

Use of a Natural Clinoptilolite Monolith as a Negative Temperature Coefficient Thermistor [†]

Loredana Schiavo  and Gianfranco Carotenuto ^{*} 

Institute of Polymers, Composites and Biomaterials (IPCB-CNR), National Research Council, Piazzale E. Fermi 1, 80055 Portici, Italy; loredana.schiavo@cnr.it

^{*} Correspondence: giancaro@unina.it

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Abstract: Geomorphic clinoptilolite, a mechanically and thermally stable mineral substance, has very useful electrical properties due to the presence of extra-framework cations in the crystal structure. Indeed, owing to the electrical transport that alkaline earth metal cations may give, this ceramic material behaves like an electrical insulator at room temperature, while it changes to an electrical conductor with increasing of temperature. Such unusual electrical property of clinoptilolite can be advantageously exploited for a number of functional applications in industrial fields. For example, clinoptilolite-based devices can be used as thermal sensors, electrical/thermal switches, NTC thermistors, etc. Here, the capability of a simple natural clinoptilolite monolith to switch from an electrical insulator to a conductor under fast temperature changes has been investigated via time-resolved a.c. electrical transport measurements.

Keywords: clinoptilolite; NTC thermistor; conduction mechanism

1. Introduction

The recent restriction of hazardous substances in the electronic industry have forced production toward ‘green’ electronic materials, such as conductors and solders, and the use of environmentally friendly manufacturing solutions [1–3]. So far, only limited academic research (at the laboratory scale) has been carried out on ‘green’ resistors and thermistors [4].

Zeolites are interesting electrical conductors (single-charge carrier ionic conductors) [5] that could be exploited for developing ‘green’ thermistors; however, to the best of our knowledge, such an application has never been proposed. A thermistor is an electrical conductor with a resistance value depending on temperature much more strictly than an ordinary resistor [6,7]. Thermistors are classified according to their conduction behaviour and the negative temperature coefficient thermistors (NTC thermistors) have lower resistance at higher temperature. Indeed, as the temperature increases, the resistance of an NTC thermistor decreases in a non-linear way, according to a particular curve known as ‘thermistor characteristics’. NTC thermistors are typically based on doped oxide semiconductors and used for temperature measurements and many other applications [8].

A variety of zeolites are available in nature (e.g., chabasite, mordenite, etc.); among them, clinoptilolite is the most convenient mineral type for use in technological applications, for example, NTC thermistors. Such choice is related to the following peculiarities: structural stability at extreme temperature (750 °C), high zeolite content, availability on the market and wide distribution in the world, low cost, non-toxic, biocompatible, low Si/Al ratio (good electrical conductivity in temperature), and stability to water. It must be pointed out that clinoptilolite is a type of zeolite quite difficult to be chemically synthesized, and therefore, the mineral form represents a convenient choice for practical applications [9].

Here, a simple experiment based on the fast heating of small clinoptilolite samples by using a high-power incandescent light bulb, has been performed in order to test the



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electrical behaviour under heating of this very common type of natural zeolite, widely available on the market. Time-resolved effective current intensity measurements have been used to evaluate the promptness of the electrical response to heating and cooling in air. In order to measure the threshold for the electrical conduction, the same type of tests have been performed also under calibrated-temperature conditions.

2. Experimental Section

Principal information on the investigated clinoptilolite mineral sample and the other materials used for the functional device fabrication are provided in Table 1. The device structure was extremely simple, and it was fabricated by cutting a thin prismatic monolith from the geomorphic stone. A mini-drill (VUM-40, Vigor, Fossano, Italy) with diamond disk was conveniently used for such an operation. The two electrodes were obtained by partially coating the monolith surface with a thin layer of a ceramic silver paste. In particular, a thermally stable type of ceramic paste was used (see Table 1).

Table 1. Information on materials used for the device fabrication.

Natural Zeolite Seller	Technische Industrie Produkte, GmbH, Waibstadt, Germany
Colour	Gray
Origin	Est-Europe
Ceramic conductive paste	XeredEx, XD-120, SGS
Copper wire	0.6 mm

A photograph of the fabricated NTC thermistor and the mineral precursor is given in Figure 1. In order to facilitate heat transfer from the heat source (i.e., the light bulb) to the clinoptilolite sample, the latter had a significantly reduced thickness, and silver paste was interposed between sample and the light bulb.



