

Dielectric Properties of $\text{Na}_{0.7}\text{CoO}_2$ and of the Superconducting $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$

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We present dielectric properties of ceramic anhydrous $\text{Na}_{0.7}\text{CoO}_2$ and the superconducting $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ materials. The presence of water which induces superconductivity also may increase the dielectric constant (ϵ) of the hydrated material. This is consistent with the predicted relationship between the high ϵ and the enhancement of T_c in high T_c superconductors. The anhydrous sample is porous and the transport is due to some percolation via the pores. The porosity is much higher for the hydrated material and the transport is ionic inside bulk water.

KEY WORDS: superconductivity; hydrates; dielectric permittivity.

1. INTRODUCTION

The subsequent discovery of superconductivity (SC) at $T_c \sim 5$ K in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ has caused great excitement [1]. Although its T_c is too low for practical applications, the structural and chemical similarities between $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ compound and Cu-based high T_c superconductors provided hope of an additional insight into the physics of SC in layered transition-metal oxides. The crystal structures of the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ family are built up of hexagonal layers composed of nonmagnetic Co^{3+} in a background of low-spin Co^{4+} ($S = \frac{1}{2}$) ions (similar to Cu^{2+} in the cuprates) that are separated by a “charge reservoir” of $\text{Na}_x(\text{H}_2\text{O})_y$. The role of this “charge reservoir” is not at all clear and further chemical and physical modifications are required to probe the stability field of this superconducting family.

Structurally, the anhydrous “parent” $\text{Na}_{0.7}\text{CoO}_2$ compound consists of alternate layers of CoO_2 and Na. The crystal structure is hexagonal ($P6_3/mmc$) with $a \sim 2.83$ Å and $c \sim 10.9$ Å ($c/a \sim 3.8$). The absence of superconductivity for the anhydrous com-

pound $\text{Na}_{0.7}\text{CoO}_2$ is intriguing. When exposed to saturated water vapor or liquid water, anhydrous $\text{Na}_{0.7}\text{CoO}_2$ intercalates water between CoO_2 layers to form the superconducting bilayer hydrate $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$. The water forms *two* additional layers between the Na and CoO_2 increasing the c -axis lattice parameter of the hexagonal structure. This induces an expansion of the c -axis from $c \sim 10.9$ Å to $c \sim 19.7$ Å ($c/a \sim 6.9$). Thus the c/a ratio is a reliable parameter to determine whether the material is a superconductor or not [2]. The Na ions are found to occupy a different configuration from the parent compound, while water forms a structure that replicates the structure of ice. The large separation enhances the two-dimensionality, which may induce the superconductivity, because high two-dimensionality is the characteristic of high T_c copper-oxide.

The copper-based high T_c superconductors (HTSC) are perovskites. The prototype perovskite is BaTiO_3 , which is the “standard” ferroelectric. The cuprates indeed possess a high dielectric constant ($\epsilon \approx 30$) at far IR frequencies (up to about 150 – 250 cm^{-1}) [3]. This feature is not included in current theories of HTSC. A large ϵ is also observed in organic superconductors, of the TMTSF-X series, as well as in the two-dimensional BEDT-X series [4]. The relationship of a very high dielectric constant to an abnormally high T_c was first pointed

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out by Cohen, predicting the superconductivity of semiconducting doped SrTiO₃ [5]. A theory accounting for a very large enhancement of T_c , due to a large ϵ , was proposed by Gersten and Weger [6]. It requires a very inhomogeneous ionic polarizability, which causes a screening of the electron–electron interaction, with much less screening of the electron–ion interaction, for ions located in parts of the unit cell (such as the planar oxygen ions in the cuprates) where the ionic polarizability is small. In this case, the McMillan [7] theory of “medium” T_c , predicting a maximum T_c of about 30–40 K, does not apply, because it is based on the properties of a nearly-homogeneous electron gas.

