss of the guest species on approaching room temperature, thus preventing in many cases good and reliable dielectric

responses in this temperature window from being obtained.^{8–11} If such elimination is avoided, for example by encapsulating the samples in Teflon-sealed cylindrical cells during the dielectric measurements,¹² very large dielectric constants can be observed at room temperature or above.

For example, the compound $[\text{Sm}_2\text{Cu}_3(\text{IDA})_6] \cdot 9\text{H}_2\text{O}$ (where IDA is iminodiacetate) has been reported to display a very large dielectric constant, $\epsilon'_{r,\text{max}} \approx 1300$ at $T = 400$ K and peculiar hysteresis loops.¹¹ Such dielectric behavior has been explained on the basis of local thermal motion of water molecules confined in the tunnels, together with an additional antiferroelectric order that would take place at 350 K.¹¹

In the same context, the hybrid $\{(\text{EMI})_2[\text{Zn}_3(1,2,4,5\text{-BTC})_2]2\text{H}_2\text{O}\}_n$ compound (where EMI is 1-ethyl-3-methylimidazolium and BTC is benzenetetracarboxylate) has been reported to display a very high dielectric constant $\epsilon'_r \approx 5 \times 10^6$ at 100 Hz that decreases various orders of magnitude as frequency increases. This compound, that at difference with the previous case is noncentrosymmetric, also displays an anomalous $P(E)$ curve, and has been described as ferroelectric.¹³

Taken into account that dielectric constant values $\epsilon'_r > 10^3$ are considered “colossal”,¹⁴ these hybrid compounds would then belong to the outstanding and desired group of colossal dielectric constant (CDC) materials.

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Apart from the obvious technical importance of CDCs for applications that require high ϵ_r electronic materials, a key issue from the scientific point of view is the microscopic origin of such a behavior, that is whether such dielectric response is really intrinsic from the bulk material, and thus is based on colossal polarizability processes, or if it is in fact a combination of intrinsic and extrinsic contributions that give rise to the observed macroscopic behavior.

Such a question of intrinsic versus apparent CDCs is not new but has in fact been at the center of an intense and extended debate and discussion in other fields of solid state and materials science. In this regard it is worth recalling the recent and very fruitful debate and controversy¹⁵ about CDC oxides such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ^{16,17} or $\text{CaMn}_7\text{O}_{12}$ ¹⁸ that display dielectric constants of $\sim 1 \times 10^6$ at 1 kHz and at 300 K. After strong discussion, it is now widely accepted that these oxides are in fact electrically heterogeneous materials, where Maxwell–Wagner polarization effects (arising from the presence of a certain electronic conductivity, formation of Schottky-like electrodes, etc.)¹⁹ markedly enhance the values of their dielectric constants. Or the case of biological materials that also show very large ϵ_r at low frequencies, not because they are ferroelectric but because they are electrically inhomogeneous and good ionic conductors due to its water content, resulting in an accumulation of electrical charge close to the contacts.²⁰

Both types of polarization effects that give rise to a substantial magnification of the materials capacitance are in fact exploited in practical applications such as in barrier layer capacitors²¹ and in supercapacitors,²² respectively.

In view of such a background and using our previous experience in the study of the dielectric properties of mixed oxides with high dielectric constants, we have carried out the present work with a two-fold purpose: (1) to clarify the real origin of the colossal dielectric constants that can be measured on MOF materials and (2) to warn about the necessity of distinguishing between intrinsic and extrinsic effects to correctly interpret their dielectric behavior.

For this purpose, we have searched in the literature for inclusion MOF compounds that display “medium” size 3D cavities, that is: cavities that are sufficiently large to allow the presence of several guest species with considerable degree of freedom, but small enough to prevent their easy loss at room temperature (to ensure that the compounds are fairly stable toward the loss of the included molecules).

Our choice has been nanoporous MOFs of formula $\text{M}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[\text{G}]$ ($\text{M}^{2+} = \text{Co}^{2+}$ or Ni^{2+} ; 1,4-bdc = 1,4-benzenedicarboxylate anions, dabco = 1,4-diazabicyclo[2.2.2]-octane, and G = DMF and H_2O , where DMF = *N,N*-dimethylformamide), whose synthesis, room temperature crystal structure, and adsorption properties have been previously reported²³ even if not their dielectric behavior.

