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Revisiting two piezoelectric salts within an eco-design paradigm for sensors and actuators applications

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Abstract

We manufactured eco-friendly piezoelectric transducers that are promising for several technological applications within an eco-design paradigm. Taking into account the environmental, eco-design and energetic constrains, two *eco-friendly* piezoelectric salts were investigated in this work: Rochelle Salt ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and Ammonium Dihydrogen Phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). The piezoelectric resonance and temperature stability of these two salts were compared. Furthermore these two salt crystals were integrated into biodegradable structural material in order to obtain several eco-friendly piezoelectric devices such as resonating cantilevers, energy harvesters, and bulk acoustic wave (BAW) filters. These three types of devices were successfully fabricated and characterized, demonstrating the potential of these piezoelectric materials. The intrinsic performance of the devices might be unbeatable taking into account the fabrication costs and ecological aspects.

Keywords: piezoelectric, salts, eco-friendly, cellulose, composite, ADP, Rochelle salt, energy harvesters, resonators, green, eco-design, fabrication.

I. Introduction

Nowadays, rare earth metals are becoming strategic and critical for the manufacturing of our technology [1]. Moreover, due to the rarity in nature and technological dissemination with small quantities, recycling and recovery of critical metals are challenging and energy consuming [2]. Therefore, some renewable energy scenarios might be unrealistic from the perspective of critical metals [3]. Would it be possible to deal with a rapid penury of such strategic resources? Would it be feasible to think to develop resilient technologies for future generations that would not include threatened resources? Concurrently, hazardous components embedded into electronics devices have an irreversible environmental impact which goes against a more sustainable world [4]. Consequently, the development of “clean” or “green” energy technology is strongly dependent of minimizing these strategic and critical resources [5].

The purpose of this work is to contribute to the emergence of “really green technology”. Not only green or efficient when used, but green on the full life cycle. The development of such technology that requires low energy and few resources during manufacturing has to be experimented now for next generation, since actual standard technology might be threatened by several shortage during this century. To place our proposed eco-design approach into perspectives, we have compared most of lead-free piezoelectric elements in term of ease of production, process complexity, biocompatibility and biodegradability, scarcity, maximum piezoelectric coefficient and maximum operating temperature range for piezoelectric applications. A comparative table including methodology is

presented in the Supplementary information. This comparative table suggests that Rochelle Salt (RS), a co-product of wine industry, is the most renewable piezoelectric material investigated herein this work. Rochelle salt is also soluble in water and non-toxic since E337 is an approved food additive by the Food and Drug Administration. Its low cost and ease of synthesis are additional assets. Our previous works have shown the possibility to grow Rochelle salt crystals into cellulose-based sheets [6] or into the naturally orientated capillaries of wood [7] to achieve eco-friendly piezoelectric transducers. Paper-based sensors [8], transducers [9] or electronic platform [10] are growing interests due to the features characteristics of cellulose-based materials namely their simplicity and abundance in our environment.

Piezoelectric salts have been studied during the 20th century [11, 12]. Rochelle Salt is ferroelectric between -18°C and 24.9°C (its two Curie points) [13]. It has high piezoelectric and dielectric constants. It has a monoclinic structure in the ferroelectric phase and an orthorhombic structure in the paraelectric phase at temperatures higher than 25°C [14].

In the middle of the 20th century, Ammonium Dihydrogen Phosphate (ADP) crystals were used in replacement of quartz and Rochelle salt crystals for some application, as Rochelle salt is deliquescent [15]. ADP and Rochelle salt optical, electro-optical, dielectric properties and more especially piezoelectric ones, were broadly investigated. [16, 17, 18].

In agriculture, ADP was used as an ingredient of fertilizers [19]. It represents the largest use of monoammonium phosphate (MAP the other abbreviation of ADP in literature), providing nitrogen and phosphorus to the plants. Thus, ADP was produced in very large quantities at relatively low cost. Both ADP and RS crystals are not hazardous and can grow at ambient temperature without sophisticated equipment. Another important asset of these two crystal salts is the possibility to employ them without poling step in contrary to the majority of the commercial piezoelectric buzzers like quartz.

In the framework of the development of lead-free and then metal-free electronics, we present fully eco-friendly piezoelectric transducers composed of abundant and non toxic elements (i.e. H, N, O, C, P, Na and K). Concretely, we studied the impedance and resonant frequencies behavior of RS and ADP crystals with respect to temperature. Then, electronic transducers made of these two piezoelectric salts are fabricated, characterized and discussed.

II. Results and discussion

II.a Study of the thermal stability of RS and ADP crystals

Impedance measurements were performed using the environmental controlled chamber (described in the Method section) at different temperatures. For all crystals, graphite-based conductive ink was used for the electrodes. The impedance of RS crystal was measured at 1 kHz for different temperatures ranging from 10°C to 50°C (Figure 1). The impedance of RS crystal decreases with increasing temperature from 10°C to 25°C, reaching a local minimum and then increases again at higher temperature up to 50°C. This local minimum observed corresponds to the change of crystal structure related to one of the Curie temperature of the RS crystal at around 25°C. This has been reported back in 1922 by J. Valasek *et. al.* where the two Curie temperatures of RS, respectively -18°C and 24.7°C were measured from dielectric spectroscopy characterization [11] and confirmed periodically with other methods such as Nuclear Magnetic Resonance (NMR) spectroscopy [20]. Additionally, we

studied the piezoelectric resonant modes of Rochelle salt crystal by recording impedance and admittance at several temperatures ranging from 10°C to 50°C by using modern apparatuses. Historically, piezoelectricity of Rochelle salt has already been measured up to 45°C [21].