The main goal of the present paper is to find out, whether a very large ionic dielectric constant is a general property of materials with an abnormally large T_c . In this regard Broad Band Dielectric Spectroscopy (BDS) covering the extremely wide frequency range (10^{-6} – 10^{11} Hz) is especially sensitive to intermolecular interactions, and cooperative processes may be monitored. It provides a link between the properties of the individual constituents of a complex material and the characterization of its bulk properties. We investigated the dielectric properties of the parent Na_{0.7}CoO₂ and the Na_{0.3}CoO₂·1.3H₂O materials. We attempt at this stage to obtain an empirical indication about the value of ϵ , both in the unhydrated and hydrated materials. In Na_{0.3}CoO₂·1.3H₂O the water may contribute to an abnormally large ionic ϵ , although this is by no means certain for isolated water molecules.

2. EXPERIMENTAL DETAILS

The parent Na_{0.7}CoO₂ compound was synthesized by solid-state reaction of Na₂CO₃ (99.5%) and Co₃O₄ (99.7%) heated for 24 h in flowing oxygen at 800°C. Hydration and deintercalation of Na to obtain Na_{0.3}CoO₂·1.3H₂O was then performed using equimolar ratio of Na₂S₂O₈ in aqueous solution with Na_{0.7}CoO₂ and stirring for 22 h in a covered beaker. Applying 4–5 drops of 1N NH₄OH in 20 ml deionized water gave us a pH 10.5, which is optimal to obtain reproducibly Na_{0.3}CoO₂·1.3H₂O [1–2]. All samples were placed in humidified containers and characterized by X-ray powder diffraction.

In the frequency band 10^{-2} – 10^6 Hz the dielectric properties were measured using an Alpha analyzer from Novocontrol GMBH. The hydrated samples were mixed with KBr in order to preserve the water content. The samples were first compacted into pellets with dimensions of 1.25 mm ×

1.8 mm × 11.2 mm, and the faces were polished and gold electrodes were evaporated on to them. Dielectric measurements were carried out at room temperature, $T = 295$ K. For the higher frequency band of 10^6 – 10^{10} Hz Time Domain Dielectric Spectrometry (TDDS) was used with an open-ended coaxial probe configuration [8,9]. The samples were densely compacted and the faces polished. The coaxial probe was terminated by a flange matched to the sample surface. The measurements were carried out at room temperature, $T = 295$ K in the frequency range 10^6 – 1.2×10^{10} Hz directly after sample preparation. Two samples were measured; the dry Na_{0.7}CoO₂ and the hydrated Na_{0.3}CoO₂·1.3H₂O/KBr at a ratio of 1:1.

3. RESULTS AND DISCUSSION

Powder X-ray patterns of the hydrated and anhydrous Na_xCoO₂ materials are shown in Fig. 1. The typical (001) reflections for the hydrated sample are shifted to lower angles indicating an increase in the c lattice parameter. Notably, there is a new reflection (002) for $d = 5.12$ Å (at $2\theta = 8.13^\circ$) for the bilayer-hydrate sample as shown in Fig. 1. Both samples are hexagonal and have the same $a = 2.82(1)$ Å lattice parameter, whereas $c = 10.81(2)$ Å for the anhydrous Na_{0.3}CoO₂ material and $c = 20.5(4)$ Å for the hydrated one, values which are consistent with the published data [1,10]. The c/a ratio for the hydrated material is related to a SC material with T_c near 4.2 K. The temperature dependence of the dc magnetic curves are in good agreement with the published data [11].

4. THE DIELECTRIC MEASUREMENTS

The complex dielectric permittivity of anhydrous Na_{0.7}CoO₂ for frequencies between 10^{-2} and 10^6 Hz is presented in Figs. 2 and 3. The data demonstrates the existence of strong dielectric relaxations in the considered frequency band with a weak contribution from dc conductivity. The main process is characterized by a power law dependence, implying that its characteristic peak frequency is in fact at a far lower range than the measurement window. There is a further relaxation centered around 10^4 Hz. The data was fitted using the Havriliak–Negami phenomenological description of relaxation processes [12], a Jonscher power [13] law term, and a dc conductivity term using the special Matfit routine [14].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^\alpha)^\beta} + A(i\omega)^{n-1} + \frac{\sigma}{i\omega\epsilon_0} \quad (1)$$