From the structural point of view, the framework of these compounds consists of two-dimensional layers of M_2 paddle wheels that are linked together by 1,4-bdc anions and dabco molecules that act as pillar ligands that connect the square nets into a 3D host structure (Figure 1).²⁴

Such a framework displays a 3D interconnected pore system²⁵ where several polar guest species are located (namely 4 DMF and 1 H_2O in the case of the Co compound). Very interestingly, such guest molecules can be removed from the compound by appropriate heating treatments without altering its 3D architecture.²⁵

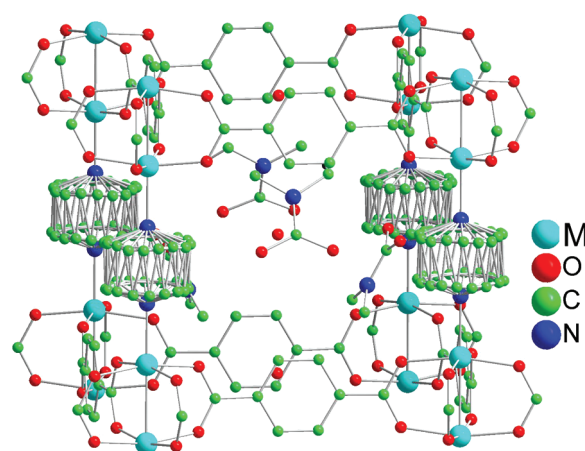


Figure 1. Crystal structure of $\text{M}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[\text{G}]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+}) at low temperature ($T = 100$ K). The carbon atoms of dabco pillars are disordered.

In addition, we have extended these studies to the derivative compounds $\text{Co}_2(\text{L})_2(\text{dabco})\cdot[\text{G}]$ whose structures are closely related to this one but where the 1,4-bdc ligand is either replaced by the NH_2 -substituted 1,4-bdc ligand (1,4-bdc- NH_2) or by the benzene-functionalized ligand 1,4-ndc [1,4-ndc = 1,4-naphthalenedicarboxylate anion; see Figure S1 of the Supporting Information (SI)]. The interest of these substitutions is that the presence of the phenyl and amine groups reduces considerably the aperture size of the pores.²⁶

EXPERIMENTAL SECTION

Synthesis. The $\text{Co}_2(\text{L})_2(\text{dabco})\cdot[\text{G}]$ compounds ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} and $\text{L} = 1,4\text{-bdc}$, 1,4-bdc- NH_2 , and 1,4-ndc) were synthesized according to the procedure described in the literature.^{23,25} In a typical experiment, 2.5 mmol of $\text{M}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 2.5 mmol of H_2bdc , $\text{H}_2\text{bdc-NH}_2$, or H_2ndc were initially dissolved in 30 mL of DMF, to which was subsequently added 1.25 mmol of dabco.

For the synthesis of $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[\text{G}]$ (compound 1) and $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[\text{G}]$ (compound 2), the resulting solutions were heated in Teflon-lined autoclaves at 403 K for 60 h, and after slow overnight cooling, the obtained products were collected, washed with DMF, and dried at room temperature. The samples were then stored in desiccators to ensure removal of any solvent molecules which could remain adsorbed on the surface of the particles.

The syntheses of $\text{Co}_2(1,4\text{-bdc-NH}_2)_2(\text{dabco})\cdot[\text{G}]$ (compound 3) and $\text{Co}_2(1,4\text{-ndc})_2(\text{dabco})\cdot[\text{G}]$ (compound 4) were carried out as follows: the initial reactants were stirred at room temperature for 3 h and then the clear solutions obtained after the removal of residual precipitates were heated in sealed glass tubes at 393 K for 65 h (compound 3) or in Teflon-lined autoclaves at 393 K for 72 h (compound 4). The obtained crystals were collected, washed with DMF, dried at room temperature, and stored in desiccators in order to remove any solvent which could remain adsorbed on the surface and avoid the adsorption of water molecules from the atmosphere.

Elemental Analysis. Elemental chemical analyses for C, N, and H were carried out using a FLASHEA1112 (Thermo-Finnigan) Analyzer.