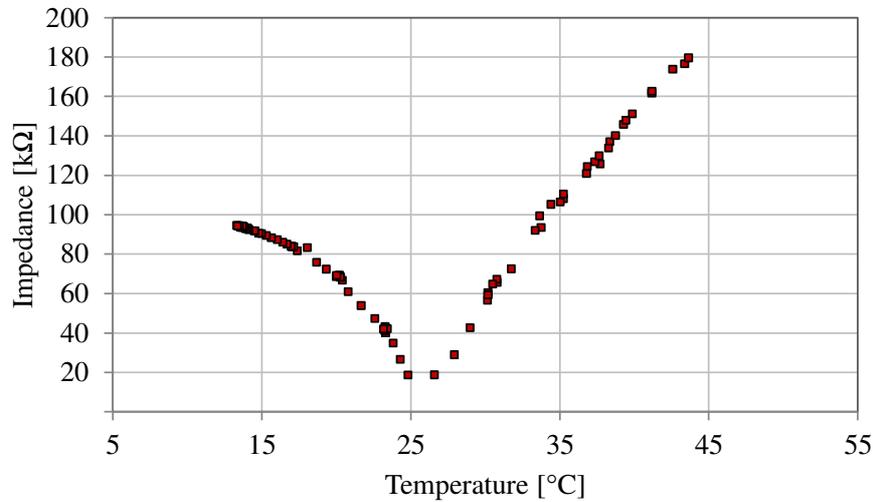


Figure 1 - Impedance measured on Rochelle salt sample as a function of temperature at 1 kHz. Driving oscillating voltage: $V_p = 1V$ (no bias voltage).

Thanks to accurate modern impedance spectroscopy, we performed the conductance measurements with frequency sweeps from 50 to 150 kHz at several temperatures. One can see on Figure 2 that the best resonant modes can be observed around 25°C, which correspond to one of the Curie temperatures of RS. These measurements also confirmed the previous studies which have demonstrated an upper temperature limit of 45°C for Rochelle salt piezoelectricity [21]. Furthermore, they highlight that the piezoelectric modes still exist up to 49°C despite their intensity was diminished (Figure 2), indicating the piezoelectricity of Rochelle salt can still be considered as residual at this temperature.

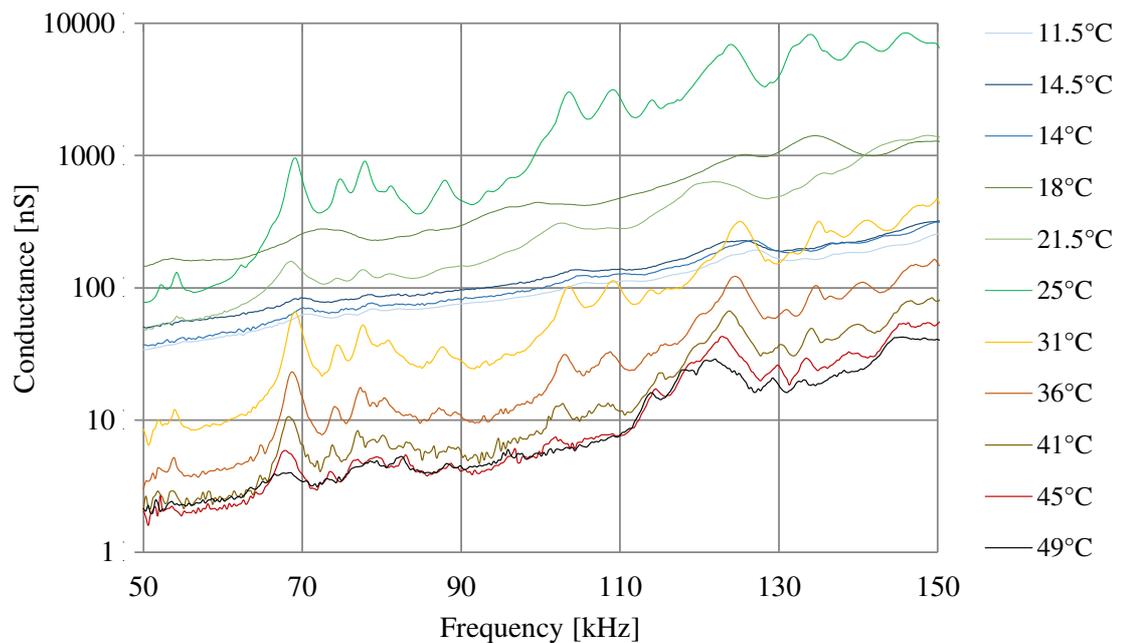


Figure 2 - Conductance spectra as a function of temperature measured on a Rochelle salt crystal between 50 kHz to 150 kHz. Driving oscillating voltage: $V_p = 1V$ (no bias voltage).

