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Experimental evidence of the pyroelectric nature of struvite

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Struvite ($MgNH_4PO_4·6H_2O$) is a mineral first identified in 1845. It is being tested for several reasons: (1) it is a problem in liquid wastewater treatment plants; (2) on the other hand, it is recovered from these wastewaters for its phosphorus, magnesium and nitrogen; (3) is the main component of microbial-induced urinary stones. We have recently shown that struvite is ferroelectric and piezoelectric. In this paper, we present the first experimental evidence of the pyroelectric nature of struvite. Using a single-diffusion gel growth technique, we grew struvite crystals as flat, parallel plates. We performed measurements of pyroelectric currents on struvite of this shape, using it as a dielectric of a plate capacitor. The occurrence of pyroelectric effects in struvite was investigated by measuring depolarization currents as a function of temperature. This technique allows the disclosure of ferroelectric/pyroelectric transitions as well as the reconstruction of the ferroelectric loop. We found that the value of the pyroelectric coefficient p attains a maximum of 22×10^{-6} C m^{-2} K^{-1} slightly below room temperature, going down to $p \cong 10 \times 10^{-6}$ C m^{-2} K^{-1} at room temperature. This value is comparable to values for other minerals. For example, the pyroelectric polarization coefficient of tourmaline, the mineral for which the pyroelectric effect was first discovered, is 4×10^{-6} C m^{-2} K^{-1}. This value is 2.5 times lower than that measured for struvite, illustrating struvite's fairly strong pyroelectricity.

1. Introduction

The pyroelectric effect is a well-known phenomenon, described in detail in the literature.[1–6] In short, the pyroelectric effect consists in a change in the spontaneous polarization $d\boldsymbol{P}_S$ of the crystal, caused by a change in its temperature dT. The spontaneous polarization $\boldsymbol{P}_S$ of pyroelectric materials, *i.e.* the polarization of the material in the absence of an external electric field, depends primarily on the temperature T. Each change in the temperature dT of the crystal causes a change in its spontaneous polarization $d\boldsymbol{P}_S$:

$$d\boldsymbol{P}_S = p\, dT \tag{1}$$

where the pyroelectric coefficient p is given by:

$$p = \frac{\partial \boldsymbol{P}_S}{\partial T}. \tag{2}$$

The pyroelectric phenomenon is also explained by the generation of free electric charges dQ on the dielectric surface under the influence of changes in its temperature dT:

$$dQ = S\, p\, dT, \tag{3}$$

where S is the surface area of the crystal. The relationship between the generated charge Q and the polarization $\boldsymbol{P}$ is as follows:

$$Q = d\boldsymbol{P}\, S. \tag{4}$$

Due to the fact that polarization is a vector quantity, the pyroelectric effect can be described by the equation:

$$d\boldsymbol{P}_{\boldsymbol{i}} = p_{\boldsymbol{i}}\, dT \tag{5}$$

where: $\boldsymbol{i}$ = 1, 2, 3 correspond to the vector component directed along the x, y and z axes, respectively.

The discoverer of this phenomenon, who was the first to determine the presence of electric charges on the surface of the crystal (which was tourmaline) after its prior heating, is believed to be Franz Ulrich Theodor Aepinus, who did it in 1756.[7] This phenomenon was named pyroelectricity (from the two Greek words pyr meaning fire and electricity) by Sir David Brewster in 1824, who studied the effect in detail in various crystals.[8]

According to the Neumann's principle,[9] the pyroelectric effect can only occur in crystals with a polar axis of symmetry, *i.e.* in crystals with the following symmetry

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elements 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm*, 6*mm*, where the numbers are the multiplicity of the axis of symmetry, and *m* the planes of symmetry (mirror).

Struvite, magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$, which is the subject of the research presented in this article, is a crystal belonging to the $Pmn2_1$ space group, and its point group is *mm*2. This means that the symmetry elements of this crystal indicate that it may exhibit a pyroelectric effect. In addition, this crystal is indicated as a pyroelectric in several bibliographic sources, for example ref. 10 and 11. Furthermore, in ref. 12, it was shown that struvite is a ferroelectric, and as it is known, ferroelectric materials are also pyroelectric. So there is no doubt that struvite is pyroelectric. However, despite our efforts, apart from stating that struvite is pyroelectric, we have not found a more precise description of this phenomenon for this crystal. Therefore, the aim of the research presented in this article is to measure this phenomenon on the struvite crystal we have grown.