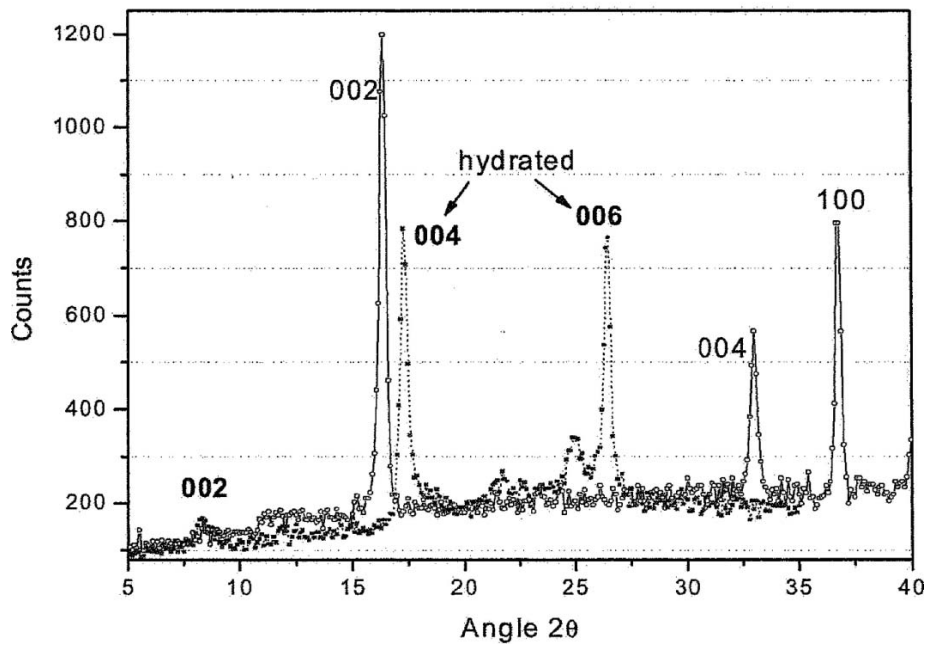


Fig. 1. XRD patterns of the anhydrous and hydrated (dash line) Na_xCoO_2 samples.

Here ε_∞ is the high frequency limit of the dielectric permittivity, τ is the characteristic relaxation time of the process, α and β are the shape parameters, $\Delta\varepsilon$ is the dielectric strength, A is a real coefficient, σ is

the dc conductivity, and ε_0 is the permittivity of free space. The fitting parameters are outlined in Table I.

The exponent of the power law, $n = 0.188$, is consistent with a very low frequency