The susceptance measurements were recorded from 1 kHz to 300 kHz at different temperatures on RS and ADP crystals. Narrow frequency sweeps centered at one resonant frequency mode were recorded for several temperatures on RS (Figure 3) and on ADP (Figure 4) in order to measure the resonance stability with respect to temperature. Both crystals (RS and ADP) have admittance spectra with well-identified resonance frequencies in ambient condition. Between 24°C and 28°C, RS has an upper frequency shift of 10%/°C (Figure 3b). The temperature shift of RS crystal modes with respect to temperature is nonlinear due to the structural phase transition at around 25°C (Curie temperature) as shown in Figure 1. As expected, Rochelle salt is not thermally stable over this temperature range and may not be used as resonant sensor. On the contrary, ADP is thermally more stable and promising to be used as resonator. The Eigen frequency of ADP crystal has a good thermal stability with a linear shift of 616 ppm of frequency per °C of temperature change (Figure 4 b and 4c). As a comparison, the dependence of a 131 kHz quartz-crystal, which includes temperature compensation mechanism, can vary by a maximum 6 ppm/°C [22]. This factor of 100 between the temperature stability of commercial quartz and raw ADP crystal could be considered as crippling. But in our case, we use graphite as electrodes on ADP crystal which can have a temperature coefficient of resistor (TCR) from -2900 to -4400 ppm/°C [23]. These ADP crystals with carbon-based electrodes may already be stable enough for numerous applications. Nevertheless, by optimizing the sample preparation process (using more stable material as electrode, employing advanced thin film deposition methods, and design), the temperature effect on resonance stability for ADP may strongly be improved.

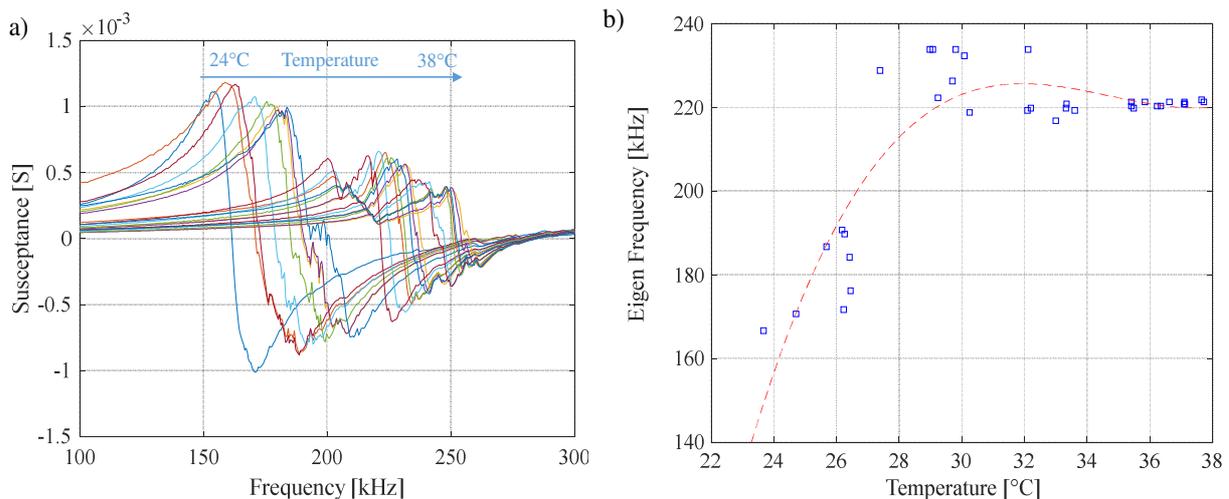


Figure 3 – a) Susceptance spectra measured on clamped Rochelle salt at several temperature, b) Eigen or major resonant frequency mode of crystal with respect to Temperature. Driving oscillating voltage: $V_p = 1V$ (no bias voltage).