Struvite has been extensively studied over the past decade for several reasons. First, struvite precipitates quite easily on uneven surfaces and in areas of high turbulence, which causes problems in wastewater treatment plants.[13–17] Struvite precipitates because carbon dioxide is released in these places and further processes locally increase the pH, and the higher the pH, the greater the crystallization potential of struvite. Therefore, in these favourable conditions with elevated pH, struvite can grow rapidly, which can lead to clogging of pipes.

On the other hand, struvite is recovered from wastewater due to its phosphorus, nitrogen and magnesium content. This is the second reason for great interest in struvite in recent years. Struvite recovered from wastewater is transformed into a useful fertilizer containing those elements (see *e.g.* ref. 18–20) that are essential for plant life. The recovery of struvite from wastewater is particularly important with regard to phosphorus,[15–21] because currently there are fewer and fewer natural sources of phosphorus that do not contain heavy metals.

A third reason for extensive research on struvite in recent years is that it is a major component of microbial-induced urinary stones, which form when the urinary tract becomes colonized by urease-positive bacteria (*e.g.*, *Proteus*). Treatment of this type of stones is usually associated with antibiotic therapy. However, microorganisms can become crystallization centres, specifically heterogeneous nucleation centres. Such centres may also be dead bacteria. Heterogeneous nucleation requires less supersaturation to initiate crystallization compared to homogeneous nucleation.[22] As a consequence, the disease may recur. It is estimated that such recurrence occurs in up to 50% of cases.[23,24]

Struvite studied in this article is also a mineral first identified in sewers in the church of St. Nicholas in Hamburg, Germany.[25] This mineral was named struvite in honour of Heinrich Christoph Gottfried Struve (1772–1851), the Russian consul of Hamburg, who held this position at the time of the discovery of this mineral.[26]

We can therefore conclude that struvite is a fascinating inorganic material, and its crystallization and properties have been extensively studied in recent years. In this article, we fit well into current research trends of struvite, presenting the results of investigation on pyroelectricity of struvite, which have not yet been confirmed experimentally.

2. Materials and methods

2.1. Struvite crystal growing method

To measure the pyroelectric effect, struvite crystals in the form of a flat plate of specific dimensions are needed. Such crystals were grown in a metasilicate gel using the method previously used by us, for example, in the case of measuring the ferroelectric effect in struvite.[12] Here we briefly summarize this method. The chemicals used were purchased from Sigma Aldrich. To prepare the gel, we used anhydrous sodium metasilicate (Na_2SiO_3; SMS), ammonium dihydrogen phosphate ($NH_4H_2PO_4$; ADP) and magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$). The reagents were dissolved in distilled water. The 0.5 M aqueous ADP solution and the 1.07 specific gravity SMS solution were mixed together in appropriate amounts until the pH reached 7.0. The mixture prepared in this way was poured into test tubes 19 cm long and 3 cm in diameter and left to gel for 24 hours. After gelation, 25 ml of 1 M magnesium acetate tetrahydrate was gently poured onto the surface of the newly formed gel and the tube was closed with a lid. The crystals, in the gel, usually took three to four weeks to grow. After this time, struvite crystals were observed in the form of rectangular plates about 1 cm long along the *b* axis. An example of such a crystal is shown in Fig. 1. The unit cell parameters are as follows: $a = 6.9650(2)$ Å, $b = 6.1165(2)$ Å, and $c = 11.2056(3)$ Å.[27]