For compound 1: calculated C, 46.32; H, 5.72; N, 9.53; found C, 46.53; H, 5.48; N, 9.75. For compound 2: calculated C, 48.04; H, 5.07; N, 9.04; found C, 48.53; H, 5.38; N, 9.30.

For compound 3: calculated C, 45.28; H, 5.67; N, 12.18; found C, 44.32; H, 4.98; N, 11.89. For compound 4: calculated C, 51.27; H, 5.41; N, 7.66; found C, 49.93; H, 5.23; N, 7.49.

Thermal Studies. Thermogravimetric analysis (TGA) were carried out in a TGA-DTA Thermal Analysis SDT2960 equipment. For these experiments approximately 25 mg of sample was heated at a rate of 5 K/min from 300 to 1023 K using corundum crucibles under a flow of dry nitrogen.

Infrared Spectroscopy. Infrared spectra were recorded at room temperature with the FT-IR spectrometer Bruker VECTOR22 over the wavenumber range 400–4000 cm^{-1} .

X-ray Diffraction Studies. The compounds were studied by X-ray powder diffraction (XRPD) at room temperature in a Siemens D-5000 diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRPD patterns were analyzed by the Le Bail profile analysis using the Rietica software.²⁷

Additionally, in the case of compound 1 (the only compound from which we have obtained crystals that are adequate for single crystal X-ray diffraction), single-crystal data sets were collected at 293 and 100 K. These experiments were carried out in a Bruker-Nonius x8 ApexII X-ray diffractometer equipped with a CCD detector and using monochromatic Mo $K\alpha_1$ radiation ($\lambda = 0.71073 \text{ \AA}$). A suitable crystal was chosen and mounted on a glass fiber using instant glue. For the 100 K set, the crystal temperature was maintained using a cold stream of nitrogen from a Kyroflex cryostream cooler. The data integration and reduction was performed using the Apex2 V.1.0-27 (Bruker Nonius, 2005) suite of software. The intensity collected was corrected for Lorentz and polarization effects and for absorption by semiempirical methods on the basis of symmetry-equivalent data using SADABS (2004) of the suite software. The structures were solved by the direct method using the SHELXS-97 program²⁸ and were refined by least-squares method on SHELXL-97.²⁹

Dielectric Properties. The complex dielectric permittivity ($\epsilon_r = \epsilon'_r - i\epsilon''_r$) of these samples was measured as a function of frequency and temperature with a parallel-plate capacitor coupled to a Solartron 1260A Impedance/Gain-Phase Analyzer, capable of measuring in the frequency range of 10 μHz to 32 MHz. The capacitor was mounted in a Janis SVT200T cryostat refrigerated with liquid nitrogen and with a Lakeshore 332 incorporated to control the temperature from 100 K up to 350 K.

As the obtained single crystals of 1 were not big enough to perform single crystal dielectric measurements, in all cases pellets made out of well-dried samples were measured instead. This latter aspect is also important as the presence of adsorbed water can greatly interfere in the observed dielectric response.

Such pellets with an area of approximately 300 mm^2 and thickness of approximately 0.6 mm were prepared to fit into the capacitor, and silver paste was painted on their surfaces to ensure a good electrical contact with the electrodes.

All of the dielectric measurements were carried out in a nitrogen atmosphere where several cycles of vacuum and nitrogen gas were performed to ensure that the sample environment was free of water.

The impedance analysis software SMART (Solartron Analytical) was used for data acquisition and processing. Impedance complex plane plots were analyzed using the LEVM program, a particular program for complex nonlinear least-squares fitting.³⁰

Polarization (P) vs electric field (E) measurements were carried out using a home-built setup based on a Sawyer–Tower

circuit where the hysteresis loops were recorded using a Keithley 6517B electrometer.