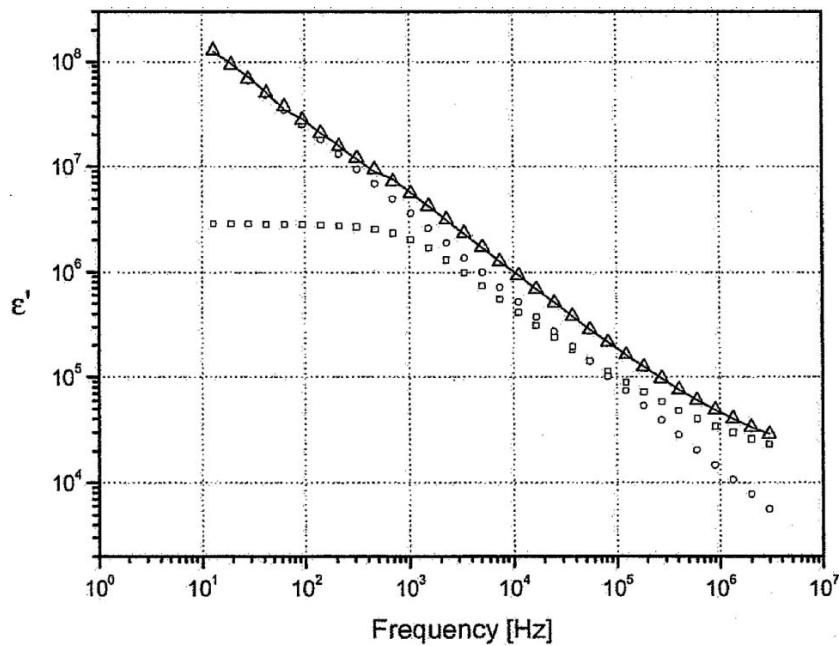


Fig. 2. The real part of the complex dielectric permittivity measured in the frequency band 1– 10^6 Hz for anhydrous $\text{Na}_{0.7}\text{CoO}_2$. The solid line is the experimental data, (Δ) Eq. (1), (\circ) the Jonscher term. The (square) is the Havriliak–Negami function.

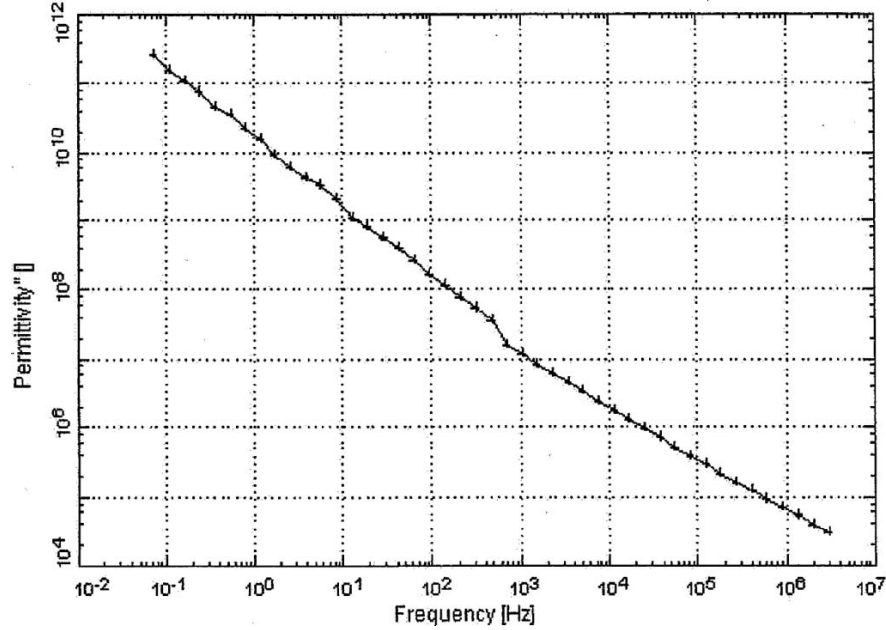


Fig. 3. The imaginary part of the dielectric permittivity for anhydrous $\text{Na}_{0.3}\text{CoO}_2$.

Maxwell–Wagner process [15]. The correspondence of ε_∞ , in Table I, to the value of the dielectric constant derived in the high frequency measurements (Table II) negated the possibility that the power law was due to surface contact effects. Given the layered structure of the crystal lattice this would suggest strong interfacial polarization at the layer interfaces. The process centered around 10^4 Hz requires further investigation. High-frequency measurements were carried out using Time Domain Spectrometry. The time domain response function to a step input is related to the dielectric permittivity by the Laplace transform

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\Delta\varepsilon} = -i\omega \int_0^\infty \phi(t) \exp(-i\omega t) dt \quad (2)$$

Fitting of the data was carried out in the time domain using the stretched exponential [16]

$$\phi(t) = \varepsilon_s \left[1 - \exp\left(-\left(\frac{t}{\tau}\right)^\nu\right) \right] \quad (3)$$

Then, the data was transformed to the frequency domain using Eq. (2). The time domain results are presented in Table II.