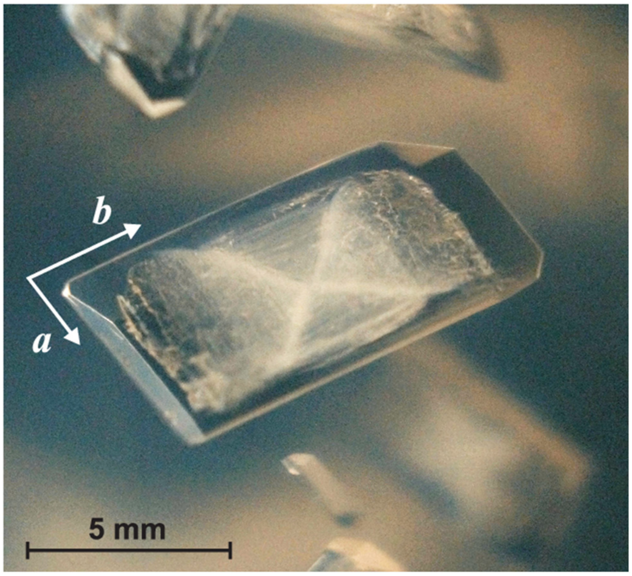

Fig. 1 Struvite crystal in a metasilicate gel (from ref. 12).

2.2. Pyroelectric effect measurement method

The measurements of pyroelectric currents have been carried out on a struvite platelet prepared as dielectric of a planar plate capacitor, oriented along the polar axis *c* of the crystal, as described in ref. 12, using a Keithley 2400 source meter for poling the sample and a Keithley 6517B electrometer for measuring the currents. Poling voltages of opposite polarities $V_p = \pm 200$ Volts have been applied at T = 373 K, and the currents have been recorded at a constant heating rate $\nu = 2$ K min^{-1}.

3. Results and discussion

The occurrence of pyroelectric effects in the compound has been explored by measuring the depolarization currents as function of temperature. This technique allows to disclose ferroelectric/pyroelectric transitions of tiny magnitude, as well as to retrace the ferroelectric loop by the application of proper poling patterns (ref. 28). The technique works as follows: as a first step a poling voltage V_p is applied to the sample well above the temperature T_c (if any) of the transition, where the electric dipoles are still free to move, then the sample is cooled down well below T_c while keeping the poling voltage applied; when low temperature is reached the poling voltage is turned off, the sample is connected to an electrometer and is brought back to the starting temperature at a constant heating rate while measuring the released depolarizing current $I(T)$. When the sample crosses T_c, a peak can be observed in the $I(T)$ curve, associated to the release of the electric dipoles. In Fig. 2 are shown the curves $I(T)$ recorded at heating rate $\nu = 2$ K min^{-1} for a sample of 0.15 cm^2 area and 0.055 cm thickness. By dividing the applied voltage by the thickness of the sample, one can get the applied electric field $E = 200$ V/0.055 cm $\cong 360$ kV m^{-1}. The two clear current peaks can be considered as a hint of a pyroelectric transition at temperature $T_c = 262$ K, which is corroborated by the inversion of the curves measured for opposite poling voltages. The linear background visible for $T < T_c$ can be ascribed to reasons unrelated to the material properties such as for instance instrumental drift. After background subtraction, the curves attain a striking symmetry even on a quantitative standpoint displaying an almost invariant trend of I *vs.* T as expected for a dielectric material. The incoming depolarization peak, centred at T_c, arises from the dielectric state and confirms the ferroelectric/pyroelectric nature of such transformation. After the peak, a tail of increasing current is triggered at 300 K, of sign concordant with the poling voltage. This could suggest the presence of a second depolarization effect coming from a further structural transformation of struvite, which would however be located above the explored temperature range, namely at $T > 330$ K.

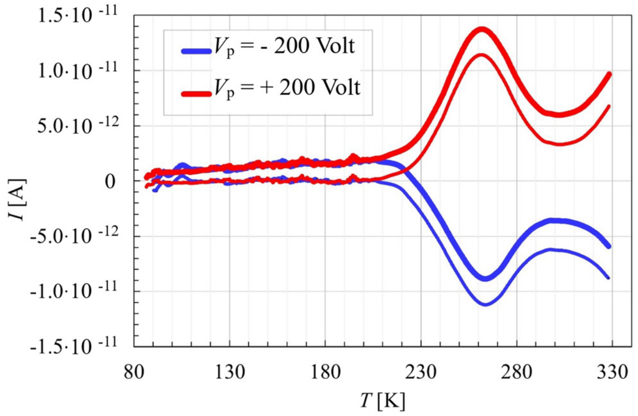

Fig. 2 Pyroelectric depolarization currents for poling voltages $V_p = \pm 200$ volts applied at T = 373 K, recorded at a heating rate $v = 2$ K min^{-1}. The applied electric field $E \cong 360$ kV m^{-1}. Thick lines: experimental data as measured; thin lines: curves after background subtraction.

