Supplementary material for "Temperature dependence of the capacitance of a ferroelectric material"

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I. INTRODUCTION

The material presented below focuses on issues that will be useful to someone wanting to build the apparatus discussed in the main text. The sections are largely self-contained and may be read in any order.

Computer codes for the data acquisition and analysis are available to instructors, on request, by writing to JB. Except for a couple of specialized routines for the PID control and curve fitting within LabVIEW, students write these codes themselves in our course.

II. SAMPLE PREPARATION

Here, we describe the synthesis of our custom ferroelectric material, whose transition temperature has been chosen to be an experimentally convenient value, 50 °C. The use of a custom material is one feature distinguishing this work from that of Dixon in Ref. [1]. As most physicists are not familiar with the techniques of solid-state chemistry, we describe the synthesis of the ceramic in some detail. Some ways to assess the quality of the sample are given in Sect. II B.

A. Material synthesis

The dielectric material we chose, a solid solution made from barium titanate ($BaTiO_3$), with 10% of the titanium ions replaced by tin ions, is one that has been the focus of recent research [2, 3]. We prepared the $Ba(Ti_{0.9}Sn_{0.1})O_3$ ceramic using a solid-state method that was derived from that of Yasuda *et al.*[2]. First, the starting materials $BaCO_3$, TiO_2, and SnO_2 [4] were mixed in stoichiometric amounts, with a mass ratio of 197.9 : 71.9 : 15.0. The materials were ground for 1 hr in an agate mortar and pestle in the presence of acetone, which served as a lubricant. An alumina mortar and pestle would also have su□ced. The reagent mixture was then put into a die and pressed into cylindrical pellets with a hydraulic press at a pressure of approximately 10^4 N/cm^2. In the first heat-treatment step, the pellets were placed on a platinum plate and calcined at 1100 °C for 4 hr, following the temperature profile shown in Fig. 1(a) [5]. After calcination, the pellets were crushed and reground in a mortar and pestle for another 1 hr, again in the presence of acetone. During the last 15 min of the grinding process, a few drops, roughly 1/2 ml, of polyvinyl alcohol (PVA) were added as a binding agent. This reground mixture was then pressed into pellets, again at a pressure of 10^4 N/cm^2. In the second and final heat-treatment step, the samples were sintered on a platinum plate by first heating for 1 hr at 500 °C, to burn o□ the PVA binder, then raising the temperature to 1400 °C and soaking at that level for 4 hr, following the temperature profile shown in Fig. 1(b). The temperature of 1400 °C allows the solid-state reaction to be complete.

Using a platinum holder is important: Any sample holder must both survive the 1400 °C sintering and not contaminate the sample at those temperatures. A ceramic holder such as alumina would contaminate the sample by allowing aluminum ions to di□use into the sample. Our platinum plate was 0.8 mm in thickness, but a smaller and thinner piece of platinum would also work [

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FIG. 1: Temperature profiles for the preparation of the $Ba(Ti_{0.9}Sn_{0.1})O_3$ ceramics. (a) Calcination. (b) Sintering. The temperature ramps in (a) were +150 and −220°C/hr. In (b), they were +150, +200, and −250 °C/hr.

B. Assessment of material quality

In practice, assessing the quality of the ceramic material is easy: one can simply use the Curie temperature and the width of the transition as a guide. Here, we include some independent ways to assess the quality of the sample that may help if something goes wrong with the synthesis. Figure

A. Sample assembly

As mentioned in the main text, the main challenges were to provide mechanical robustness so that the sample could survive sometimes-rough handling by students, give good thermal contact between the heater and both the thermistor and capacitor, and be able to withstand the repeated heat shocks created during heating and cooling cycles.

The silver paint provided a good electrical connection between the leads and the capacitor, but the leads could easily be pulled o if the capacitor was handled roughly. The lead for the outer face of the capacitor was bent into a flat coil and glued to the ceramic in an attempt to provide a greater length of wire for bonding. Since such a coil would interfere with the contact between the ceramic and the heater resistor on the inner face of the capacitor, the inner lead was bent into an arc and glued along the lower, curved, edge of the ceramic so that the heater resistor was in direct contact with the ceramic. Care was required when applying the silver paint to prevent the paint from spilling over the edge of the ceramic, thus shorting out the capacitor.

In order to provide good thermal contact, the three components—thermistor, resistor, and capacitor—were glued together with a UV-activated adhesive putty [12]. Usually the components could be pressed into good contact by bending the leads but, if not, wrapping thread around the leads just below the components would pull them together. The putty was applied with a toothpick over the components, and on the outer face of the capacitor in an attempt to reinforce the connection of the outer lead. The putty was cured under a UV lamp. Sunlight, if available, should also work.