Figure 1. Fabricated NTC thermistor and starting clinoptilolite mineral.

3. Results

The SEM micrograph of the clinoptilolite sample surface (see Figure 2a) clearly shows that the mineral is made of randomly oriented stacks of lamellar crystals. All lamellas have the same thickness (40 nm) and the other two sizes are of a few hundred microns. Owing to the high clinoptilolite content, the electrically conductive zeolite lamellar crystals are interconnected and form a percolation network, with paths crossing the full solid structure.

Since the Al-O bond is weaker than the Si-O bond because the Al-O bond is longer and less polarized, the Si/Al atomic ratio is a determining factor for the zeolites properties; indeed, it defines the mechanical/chemical stability, the ion exchange capability, and the electrical conductivity of these materials. Therefore, the Si/Al atomic ratio of the investigated clinoptilolite sample has been determined via EDS analysis (see Figure 2b), the

result being 5.6, which is a characteristic value for this mineral. In addition, the chemical analysis of the clinoptilolite sample performed via EDS has shown that K^+ and Ca^{2+} are the most abundant types of charge compensating cations, and therefore, the mineral sample consists of clinoptilolite-K,Ca.

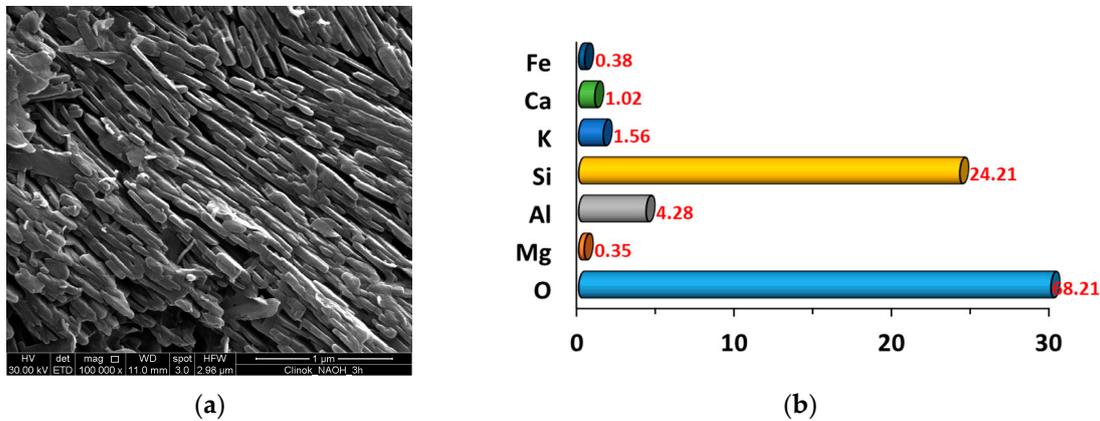


Figure 2. SEM-micrograph showing the lamellar texture of the clinoptilolite mineral (a) and its chemical composition obtained via EDS-analysis (b).

Two electrodes were placed on the surface of a prismatic clinoptilolite monolith in order to test the clinoptilolite electric behaviour under fast uncontrolled heating and this simple device was put in contact with the surface of a light bulb. The electric current intensity was measured using a true-RMS digital multimeter (DMM) placed in series with a sinusoidal signal generator. Electric signals were measured and recorded during the time by using the devoted DMM datalogger software.

The effect of a fast increase in temperature on the mobility of the extra-framework cations (actually, K^+ is the principally involved charge carrier) has been investigated by monitoring, during a rapid heating process, the variation in the effective current intensity flowing in the sample, biased by a constant a.c. sinusoidal voltage value. In particular, the small piece of clinoptilolite was polarized by using an a.c. voltage source (sinusoidal voltage signal of $20V_{pp}$, 5 kHz), and the current intensity flowing in it was measured by connecting a wide-band true-RMS digital multimeter (DMM), set as an a.c. micro-ammeter, in series with the sample (see Figure 3).