RESULTS

Characterization. The XRPD patterns show that the obtained samples are single phase materials (Figure 2). In

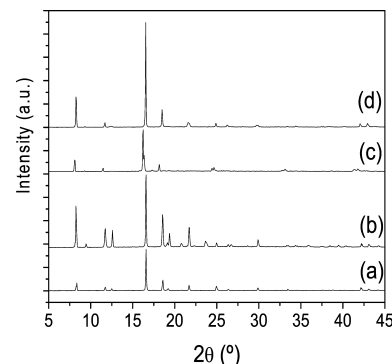


Figure 2. Room temperature XRPD pattern of (a) compound 1, (b) compound 2, (c) compound 3, and (d) compound 4.

addition, the structural data obtained from the LeBail refinements are in full agreement with those already reported in the literature.²⁰ In this context, compounds 1 and 2 show tetragonal symmetry (S.G.: $I4/mcm$) and the following cell parameters: $a = 15.181(1) \text{ \AA}$ and $c = 19.085(1) \text{ \AA}$ for $M = \text{Co}^{2+}$ and $a = 15.127(1) \text{ \AA}$ and $c = 18.667(1) \text{ \AA}$ for $M = \text{Ni}^{2+}$. Therefore, the substitution of the Co^{2+} ion ($^{\text{VI}}r_{\text{Co}^{2+}} = 0.74 \text{ \AA}$)³¹ by the relatively smaller Ni^{2+} ion ($^{\text{VI}}r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$)³¹ results in a slight contraction of the corresponding cell parameters, as expected.

As for the closely related compounds 3 and 4, whose structure had not been published before, the corresponding LeBail refinement indicates that they also show tetragonal symmetry with cell parameters $a = 15.2649(6) \text{ \AA}$ and $c = 19.1212(5) \text{ \AA}$ (S.G.: $I4/mcm$) in the case of compound 3 and $a = 10.8997(7) \text{ \AA}$ and $c = 9.7794(8) \text{ \AA}$ (S.G.: $P4/mmm$) in the case of compound 4.

The structure of compound 1 could also be solved by single crystal X-ray diffraction both at room temperature and at 100 K (see the SI, Tables SI and SII and Figures S2–4). The room temperature structure that is reported for the first time in this work presents two major structural differences with respect to that found at low temperature (and that is in agreement with that already described):²⁵ (1) The 1,4-bdc ligand is split into two different possible positions of equal electron density, effect that is not present at 100 K (see the SI, Figure S4). (2) At room temperature the guest molecules (DMF and water) seem to be randomly distributed inside the MOF cages, and even if their electron density is clearly detected, a satisfactory refinement including their atomic positions could not be obtained. Meanwhile, at low temperature, the location of these molecules could be established (see the SI, Figure S3).

At both temperatures the C atoms of the dabco pillars are found to be disordered, as it had already been reported for the low temperature structure.^{23–25}

IR spectra for the four $M_2(L)_2(\text{dabco}) \cdot [G]$ compounds are quite similar and in agreement with those reported in the literature for $M_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [G]$ ²³ (see the SI, Figure S5). The presence of water is clearly detected by the presence of a broad band around 3500 cm^{-1} , whereas the band at 1095

cm^{-1} could be ascribed to the asymmetric stretching vibration of the methyl group of DMF molecules.

A typical TGA curve for these compounds is shown in the SI, Figure S6. Combining the TGA results with elemental analysis data, we have estimated the amount of DMF and H_2O present inside the pores of the structures. According to those results, the complete chemical formula of these compounds can be written as follows: **1**, $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [4\text{DMF} \cdot 1\text{H}_2\text{O}]$; **2**, $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 1/2\text{H}_2\text{O}]$; **3**, $\text{Co}_2(1,4\text{-bdc-NH}_2)_2(\text{dabco}) \cdot [7/2\text{DMF} \cdot 1\text{H}_2\text{O}]$; and **4**, $\text{Co}_2(1,4\text{-ndc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 2\text{H}_2\text{O}]$.

Moreover TGA results reveal that these compounds are stable up to 373 K. Above this temperature they start to lose H_2O and DMF, to finally decompose around 523 K.^{23,25}

As for their stability in air, it should be mentioned that only compound **1** is seen to evolve with time rather quickly, so that it should be handled with care. Meanwhile the rest of the compounds are stable, specially the Ni-one. Therefore, we have chosen compound **2** to carry out further experiments by eliminating the guest molecules.