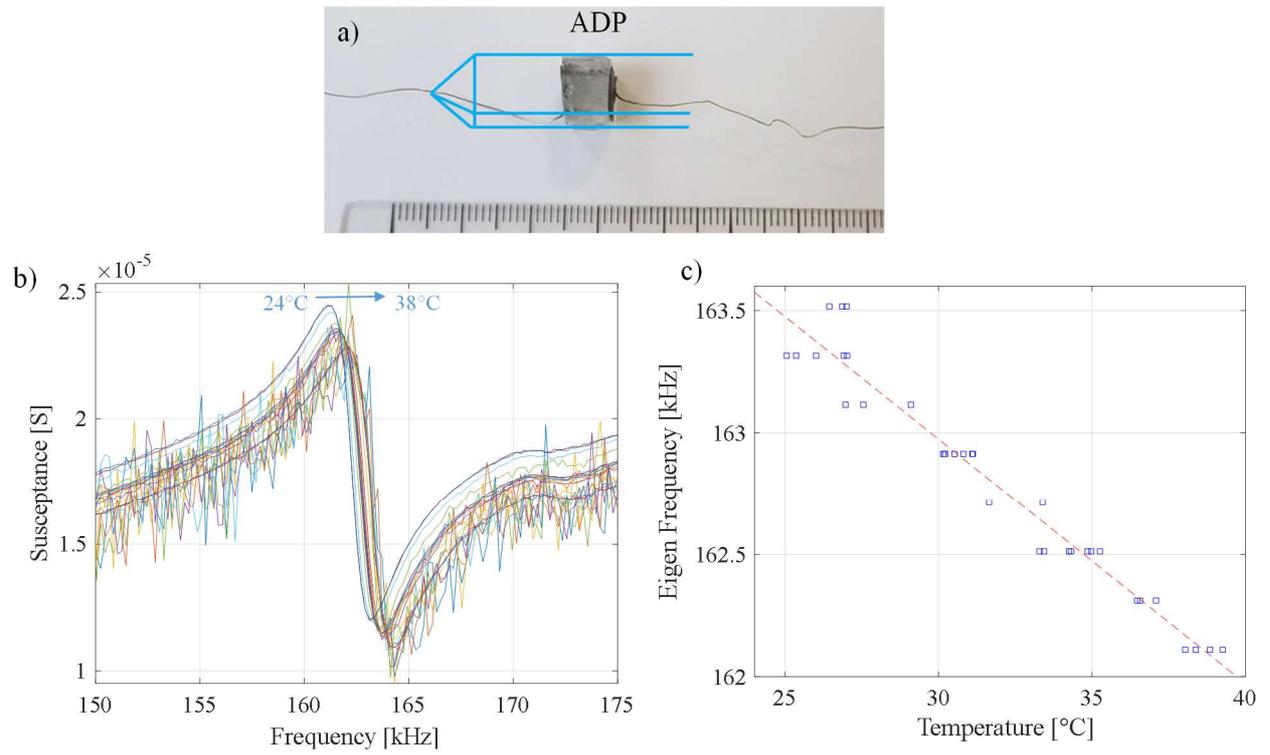


Figure 4 - a) ADP crystal with graphite-based electrodes, b) Susceptance spectra measured on clamped ADP at several temperatures for a frequency sweep between 150 kHz-175 kHz , c) Eigen or major resonant frequency mode of crystal versus Temperature. Driving oscillating voltage: $V_p = 1V$ (no bias voltage).

II.b RS-based transducers

II.b.1 Impact energy harvesters

As low cost impact energy harvester, we used some commercial wood rattles on which we fixed our piezoelectric samples on the cantilever clamping area using double side adhesive tape. The RS-based composite samples were prepared by incorporation of RS into paper sheets and into natural wood and named “*PiezoPaper*” and “*PiezoWood*”, respectively as previously reported [6, 7]. Then the top and bottom electrodes were patterned by deposition of carbon-based conductive ink (*Electric Paint* from Bare conductive). For comparison, we also used a pure RS crystal, a commercial flexible sample of PVDF-TrFE (*DT series of piezo film sensors* provided by Measurement Specialties, Inc.) and a commercial piezoelectric buzzer (15Vpp, 4.2 kHz *Piezo Electric Transducers*, provided by Radiospares). The output signals produced when actuating the rattle for one impact were recorded on an oscilloscope with an input load of 1 MΩ. Therefore, samples are not loaded with their respective optimal load but each piezoelectric sample undergoes the same experimental conditions, since then the energy harvested in each device has been integrated with the same load. Moreover, dimensions of the piezoelectric samples are not the same, so the produced results are not a rigorous comparison of performance but an illustration of several (green) technological options. The results of voltage curves are shown in Figure 5 (from a to e) and harvested energy in Figure 5 f. The lowest voltage is obtained with “*PiezoPaper*”, a maximum of 500 mV peak-to-peak voltage (V_{pp}) is recorded corresponding to 0.7 μJ per impact. It is noteworthy that due to the random arrangement of cellulose fibers, the RS crystals are also randomly orientated [6]. The global electric response should thus be due to the combination of the three piezoelectric coefficients oriented in three orthogonal spatial directions. Therefore, direct piezoelectric response is relatively low (in the range of 2 to 5 pm/V [6]). For the “*PiezoWood*” harvester, electrical response is stronger, namely more than 1 V_{pp} and 3 μJ per impact. This increase of performance can be attributed to the anisotropic structure of wood [7]. With almost 2 V_{pp} and 8 μJ per impact, the commercial flexible piezoelectric PVDF sample still exhibits better performance than the presented “*PiezoWood*” and “*PiezoPaper*” samples. Efforts on electrodes thickness, formulation and interface between matrix and RS crystals must continue in order to compete with PVDF material. However, Rochelle salt single crystal harvests more energy than the PVDF-based harvester: >10 V_{pp} and 56 μJ/impact. This versatile electromechanical energy harvester is able to turn on LEDs. With more than 20 V_{pp} and 710 μJ/impact, the piezoelectric ceramic of the buzzer largely overpass the piezoelectric response of all the green piezoelectric materials presented. The aim of this work is not to produce a comparative life-cycle-analysis of the five harvesters presented here. In this framework, others parameters have to be considered. In fact, why should we consider only the output energy provided by the harvester? What level of technological complexity and how much energy do we need to realize these piezoelectric energy harvester? Their simple process to synthesis and easy fabrication, full recyclability and biodegradability combined with their non-toxicity and eco compatibility outbalance the lower intrinsic performances of RS-based harvester present unbeatable energy return on investment (EROI). RS-based Composite could still be optimized in order to compete with PVDF-based technology. With some improvements, might the RS-based structures be the “greenest” piezoelectric energy harvester with the smallest energy budget? At least, among the devices of Figure 5, it is our best candidate.