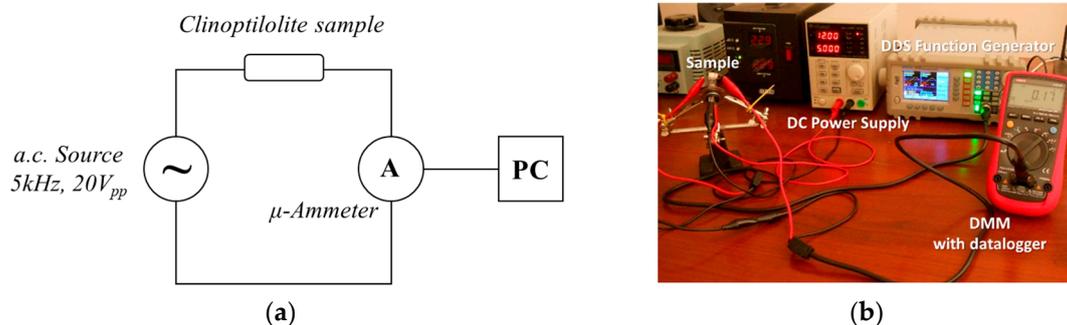


Figure 3. Schematic representation of the electric circuit used for tests (a) and experimental setup (b).

A direct digital synthesis (DDS) function generator (Gratten, ATF20B+) was used as the voltage source, and a true-RMS, 10kHz bandwidth, DMM (Uni-Trend, UT61E) was used as an a.c. micro-ammeter. The effective current intensity value (I_{eff}) was recorded on a PC using a devoted datalogging software application (see Figure 4).

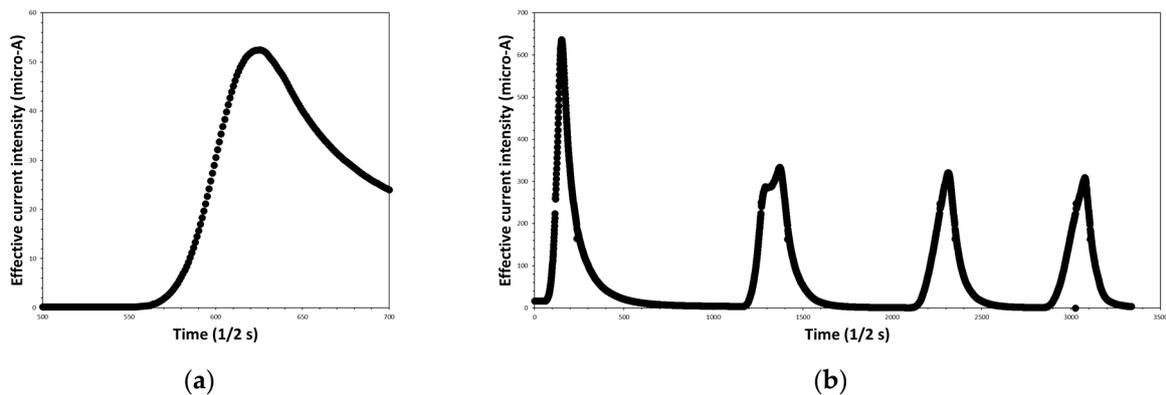


Figure 4. Change in the effective current intensity as a result of the turning on/off of the incandescent light bulb (a) and behaviour of the NTC material under four successive thermal pulses (b).

A fast specimen heating was achieved by placing its free-from-electrodes surface in contact with the glass bulb surface of a high-power halogen lamp (NT U H4, 12 V, 60/55 W, P43T), powered up using a D.C. power supply (Velleman, LABPS 3005D, 30 V/5 A). The same electrically conductive ceramic silver paste used for painting the electrical contacts on the clinoptilolite sample (XeredEx, XD-120, SGS) was used to thermally connect the specimen with the glass bulb surface in order to have efficient heat transfer to the prototypal device.

As visible in Figure 4a, the application of a thermal pulse to the clinoptilolite monolith promptly generates an electrical micro-current in the ceramic sample. Such a micro-current built up with the turning-on of the lamp. During the successive cooling step in air (i.e., the turning-off of the incandescent lamp), the micro-current intensity readily decreased until reaching the starting negligible value. The resulting peak in the current intensity had a slightly asymmetric profile since the process of the sample cooling in air resulted in being slower than the previous heating process. In particular, the heating step followed a linear law, while the cooling step followed a parabolic law. Figure 4b shows the sample behaviour under repeated heating/cooling cycles; as visible, four repeated cycles were unable to modify the electric behaviour of such a simple NTC device.