For this purpose we have heated the as obtained compound **2** at 473 K for 2 h, obtaining $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco})$ (compound **5**). The XRPD pattern of **5** reveals that its structural framework basically remains unchanged after this thermal treatment, although there is a slight peak broadening and a shift of the diffraction maxima (see the SI, Figure S7). Also, in the IR spectrum of this compound the bands from the carboxylate groups and the benzene rings are still present, thus confirming the integrity of the 3D skeleton of the metal organic framework. Meanwhile the disappearance of the broad band around 3500 cm^{-1} , previously detected in compound **2**, corroborates the elimination of the guest H_2O molecules initially located inside the pores (see the SI, Figure S5).

Dielectric Behavior. Figure 3 shows the temperature dependence of the real part of the complex dielectric

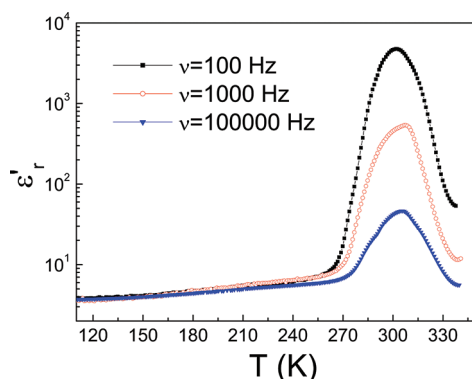


Figure 3. Temperature dependence of the dielectric constant of compound **1** measured at different frequencies in the temperature interval $100 < T(\text{K}) < 350$.

permittivity ϵ'_r (the so-called dielectric constant) of pressed pellets of $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [4\text{DMF} \cdot 1\text{H}_2\text{O}]$ (compound **1**). As it can be seen, the dielectric constant goes through a broad and pronounced maximum close to room temperature, giving rise to very large colossal values at 300 K, especially at low measuring frequencies, for example $\epsilon'_r \approx 5000$ at 300 K for $\nu = 100\text{ Hz}$.

Compound **2**, which contains Ni^{2+} instead Co^{2+} , shows a similar behavior, although the increase of its dielectric constant

at room temperature is considerably smaller, with values almost 2 orders of magnitude lower than those observed in compound **1** (see Figure 4).

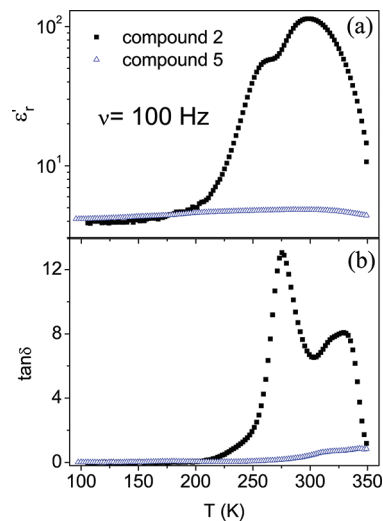


Figure 4. (a) Dielectric constant and (b) loss tangent of the compounds **2** and **5** in the temperature interval $100 < T(\text{K}) < 350$ (measuring frequency $\nu = 100\text{ Hz}$).

In the case of compounds **3** and **4**, their dielectric constants also go through a small maximum close to room temperature, but with very reduced values compared to those of compound **1** (see Figure 5).

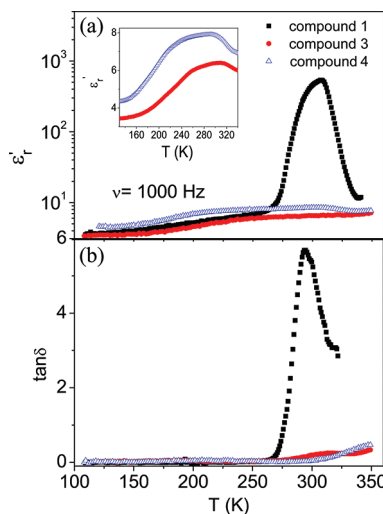


Figure 5. Comparison of the (a) dielectric constant (b) and loss tangent of $[\text{Co}_2(\text{L})_2(\text{dabco})] \cdot [\text{G}]$ compounds with different ligands L: 1,4-bdc (compound **1**), 1,4-bdc- NH_2 (compound **3**), and 1,4-ndc (compound **4**), in the temperature interval $100 < T(\text{K}) < 350$ and measuring frequency $\nu = 1000\text{ Hz}$.