We mounted the sample in an IC socket to prevent stress on the leads, which could fracture the assembly or change the thermal contact [13]. The IC socket containing the samples was mounted in a standard breadboard. We increased the stability of the temperature regulation more than ten-fold by shielding the sample from air currents, using a length of Tygon tubing (3/4" diameter, 1/16" wall, ≈ 1.5" long), with clear tape covering the top. The dimensions of the tubing are such that it stretches over the IC socket, making a good seal. The transparent shielding also leaves the sample visible, which is important in not having it appear to be a "black box" to students. For similar pedagogical reasons, when gluing the components together, we left small bits exposed so that the shapes of each object could be discerned under the adhesive. On the other hand, while the thermal insulation provided by Tygon tubing was a significant improvement compared to not having any insulation at all, it was not good enough to eliminate all e ects of environmental perturbations, as we now discuss.

B. Comments on the thermal design of the set-up

An "ideal" set-up would have equal masses for thermistor and capacitor and equal thermal contacts, or thermal resistances, between each mass and the heater in the center. The thermistor and capacitor would also be subject to identical thermal perturbations. Under all these conditions, the temperature of the capacitor would equal that of the resistor and, thus, the level of temperature control for the capacitor would equal that of the thermistor. In practice, there were two reasons that our control of the capacitor temperature was worse than that of the thermistor: First, when we developed the home-built capacitor discussed in the main text, the new capacitor ended up having a mass roughly three times that of the thermistor. By contrast, in the version of the experiment developed by Dixon in Ref. [1], the masses of the thermistor and capacitor were roughly equal. The inequality in masses meant that the time constant for responding to temperature fluctuations was three times slower for the capacitor than for the thermistor. In principle, we could restore the symmetry in the masses either by reducing the mass of the capacitor or increasing the mass of the thermistor. Doing the former is problematic with the DAQ we chose, as its limited input impedance and A/D sampling rate set a lower limit to the capacitance that could be measured. Reducing the mass of the capacitor would reduce its capacitance and thus increase systematic errors in the capacitance measurement [14]. On the other hand, increasing the mass of the thermistor would result in longer time constants for the temperature-control process. But having short time constants is important for building student intuition into control processes. Thus, in the end, we decided to tolerate a small imbalance in the thermal loads.

The second problem, as discussed briefly in the main text, was that our use of a piece of transparent silicone tubing as insulation did not isolate very well the experimental set-up from the environment. Because being able to see the set-up has pedagogical advantages and because the resulting temperature stability of the capacitor was good enough for our purposes, we accepted this compromise. The poor insulation leads to worse temperature control by allowing environmental perturbations that differentially change the temperatures of the thermistor and capacitor. The condition for eliminating such imbalances is that the time constant associated with the insulation from the environment exceed the "internal" time constant for heat to di use from the thermistor to the capacitor. This could be achieved, for example, by placing one or more styrofoam co ee cups over the apparatus, as discussed in Ref. [1].

In addition to allowing students to see the apparatus, one other advantage of our "bad" insulation is that blowing sharply on the apparatus from a distance of roughly 10 cm produced "impulse" thermal perturbations of 0.1–0.2 °C to the thermistor temperature. These could be used to evaluate quickly the quality of the temperature

control for a given set of feedback parameters. The cycle of setting feedback parameters, perturbing (blowing), and watching the response took only about 10 s. Students could then easily develop intuitions about the system dynamics and find optimal values for the proportional, integral, and derivative gains. The traditional way to achieve good temperature stability and uniformity is to use a large, high-thermal-conductivity mass for the apparatus, such as a block of copper. The high thermal conductivity of the apparatus then implies small gradients if losses to the environment are low. The latter condition is achieved, as discussed above, by insulating very well the apparatus from the environment. The result, however, is a system with much longer time constants, leading to a much longer cycle for adjusting the feedback parameters.

The important point, as discussed in the main text, is that the design compromises we made in trading performance for pedagogy led to a thermal stability for the capacitor that was nonetheless adequate for our purposes. In particular, we could measure the capacitance accurately enough to study its variations in response to controlled temperature changes and to observe slow aging effects when the temperature set-point was held at a fixed value.

C. Power amplifier

The power amplifier we built used a high-power op amp [15] in a standard single-supply design [16] that was

use an electronic bu□er circuit, but our students have not taken an electronics course and thus have

[13] ACT, Model DM-314STG30 14-pin low-profile IC socket. It was important to use a socket with strong legs that can be repeatedly inserted into breadboards. Sockets with spring contacts did not work—the component leads tended to pop out of the spring contacts. Although only 6 pins are used, the extra pins made it easier to handle and insert the sockets.

[14] The problem of systematic errors in the measurements of small capacitance is actually worse than one might guess looking at the RC decays presented in the main article. As the impedance of the RC circuit increases, the A/D input of the NI 6809 DAQ shows oscillations of ever greater amplitude. These are already apparent if one looks carefully at Fig. [2] of the main article, where small,