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Dehydration products of gypsum: positron annihilation and dielectric measurements

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Bassanite ($CaSO_4 \cdot \frac{1}{2} H_2O$) and anhydrite ($CaSO_4$) are the low-temperature products of gypsum ($CaSO_4 \cdot 2H_2O$) dehydration, which are obtained at about 373 and 433 K, respectively. These sulphates have non-centrosymmetric crystallographic point groups, but dielectric measurements do not reveal any piezo- or ferroelectric characteristic, and they practically behave like linear dielectrics. Positron lifetime spectra exhibit the existence of two different positron states, besides a free positron state. There is positronium formation in the three sulphates, and there is also evidence for the presence of a highly populated positron bound state which may be a complex state associated with positrons bound to SO_4^{2-} ions. Parameter *S* estimated from the Doppler curve and the average positron lifetime show unquestionably the sensitivity of positrons to the phase transitions gypsum–bassanite and bassanite–anhydrite.

1. Introduction

Calcium sulphate occurs in nature as anhydrite, $CaSO_4$, and, in the dihydrate form, it is known as gypsum, $CaSO_4 \cdot 2H_2O$. Generally, it has been established (e.g. [1, 2]) that gypsum loses $1\frac{1}{2} H_2O$ molecules at ~400 K, becoming hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, which is also known as the mineral bassanite; the rest of the water, $\frac{1}{2}H_2O$, is lost at 436 K. However, the technical importance of this system has provided an extensive but confusing literature which has left many basic problems unresolved. Although thermochemical data [3] were not of much help to fix the gypsum–bassanite transition point, some other studies have found that gypsum [4] begins to lose water at 348–353 K and no detectable change in the hemihydrate is observed when heating from 323 to 373 K, but soluble anhydrite, γ-$CaSO_4$, may be formed between 348 and 378 K [5]. It has been established more recently that water starts to escape from gypsum at ~363 K [6] and stability with bassanite is reached near 371 K at a pressure of one atmosphere [7].

Similarly, crystallographic data supposed that gypsum was monoclinic [4, 8, 9] and soluble anhydrite, γ-$CaSO_4$, was considered orthorhombic [8, 9]. However, it was recently found that gypsum is orthorhombic [10, 11], bassanite is monoclinic [6], and anhydrite is hexagonal [6]. Furthermore, bassanite and anhydrite have non-centrosymmetric point groups of symmetry, 2 and 622, respectively, which makes them good candidates as piezoelectric and/or pyroelectric compounds [12].

It is well known that positrons are particularly sensitive to the electronic state of solids, and positron techniques are successfully applied to the understanding of the nature of phase transitions. Thus, in the light of these facts, the present work is trying to study these phase transitions gypsum–bassanite and bassanite–anhydrite by means of positron annihilation techniques. At the same time, dielectric measurements are carried out in these low-temperature dehydration products of gypsum, bassanite and anhydrite, in order to gain acquaintance with their dielectric properties and know their possible pyro- or piezoelectric characteristics.

2. Experimental procedure

2.1. Sample preparation

Gypsum has a layered structure, the layers being parallel to the (0 1 0) crystallographic planes. Every two sheets of the sulphate ions are bound together by calcium ions and each pair of sheets is bound to other sheets by the weak hydrogen bonding of water molecules, allowing then an easy cleavage at (0 1 0) planes. All samples were obtained by simple cleavage on these planes, from a large block having good optical quality and transparency, free from any visible defect or aggregation of impurities.

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Samples for dielectric measurements had thicknesses varying from 0.3 to 0.8 mm and an area around 0.5 cm^2. Before electrodes were painted on to the faces with a silver paint curing at room temperature (RT), samples were annealed during periods of time varying between half an hour to several hours, from RT to 473 K, in order to partially or completely dehydrate the specimens.

For positron annihilation techniques, samples had a thickness of about 1.5 mm, which is enough to stop all positrons, and an area of approximately 1 cm^2. These samples were also subjected to similar thermal treatments, and all specimens were maintained in a dry box after the annealing, to avoid their possible hydration.

2.2. Dielectric measurements

Capacity measurements were carried out at 10 kHz in an HP4262A LCR meter, with samples in a liquid N_2 cryostat in order to determine the temperature dependence of the dielectric constant, ε', between approximately 90 and 300 K. The rest of the measurements were made at RT.

Data for remanent polarization were obtained from hysteresis loops measured at 10^{-2} Hz. They were traced by applying to the sample a sinusoidal voltage from an HP3310A function generator, amplified to 1 kV with a Kepco BOP1000M, and measuring the current passing through the sample. Charge integration was performed in a personal computer.