If we now compare the behavior of compound **2** (fresh sample) with that of compound **5**, from which the guest molecules have been removed, we can see that the broad peak that is observed in the fresh sample close to room temperature has completely disappeared, and no anomaly is detected in the dielectric constant that is very low and temperature independent (see Figure 4).

To investigate further the dielectric behavior displayed by these samples, we have carried out impedance spectroscopy studies as a function of frequency and temperature. As it is well-known, this technique is a very powerful tool to unravel the dielectric response of materials^{15b} and to avoid misinterpreting results such as apparent hysteresis loops displayed by electrically inhomogeneous samples.^{32,33}

The behavior displayed by $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[4\text{DMF}\cdot\text{H}_2\text{O}]$ (compound 1) that is again different from the rest will be presented first.

Figure 6 shows typical impedance complex plane plots for compound 1 in the temperature interval $110 \leq T(\text{K}) \leq 260$

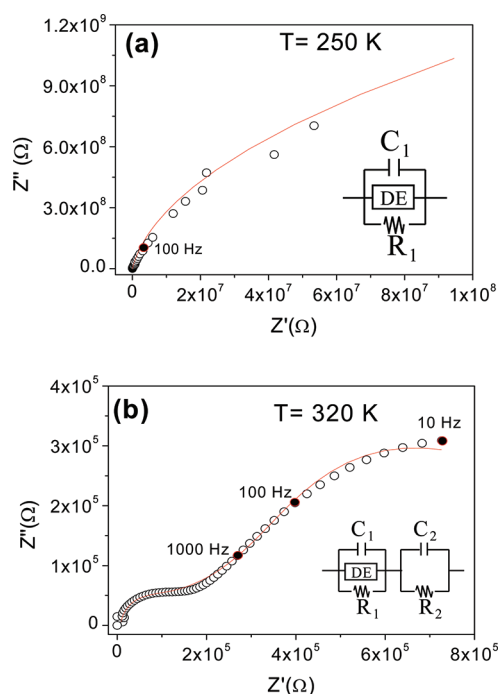


Figure 6. Typical impedance complex plane of compound 1 in the temperature ranges (a) $110 \leq T(\text{K}) \leq 260$ and (b) $260 < T(\text{K}) \leq 350$.

(Figure 6a) and $260 < T(\text{K}) \leq 350$ (Figure 6b). As it can be seen, in the interval $110 \leq T(\text{K}) \leq 260$, the corresponding impedance complex plane plots show a single large arc (Figure 6a), whereas for $T > 260$ K an additional second small arc appears in the low frequency range (Figure 6b).

The large arc can be modeled by an equivalent circuit containing three elements connected in parallel: a resistance (R) and a capacitance (C) that is frequency independent, and a frequency-dependent distributed element (DE). As this large arc intercepts zero for $T \leq 260$ K and the order of magnitude of its capacitance is pF cm^{-1} , it seems to be associated with the material bulk response.^{15b} The intrinsic dielectric constant (ϵ') calculated from the value of the obtained capacitance is around 4.6. Taking into account that this is the only contribution present for $T \leq 260$ K, the observed dielectric response is purely intrinsic in this low temperature interval.

The second arc observed for $T > 260$ K can be modeled as a single RC connected in series with the circuit that describes the bulk arc. The capacitance of such a low frequency arc is about μcm^{-1} , typical of extrinsic contributions such as electrode effects, blocking electrodes, etc.^{15b} This means that in the higher temperature interval, including room temperature, the

dielectric response of compound 1 contains both intrinsic and extrinsic contributions.

In this regard, it should be emphasized that although for $110 \leq T(\text{K}) \leq 260$ compound 1 behaves as an insulator ($\sigma < 10^{-9}$ S/cm for $T < 260$ K), for $T > 260$ K it becomes semiconducting (i.e., $\sigma \approx 0.5 \mu\text{S/cm}$ for $T = 320$ K).

These results, together with the very large values of the dielectric constant measured for $T > 260$ K at low frequencies, signal the activation of interfacial polarization effects in the $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[4\text{DMF}\cdot\text{H}_2\text{O}]$ compound close to room temperature.