Heating tests at known temperature values were similarly performed by using time-resolved effective current intensity measurements (see Figure 5). However, in this case, temperature was also measured during the time and sample heating was achieved by using an aluminium block containing a ceramic heater cartridge, and the sample was thermally insulated by a layer of Kapton/cotton wool (the heating block set of a 3D printer was used for this purpose). A digital datalogger thermometer (Uni-Trend, UT-325) was used to measure and record the temperature during time. As is visible in Figure 5, a slow/controlled heating process was also capable of giving a quite asymmetric $I_{\text{eff}}-T$ peak, just like in the case of a thermal pulse.

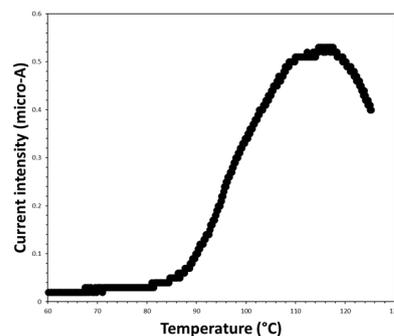


Figure 5. $I_{\text{eff}}-T$ curve obtained with tests at known temperature values.

4. Discussion

Zeolites are low-density crystalline aluminosilicates. They have a covalent crystalline structure with extra-framework positive charges (charge balancing cations). Vučelić defined this particular structure as a ‘reverse’ metal lattice [10]. According to the electrical conduction model of Vučelić [11,12], only those extra-framework charges moving in a ‘free ionic conduction zone’ (i.e., the free cationic conduction band located in the middle of channels) can promote electrical conduction. Indeed, ions at the centres of cavities are carriers of current and move through the zeolite with a low activation energy. The Vučelić model is analogous to the behaviour of electrons in a fixed cation electromagnetic field and to their conduction through conduction zones. More properly, the zeolite structure could be described as that of a doped-metalloid (n-type) with inverted charge signs: the negative charges (Al⁻) are located in the covalent crystal lattice and do not move, while the excited extra-framework positive charges (Meⁿ⁺) (i.e., cation at cage centres), which constitute a cationic conduction band, cause electrical transport.

The electrical properties of zeolites mainly depend on the contained monovalent metal ions because they are less strongly held by the negatively charged lattice and can easily migrate between two neighbouring negative sites. In more detail, the clinoptilolite electrical conductivity, $\sigma(T)$, depends only on the following three factors, namely, (i) charge of the electrical carriers, $Z \cdot e^-$, where e^- is the elementary charge ($e^- = 1.602 \times 10^{-19}$ C), (ii) concentration of the electrical carriers, $[Me^{Z+}]$, and (iii) mobility of the electrical carriers, μ , according to the following physical law $\sigma(T) = \sum_i [Z_i \cdot e^- \cdot [Me^{Z+}]_i \cdot \mu_i]$, where the sum is formally extended to all extra-framework cations present in the substance. However, since the tested sample is clinoptilolite-K,Ca, potassium ions located in the super-cages are principally involved in the migration under the applied sinusoidal signal (5 kHz, 20V_{pp}). Indeed, the contribution of Ca²⁺ and Mg²⁺ cations is negligible because they have a larger charge and are present in the clinoptilolite sample at concentrations lower than K⁺. Iron atoms do not participate to the electrical transport mechanism because they are located in the framework (isomorphous substitution), just like the aluminium atoms. Finally, it is possible to approximately write:

$$\sigma(T) = e^- \cdot [K^+]* \cdot \mu_K$$

where $[K^+]*$ is the concentration of excited K⁺ cations. Each K⁺ ion is located in a potential well generated by the four negatively charged oxygen atoms [10] and the concentration of excited K⁺ present at zeolite cage centre is temperature-dependent; indeed, it increases with the rise in temperature, thus determining an increase in the material electrical conductivity.

5. Conclusions

Zeolites have a temperature-dependent electrical conductivity that can be exploited to fabricate useful thermal devices of NTC type. Here, a thermal switch has been fabricated simply by painting two silver electrodes on the surface of a piece of geomorphic clinoptilolite. Fast heating tests showed a prompt and completely reversible change in the device electrical conductivity. In particular, this simple device rapidly switched from an electrical insulator to a good electrical conductor above a certain temperature threshold. This temperature threshold for electrical transport was determined via electrical measurements at known temperature values, and the result was ca. 90 °C.

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