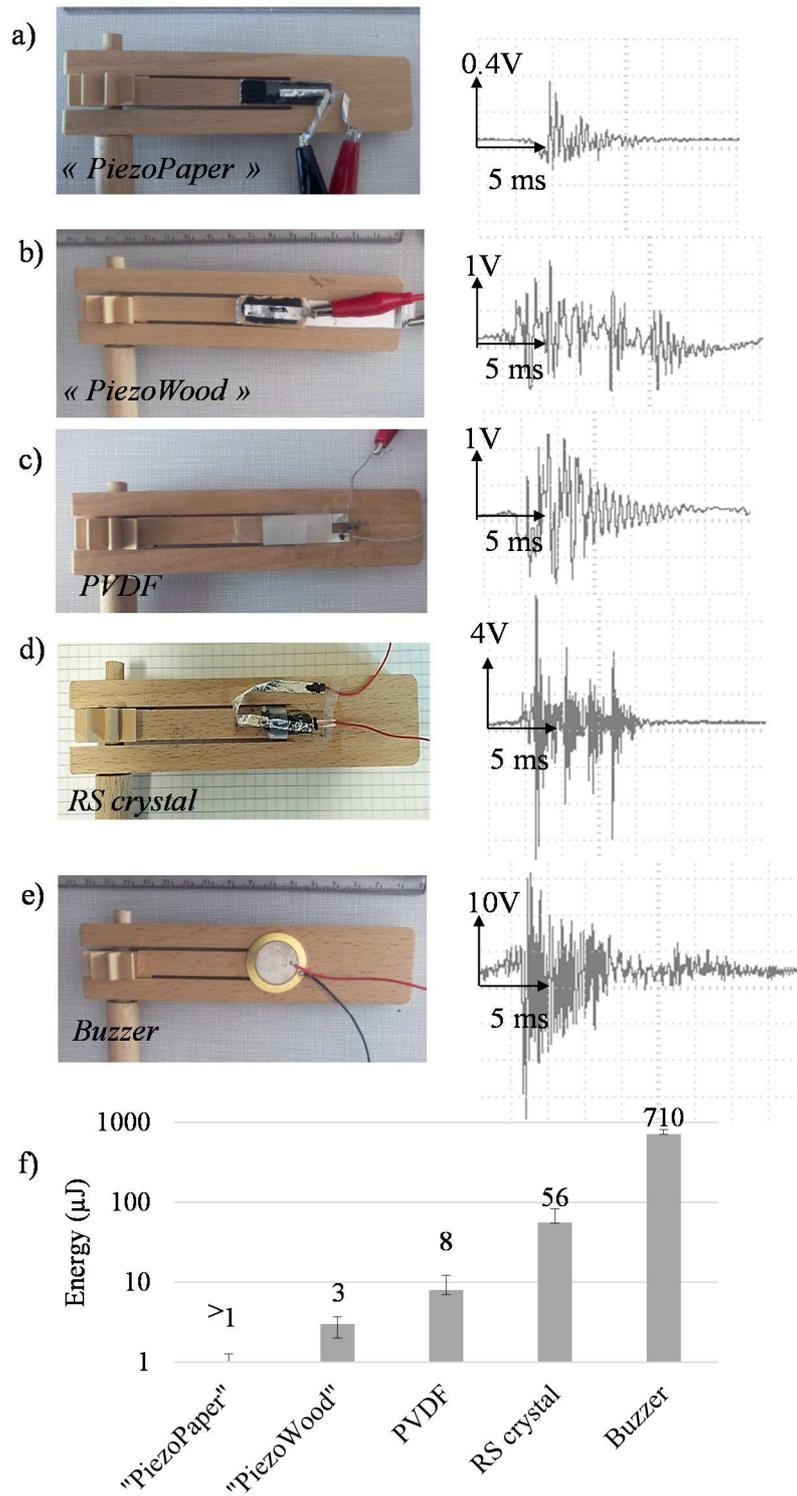


Figure 5 – Image and example of output voltage for a) RS impregnated piezoelectric paper, b) RS impregnated wood, c) commercial PVDF film, d) RS single crystal with electrodes, e) commercial piezoelectric buzzer clamped on rattle, and f) comparative averaged energy per impact harvested with the five different harvesters. Harvesters have been loaded directly on 1 M Ω oscilloscope input. Upward cantilever excitation are performed at 1 Hz (1 impact per second or 5.5 gear turn per minutes)

II.b.2 PiezoPaper cantilevers

“PiezoPaper” foils were prepared as previously reported [6] and then cut with a laser cutting machine (Speedy 500 from Trotec) in order to pattern any 2D shape structure. A conductive ink layer was deposited on RS impregnated paper sheet and an aluminum foil covered both sides of the foil as electrodes. One extremity of cantilever was clamped as illustrated in Figure 6. In order to compare our graphite-based electrodes, we also used aluminum scotch tape for some RS impregnated paper cantilever (Figure 6 a). Out-of-plane vibration of the RS impregnated cantilevers was measured using a laser vibrometer (MSA-500 from Polytec), as presented in Figure 6. Cantilevers were driven with $10 V_{pp}$ periodic chirp. It appears that the electrodes made with aluminum tape are insulating due to the adhesive layer at the rear side of aluminum tape (compared to resistive carbon-based electrodes): the first mode of vibration amplitude was measured to be 1.6 pm (Figure 6 a). A longer cantilever with the same configuration reaches more than the nanometer of out-of-plane deflection (Figure 6 c). In term of quality factors (Q-factors), the stiffness of aluminum tape is dominating. Therefore, the cantilever with aluminum tape reaches a Q-factor of 21 whereas cantilevers with carbon-based-electrodes cannot overpass 10. Geometrical and structural optimizations have to be made in order to produce bilayer cantilevers including a stiff layer and an efficient piezoelectric layer for the vibrational driving. It is worth noting that cantilevers with graphite-based electrodes are metal free and