Meanwhile, in the case of compounds 3–5, in the whole temperature interval studied, the impedance complex plane plots only show a large single arc that intercepts zero, and the samples remain insulating even at room temperature (see the SI, Figure S8a). This result implies that the dielectric response of these compounds 3–5 is purely intrinsic.

Finally, the impedance complex plane plots of compound 2 in the temperature interval $260 < T(\text{K}) \leq 350$ K reveal a scenario that seems intermediate between the two presented above. They show a large single large arc (see the SI, Figure S8b) that can be equally well modeled on the basis of two different equivalent circuits: the first one typical for a purely intrinsic response (containing three elements connected in parallel R , C , and DE) and the second one typical for the coexistence of extrinsic and intrinsic contributions (containing a single RC connected in series with the circuit that describes the intrinsic response). The agreement factors do not give a clear advantage of one over the other, so that the situation seems to be intermediate between the two. These results, together with the relative large values of the dielectric constant measured at $T > 260$ K at low frequencies, point toward the presence of interfacial polarization effects in $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[4\text{DMF}\cdot\text{H}_2\text{O}]$, even if their contribution is smaller than in the case of compound 1.

DISCUSSION

The chemical characterization of the obtained samples fully confirms that we have obtained the desired porous hybrid materials $\text{M}_2(\text{L})_2(\text{dabco})\cdot[\text{G}]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} and $\text{L} = 1,4\text{-bdc}$, $1,4\text{-bdc-NH}_2$, or $1,4\text{-ndc}$) as single phase pure materials. Evenmore, starting from $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[3\text{DMF}\cdot 1/2\text{H}_2\text{O}]$, we have been able to progressively eliminate the guest molecules from the cavities while retaining the integrity of the 3D structural skeleton.

The obtained hybrid compounds $\text{M}_2(\text{L})_2(\text{dabco})\cdot[\text{G}]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} and $\text{L} = 1,4\text{-bdc}$, $1,4\text{-bdc-NH}_2$, or $1,4\text{-ndc}$) show a maximum in their $\epsilon'_r(T)$ curves around 300 K that in the case of $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco})\cdot[4\text{DMF}\cdot\text{H}_2\text{O}]$ gives rise to a very large (colossal) dielectric constant at room temperature.

Very interestingly, the appearance of such a maximum of ϵ'_r around 300 K is related to the presence of the guest molecules located inside the cavities, as the elimination of those molecules results in its disappearance. As the dielectric constant of H_2O is known to exhibit an abrupt jump from 273 K,⁸ in principle the appearance of this peak seems to be related to changes in the polarizability of the H_2O molecules confined in the cavities. The interaction of those H_2O molecules with DMF, or even with the framework, could slightly broaden and shift the peak toward higher temperatures.³⁴

However, what is indeed remarkable is the elevated values of the dielectric constant displayed by compound 1, much higher

than those corresponding to pure H₂O ($\epsilon'_r \approx 88$) or to DMF ($\epsilon'_r \approx 38$).

Impedance spectroscopy studies are most revealing in this context: they unambiguously show that such a very high dielectric constant is not purely intrinsic but is greatly enhanced by the activation of extrinsic dielectric effects close to room temperature. When such extrinsic contributions disappear, the dielectric constant values turn out to be much smaller, as observed in the case of compounds 3 and 4.

With all of this information in hand, we attribute the intrinsic dielectric response of these materials to the presence of dipolar guest molecules inside the cavities and to their concomitant orientational polarizability. This latter will be small at low temperatures when the guest molecules are frozen in specific positions with very reduced thermal motion. Nevertheless, their degree of freedom will markedly increase with temperature, resulting in a higher polarizability close to room temperature.

As for the origin of the extrinsic effects, that magnify the intrinsic response and that in the case of compound 1 give rise to a colossal dielectric constant, our explanation is the following: we relate it to the characteristics of the porous structure and to the presence of the guest molecules.