Piezoelectric coefficients d_{33} were measured with a CPDT 3300 Berlincourt meter. Finally, electric impedance, $|Z|$, was measured with an HP4192A impedance analyser, also interfaced to a personal computer, covering the frequency spectrum from 50 kHz to 13 MHz in small steps.

2.3. Positron annihilation measurements

Positron annihilation lifetime measurements were carried out using an EG&G Ortec fast timing coincidence system. The windows of the constant-fraction differential discriminator, CFDD 583, were set for the start channel on LL:900 keV–UL:1150 keV, and for the stop channel on LL:280 keV–UL:360 keV. The outputs of the CFDD were connected to the fast coincidence unit 414A with 60 ns resolving time. The timing output of each CFDD was delayed by a precision delay unit (Ortec DB 463) set on 64 and 96 ns for the start and the stop channels, respectively. The delayed start and stop signals were connected to a time-to-amplitude converter (TAC Ortec 566) set on a 100 ns range for conversion. The data acquisition system comprised an EG&G Ortec 918A MCB and a personal computer. A 220 ps timing resolution at full-width half maximum (FWHM) for ^{60}Cu was obtained.

The ^{22}NaCl positron source of 1.1×10^6 Bq was placed on a thin nickel foil which had a density of 0.89 mg cm^{-2} and a purity of 99.95%, and sandwiched between two identical specimens. The source correction was 0.180 ns (8%) and 0.401 ns (4.63%) for nickel and NaCl, respectively. The total number of counts for each spectrum was around 1.5×10^6. Spectra were analysed by the program PATFIT-88 [13].

The Doppler broadening annihilation radiation line (DBARL) measurements were carried out with a high-purity Ge detector with 1.4 keV energy resolution for the 661 keV gamma-transition line of ^{137}Cs. The Doppler spectra obtained were analysed in terms of the S parameter, defined as the counts in a central part of the spectrum, 10 channels, divided by the total number of counts, 88 channels.

3. Results and discussion

After annealing treatments, mainly at temperatures higher than 323 K, the physical aspect of the samples changes. They lose transparency and become milky in appearance, which may be an indication that they begin to lose water. In samples annealed over 353 K, if the increase or decrease of temperature is not carried out slowly, at rates of about 1 K min^{-1} or less, the layered structure of samples appears. They become a set of separated sheets and samples must be rejected. In any case, and after thermal treatments, placing the radioactive source between two specimens or painting the electrodes on to the faces must be performed with special care due to the brittle state of the samples.

3.1. Dielectric properties

Measurements carried out at RT give low values for the dielectric constant of these materials: 8–9 for gypsum, 4–5 for anhydride, and intermediate values for hemihydrate. Although the samples studied had a large variety of thermal treatments, since they were annealed under very different conditions, dielectric studies were conducted mainly on bassanite and anhydrite due to their crystallographic characteristics. Actually, in gypsum, the sulphate ion is not a regular tetrahedron and the water molecules are asymmetric [10]. For this reason, when some water molecules escape along [1 0 1] directions during annealing treatments, one would expect that a dipolar moment may appear in the specimens. On the contrary, this is not so; it seems that water molecules lost during dehydration have greatly contributed to the natural polarizability of gypsum. This polarizability decreases when water escapes from the samples which, together with the low absolute values of the dielectric constants, does not suggest any piezoelectric or ferroelectric behaviour of dehydrate samples.

The character of linear dielectric is maintained when the temperature is lowered from RT to that of liquid nitrogen (Fig. 1). No maximum is observed that could be associated with a ferroelectric phase transition, not even a slight increase in ε' that would allow one to predict a transition at 30 or 40 K below the minimum temperature achieved. The only thing observed is an almost linear decrease of ε' with temperature, of the order of 6 to 7% between 300 and 90 K, which is common in normal dielectric materials.

Experimental points are easily replaced by lines in Figs 1 and 2 because they are obtained at very small steps of the temperature or the frequency, re-

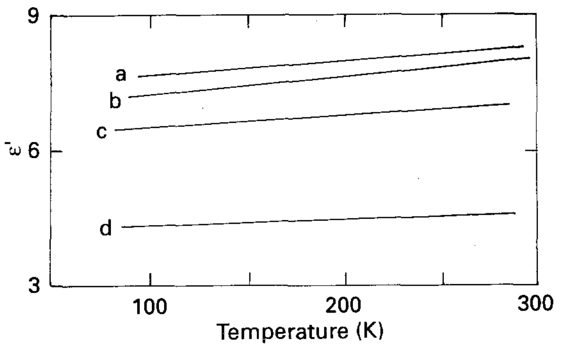

Figure 1 Values of the dielectric constant, ε', for four different samples: (a) virgin RT gypsum sample and samples annealed for 1 h at (b) 363 K, (c) 373 K and (d) 453 K.