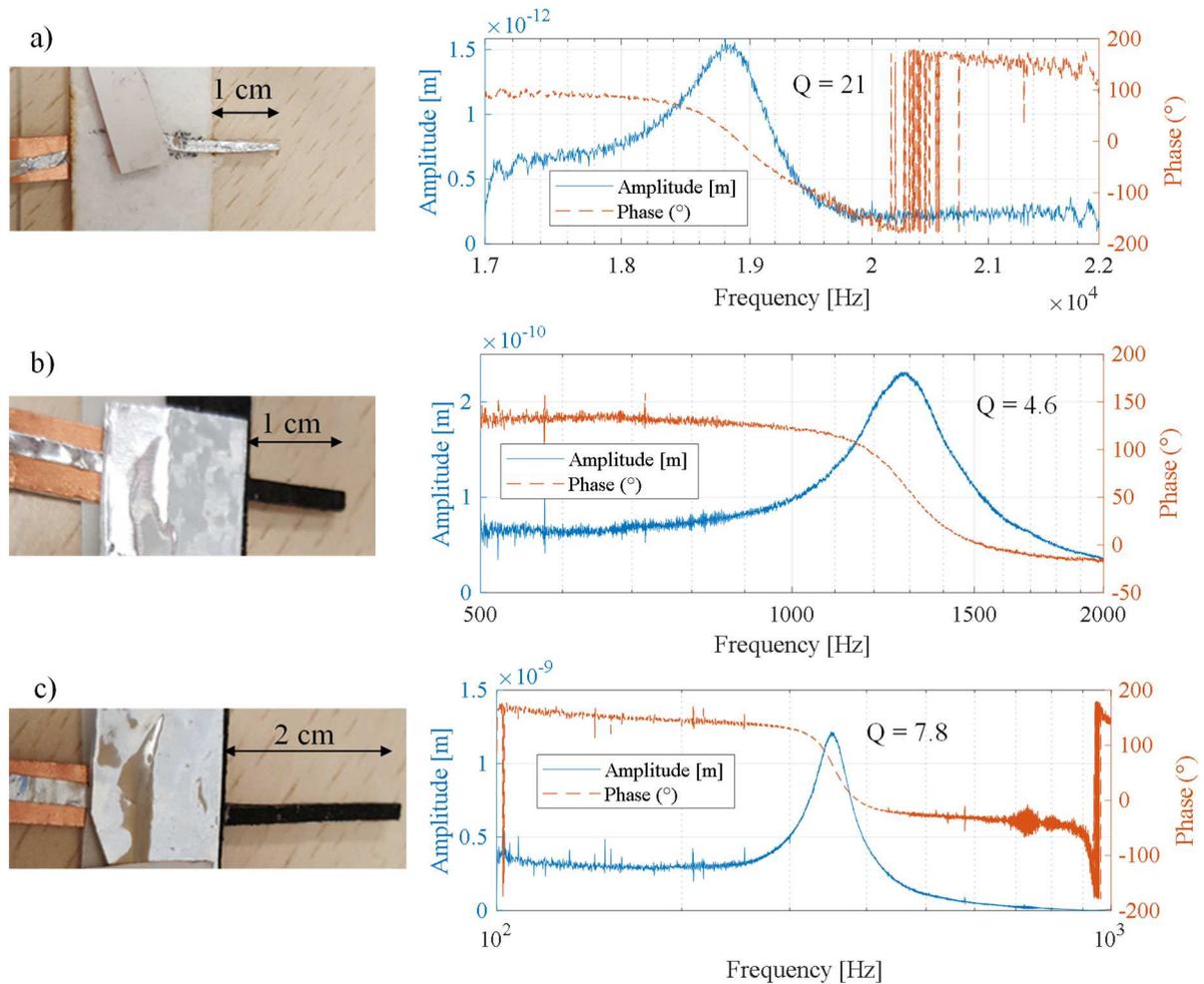


Figure 6 – Images of a) b) and c) out-of-plane displacement spectrum of a) 1 cm long “PiezoPaper” cantilever with Al-tape electrodes, “PiezoPaper” b) 1 cm long and c) 2 cm long cantilevers with conductive ink electrodes (and Al tape for optical signal reflection). Driving oscillating voltage applied, $V_p = 10 V_{peak-to-peak}$

II.c ADP-based piezoelectric transformer or BAW filter

We have shown in section II.a that ADP single crystals could be quite stable oscillators. Therefore, ADP resonator could replace quartz disk or tuning fork if lower energy budget for fabrication is required. More complex device than dipoles can be manufactured on ADP substrate. For instance, narrow band pass filter can be developed by implementing Surface-Acoustic-Wave (SAW) or Bulk-Acoustic-Wave (BAW) devices (filters, sensors, transformer, etc.). Therefore, to illustrate the feasibility of this concept, we built an ADP-based piezoelectric transformer (Figure 7) using transversal vibrational mode by shaping graphite-based electrodes on top and bottom of the long faces of ADP crystals. Such a rudimentary BAW device fabricated from ADP crystal, diced manually and covered by carbon-based electrodes led to a promising Q-factor of 75. Last but not least, this device is entirely biodegradable: ADP crystal are biodegraded by soil as it is used as fertilizer in agriculture, graphite ink is water soluble and could be harvested or diluted and disseminated, steel wires could be oxidized and degrade rapidly into a humid soil.