Dividing by the sample area and the heating rate, one can estimate the pyroelectric coefficient. The value obtained at the transition temperature T = 262 K is $p \cong 22 \times 10^{-6}$ C m^{-2} K^{-1}, while at room temperature T = 293 K one gets $p \cong 10 \times 10^{-6}$ C m^{-2} K^{-1}. The pyroelectric coefficient (p) for selected crystals that are also minerals is within a fairly wide range of values. The pyroelectric polarization for tourmaline, the mineral for which the pyroelectric effect was first discovered, is 4×10^{-6} C m^{-2} K^{-1} at room (ambient) temperature (RT).[10] For wurtzite p is an order of magnitude smaller and is 0.43×10^{-6} C m^{-2} K^{-1} for RT.[10] And for example, for boracite, the p-value is negative and is -2.4×10^{-6} C m^{-2} K^{-1} for RT.[10] There are also crystals for which p reaches much higher values, for example, for chambersite p is 850×10^{-6} C m^{-2} K^{-1} for a temperature of 135 °C.[10] Note that the pyroelectric coefficient is negative when the polarization decreases with increasing temperature.

It should be noted that the value of the pyroelectric coefficient results from the sum of the so-called primary and secondary pyroelectric effect. Primary effect is the amount of charge expressed *via* the primary pyroelectric effect. The secondary effect is the result of crystal deformation, *i.e.* expansion or contraction of the crystal resulting from a change in temperature. The sum of these effects, the so-called total pyroelectric effect at constant stress, is usually expressed as p.

4. Conclusions

Our research presented in this paper shows that struvite meets all the basic requirements to be considered as pyroelectric crystal. Measurements of pyroelectric effects were made on struvite crystals in the form of flat-parallel plates grown by single diffusion in a silica gel environment. The occurrence of pyroelectric effects in struvite was investigated by measuring depolarization currents as a function of temperature. The measurements performed indicate that the value of the pyroelectric coefficient p of struvite at room temperature is $\cong 10 \times 10^{-6}$ C m^{-2} K^{-1}, attaining a maximum value $p \cong 22 \times 10^{-6}$ C m^{-2} K^{-1} at the pyroelectric transition at temperature $T_c = 262$ K. The value of the coefficient p for struvite at room temperature is 2.5 times higher than that of tourmaline, the mineral for which the pyroelectric effect was first discovered, illustrating that relatively strong pyroelectricity is present in struvite.

Challenges and limitations in using struvite's pyroelectricity in practical applications may arise from temperature limitations of struvite's stable pyroelectric properties, as well as the fact that in air, over time, struvite loses water of crystallization and most often turns into dittmarite, which is monohydrate. However, the pyroelectric properties of struvite may be important in aqueous solutions such as liquid sewage or urine, considering that the ferroelectric/pyroelectric transition takes place in the proximity of room temperature.

For example, in the human urinary tract, struvite (a component of urinary stones induced by bacteria – see Introduction) subject to temperature fluctuations consistent with human body temperature fluctuations, as a pyroelectric material, can generate an electric charge in response to these fluctuations. The electric charge accumulated on the struvite surfaces may affect the capture of impurities, especially those with an electrical charge, *i.e.* ions. As a consequence, this may lead to a change in the morphology and habit of these crystals. The surface charge of struvite can also affect bacterial adhesion (in urine in case of infection), as well as the aggregation of struvite crystals with each other and with bacteria. These phenomena may have a real impact on the development of urinary stones and perhaps also on the behaviour of struvite in liquid sewage.

Data availability

The data that support the findings of this study are available within the article.

Conflicts of interest

The authors have declared that no competing interests exist.

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