In the Co compound the “medium” size 3D interconnected pore system inside its framework presents relatively wide open channels (of pore diameter $7.6 \times 7.6 \text{ \AA}$ along the *c* axis intersected by smaller channels of $3.7 \times 5.1 \text{ \AA}$ along the *a* and *b* axes), and recent molecular dynamic simulations have shown that small molecules can diffuse through them.³⁵ Should this occur with the H₂O and DMF species, an almost liquid-like state would be present throughout the skeleton framework, which could be readily polarized in the presence of an electric field. This effect could also account for the increase in the electrical conductivity that is observed above 260 K and that finally gives rise to the appearance of extrinsic effects associated with the formation of an electrical double layer at the electrodes.

If we prevent such diffusion from occurring the extrinsic contribution will disappear, the dielectric response will turn out to be purely intrinsic and the magnitude of the $\epsilon'_r(T)$ maximum will substantially decrease.

This is in fact what is observed in samples 3 and 4, where such extrinsic contribution is totally eliminated by blocking the channels window, so that the guest molecules can no longer diffuse. As a result, the dielectric response is purely intrinsic and the dielectric constant small ($\epsilon'_r \approx 6$ at 300 K for $\nu = 1000 \text{ Hz}$).

Meanwhile in the case of compound 2, the extrinsic contribution is only partially eliminated by reducing the size of the cavities, so that a small diffusion can still occur. This results in a small enhancement of the dielectric constant at room temperature that achieves higher values than in the case of compounds 3 and 4 ($\epsilon'_r \approx 150$ at 300 K for $\nu = 100 \text{ Hz}$), even if they are much smaller than those of compound 1.

Very importantly, extrinsic contributions are going to be present in the dielectric response of any porous MOF that presents a certain conductivity; most probably in the CDC porous MOFs cited in the introduction of this paper whose structures are open enough to allow the long-range migration of the guest molecules through their channels.

All of these extrinsic effects need to be taken into account to adequately describe the dielectric behavior of MOF samples avoiding, among others, the misinterpretation of closed P(E) curves measured on such systems (see SI, Figure S9, which shows the apparent P(E) curve displayed by compound 1). If

not, we would just be repeating the errors that gave rise to the celebrated and extremely critical viewpoint articles “Ferro-electrics go bananas”³² and “Bananas go paraelectric”³³ written in view of the proliferation of errors in the papers published in those days in the context of oxides with magnetoelectric multiferroic behavior.

CONCLUSIONS

In conclusion, we have shown that the hybrid material $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [4\text{DMF} \cdot 1\text{H}_2\text{O}]$ shows a colossal dielectric constant at room temperature ($\epsilon'_r \approx 5000$ at 300 K for $\nu = 100 \text{ Hz}$). We attribute these colossal values to an order–disorder process of the dipolar guest molecules allocated in the cavities of the framework structure that is further enhanced by the activation of extrinsic interfacial polarization effects in that temperature window associated with the diffusion of numerous guest molecules through the channels and the formation of the concomitant electrical double layer.

Therefore, it is an apparent colossal dielectric behavior that does not imply colossal polarizability processes, as the dielectric constant is not purely intrinsic but is greatly enhanced by the activation of extrinsic dielectric effects close to room temperature. If such extrinsic contributions are eliminated or reduced, the values of the dielectric constant turn out to be much smaller, as observed in the closely related compounds $\text{Co}_2(1,4\text{-bdc-NH}_2)_2(\text{dabco}) \cdot [7/2\text{DMF} \cdot 1\text{H}_2\text{O}]$, $\text{Co}_2(1,4\text{-ndc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 2\text{H}_2\text{O}]$, and $\text{Ni}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [3\text{DMF} \cdot 1/2\text{H}_2\text{O}]$.

On this basis, we identify the basic “ingredient” that is present in MOF materials with apparent CDC constants: a certain conductivity that can arise from diffusion of guest molecules through the channels.

Therefore, we warn about the imperious necessity of distinguishing between intrinsic and extrinsic effects in electrically inhomogeneous MOF materials that display a certain conductivity in order to adequately interpret their dielectric behavior.

ASSOCIATED CONTENT

Supporting Information

Single crystal X-ray diffraction information and structure views of the $\text{Co}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot [\text{G}]$ compound at different temperatures (100 and 293 K). Infrared spectra of compounds 2 and 5. TGA analysis of compound 2. XRPD pattern at room temperature of compounds 2 and 5. Typical impedance complex plane of compounds 2 and 4. “Apparent” P(E) hysteresis loop of compound 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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