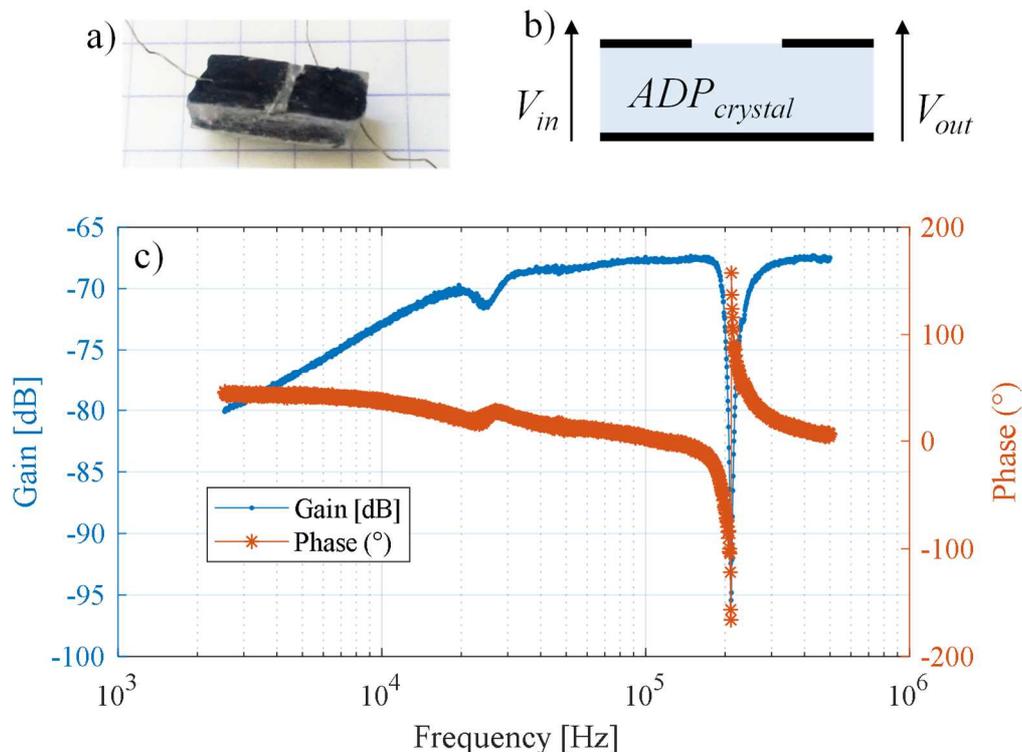


Figure 7 – a) Image of the tested BAW device b) schematic design of the device with electrodes and voltages c) Gain-Phase spectra of fully biodegradable ADP-based BAW piezoelectric transformer/filter transformer using transversal vibration mode. Driving AC voltage: $V_{in} = 1V$; frequency range [3-400] kHz

The gain-phase spectra as a function of frequency obtained for the ADP-based BAW filter (Figure 7c) highlight sharp bandwidth at the resonant frequency of the filter. This material could be reconsidered for specific band-pass filter applications such as biodegradables sensing purposes.

III. Material and Methods

RS and ADP powders (purity 99%) were provided by APC Pure. Graphite-based conductive ink (commercial name: Electric paint) was provided by Bare Conductive and bought on Radiospares. Saturated RS and ADP solutions were prepared by introducing the powders into the distilled water and crystals were grown in a crystallizer at ambient temperature. Then some crystals were diced manually with a scalpel and dark conductive ink has been deposited manually in order to shape the electrodes. Wood or paper-based composite samples were prepared by impregnation of substrates into RS or ADP saturated solutions and dried at ambient temperature during at least 48 hours. The composite preparation processes have already been detailed [6,7]. Trotec speedy 300 laser-cutting machine was employed to shape the paper cantilevers by patterning the dried substrates obtained previously.

A precision LCR Meter (E4980A, from Keysight or calibrated Red Pitaya board was used to measure the impedance characteristics of RS and ADP crystals and to perform impedance or admittance spectra. In order to monitor and control precisely the sample temperature, a low cost apparatus was built: a modified driving electronics of a commercial 12V Peltier fridge and controlling it using a MBED microcontroller by implementing a simple proportional coefficient corrector. A commented picture of the setup is shown on Figure 8. This setup permitted to control the temperature of a 5 liters chamber in the range of 10-60°C within an accuracy of 0.5°C. The gain-phase spectra were also obtained by using a Red Pitaya board.