For the hydrated sample, the following mixing formula was used to extract the response due to the hydrated $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ from the influence of KBr

$$\varepsilon_{\text{measured}}^*(\omega) = p \varepsilon_{\text{Na}_{0.3}\text{CoO}_2}^*(\omega) + (1-p) \varepsilon_{\text{KBr}}^*(\omega) \quad (4)$$

where p is the fraction of $\text{Na}_{0.3}\text{CoO}_2$. Due to the low permittivity of KBr ($\varepsilon \approx 4$) this translates to

$$\varepsilon_{\text{NaCO}_2}^*(\omega) = 2\varepsilon_{\text{measured}}^*(\omega) \quad (5)$$

The complex dielectric permittivity results are presented in Fig. 4. The stretched exponential model of dielectric response has been linked to the transport of charge carriers in the medium [17,18]. To understand the transport mechanism fully, temperature measurements are required. However, from the value of the exponent we can derive the fractal dimension of the matrix and its resulting porosity [19]. The fractal dimension D is governed by

$$D = 3\nu \quad (6)$$

The value then for the anhydrous sample $D = 1.59$, is indicative of transport in a plane. In the hydrated sample $D = 3$ and the transport would then be

Table I. The Fitting Parameters Derived in the Frequency Band 10^{-1} to 10^6 Hz

ε_∞	$\Delta\varepsilon$	α	β	τ [s]	A	n	σ [S/m]
1.38×10^4	2.84×10^6	0.912	0.713	1.28×10^{-4}	1.53×10^{10}	0.188	9.03×10^{-11}

Table II. The Fitting Parameters of Na_xCoO_2 Samples Derived From TDDS Measurements

Parameter	$\text{Na}_{0.7}\text{CoO}_2$	$\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$
Dielectric constant ϵ_s	12355 ± 36	14726 ± 14
Relaxation time τ [s]	$1 \pm 0.01 \times 10^{-6}$	$0.157 \pm 0.001 \times 10^{-6}$
Stretch exponent ν	0.530 ± 0.003	0.966 ± 0.006

throughout the sample. The porosity ϕ is given by

$$\phi = (4 - D)^{-1} \quad (7)$$

For the anhydrous sample, we have a porosity of $\phi = 0.414$ —the sample is very porous and the transport is likely to be some form of percolation via the pores. For the hydrated sample the porosity is 1—the pores are most likely filled with water and the transport is ionic inside bulk water, or the presence of KBr radically changes the structure of the ceramic.

5. CONCLUSIONS

$\text{Na}_{0.3}\text{CoO}_2$ demonstrates a rich and varied dielectric landscape. The origin of exceptionally high static permittivity probably lies in the layered structure of the crystal lattice. Interfacial polarization of internal charge carriers trapped at the layer boundary would lead to the sort of relation noted in Fig. 4. Intriguingly, the results of the high-frequency

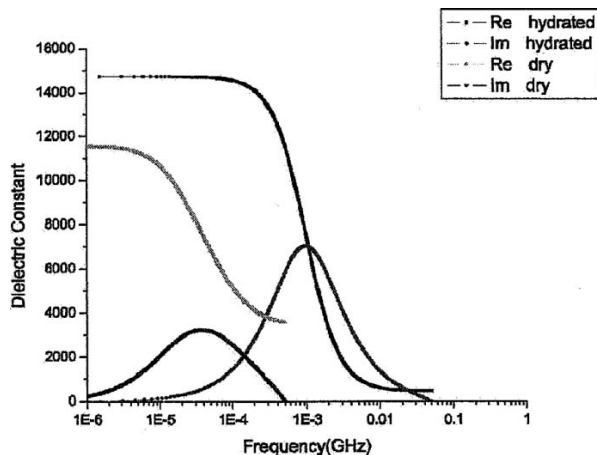


Fig. 4. The dielectric permittivity of anhydrous and hydrated Na_xCoO_2 in the frequency band 1 MHz to 10 GHz.

measurements reflect charge carriers that are mobile, their transport being heavily influenced by the state of the background matrix. The resolution of such a dilemma would be the existence of two separate systems of charge carriers inside the lattice. Temperature-based measurements would be required to investigate the true nature of these relaxations.

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