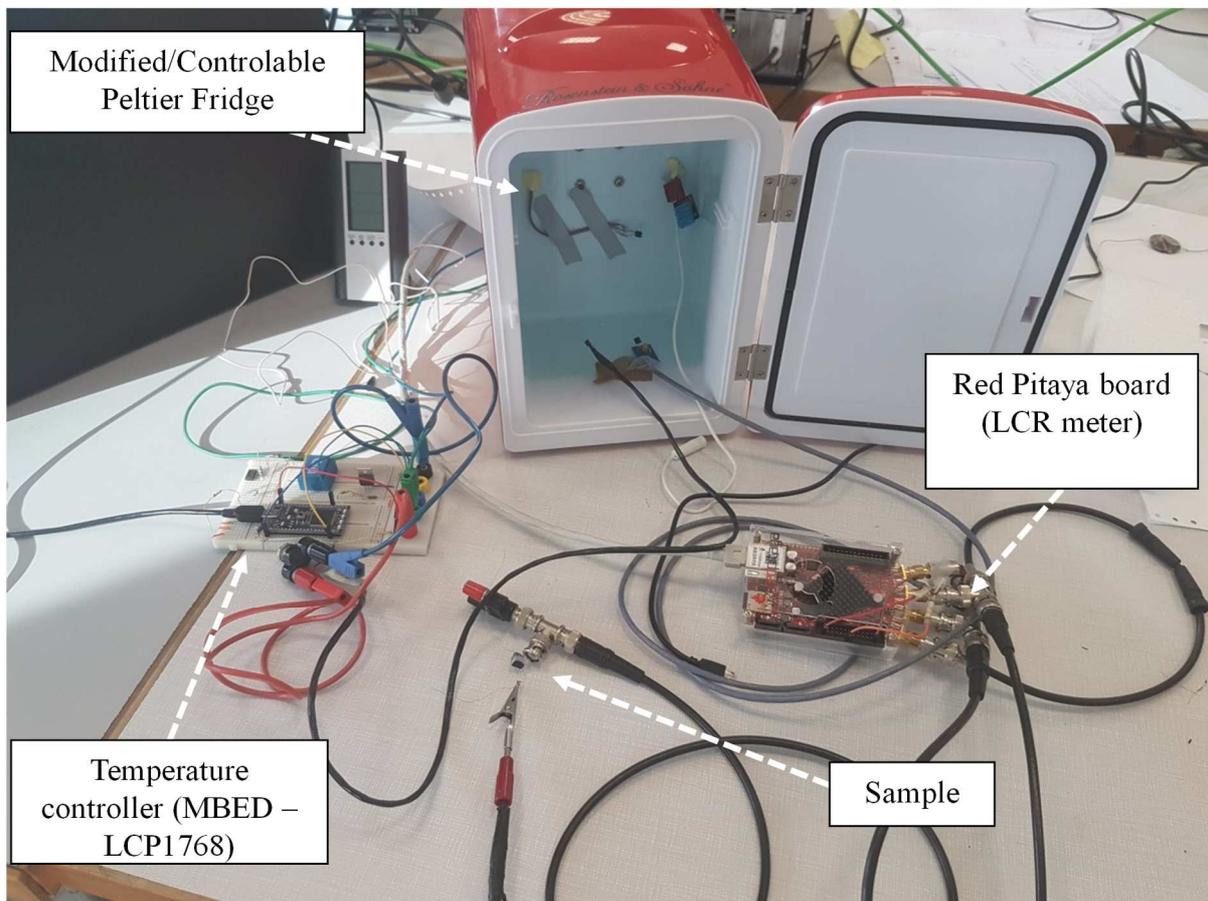


Figure 8 – Environmental controlled chamber and setup for impedance measurements.

IV. Conclusion

In this work, authors re-explored two piezoelectric salts: RS and ADP. The idea is to redesign eco-friendly and sustainable technological opportunities that could have interests for energetical and environmental concerns. We manufactured and characterized several simple demonstrators that could initiate the development of new “green applications” with low energy budget. RS and ADP-based simple devices were fabricated with very limited resources: resonating crystals, several type of biodegradable piezoelectric energy harvesters, resonating paper cantilevers and filter or transformer. The output characteristics of three electromechanical energy harvesters using pure RS crystal or RS incorporated composites (RS incorporated paper or wood) were characterized and discussed. Then composite paper cantilevers were fabricated and characterized as actuators. Finally, two applications with ADP (oscillator, bulk or surface acoustic wave devices) are also presented. ADP-based devices could be an ecofriendly alternative for the replacement of quartz or silicon technology with lower environmental and energy costs.

Although the relative thermal instability of RS, basic impact energy harvesters fabricated by using RS crystals show a spatially distributed piezoelectricity and a huge amplitude (up to 300 pm/V) measured at specific temperature and orientation. Piezoelectric actuator and energy harvesting systems, usually built with high environmental impact materials, could be greener with Rochelle salt and efficient enough if well integrated and well used for applications with optimal environmental conditions (acceptable deprecation of performance when temperature and moisture change).

Manufactured RS-incorporated paper cantilevers were only tested as actuators. However, in the future those paper-based structure could integrate piezoelectric or piezoresistive readout in order to obtain a fully biodegradable paper-based micro electromechanical systems (MEMS) which include driving and readout transduction. If the stability over temperature changing conditions are problematic, those resonators could find application for a single use or disposable low-cost temperature sensors.

We also demonstrated that ADP is thermally stable piezoelectric crystal that could be used for oscillator based-devices involving eco-friendly concerns or small energy budget in replacement of quartz or silicon based technology. Piezoelectric transformers, SAW, BAW or filters may have application in the sensors or telecommunication fields for the development of eco-friendly or disposable electronics. This work opens the new horizons and opportunities to develop slightly less efficient technologies, but sufficiently effective and perfectly integrated into a sustainable ecosystem. Design optimization, eco-responsible manufacturing techniques and accurate characterizations must be used and re-appropriated in order to fulfill the challenge of developing a new circular and sustainable technology within the limited physical and environmental restrictions. Authors think that piezoelectric salts and more generally renewable salts are good candidates to be integrated into sustainable (re)designs of (piezo-)electronics. These achievements open new opportunities for manufacturing low cost green electronic components with low environmental impacts, acceptable performances and thermal stability.

V. Acknowledgments

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