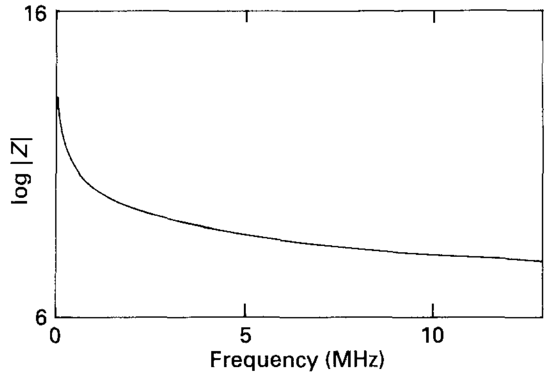

Figure 2 Values of log|*Z*|, |*Z*| being the dielectric impedance, for the sample of Fig. 1b. Measurements covered a wide spectrum of frequencies from 50 kHz to 13 MHz.

spectively, and there is overlapping between these points at the scale of the drawing. It is observed in Fig. 2 how these measurements also failed to show any piezoelectric resonance: in the decrease of |*Z*| from about 1 MΩ at 50 kHz to ~10 kΩ at 13 MHz there is no trace of discontinuity that could be associated with a piezoelectric vibration in any of the samples.

Correspondingly, values of d_{33} are monotonously zero for all samples, never surpassing the noise level of the Berlincourt meter.

Finally, measurements of polarization do not show any sign of dipolar moment in the samples. No ferroelectric hysteresis loops are detected and only simple elliptic loops are observed, which may be explained in terms of the accumulation of charge due to losses in normal dielectrics, with total values of the order of 0.01 μC cm^{-2}.

3.2. Positron annihilation results

Lifetime spectra could be analysed into two or three components. In general, a three-component analysis always converges but, if the short lifetime τ_1 is fixed at 0.100 ns, similar results are obtained, with lower standard deviations and the best fits. In this case lifetimes, τ_2 and τ_3, and intensities, I_2 and I_3, are represented in Figs 3 and 4, respectively, as a function of the annealing temperature given to the samples. The annealing time was one hour for all measurements represented in these figures and in Fig. 5 below.

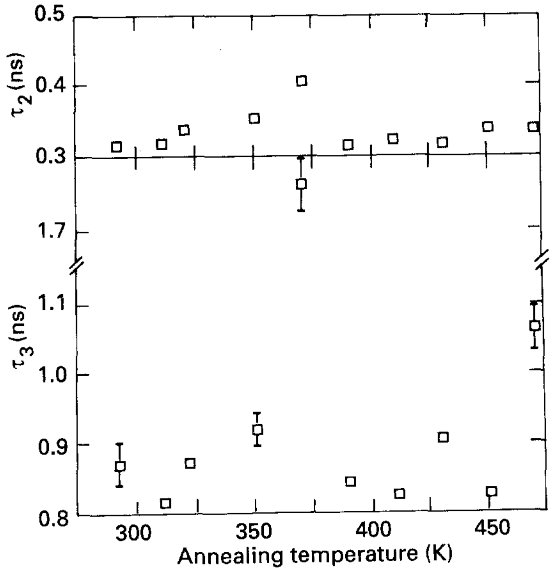

Figure 3 Positron lifetimes, τ_2 and τ_3, for samples annealed for 1 h at the temperatures indicated. τ_1 is fixed at 0.100 ns. Error bars are only drawn where they are required.

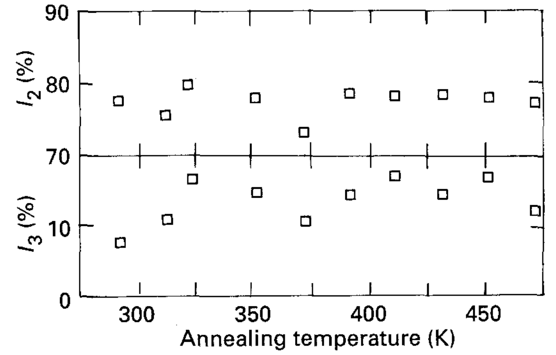

Figure 4 Positron intensities, I_2 and I_3. Errors practically coincide with the size of the square.

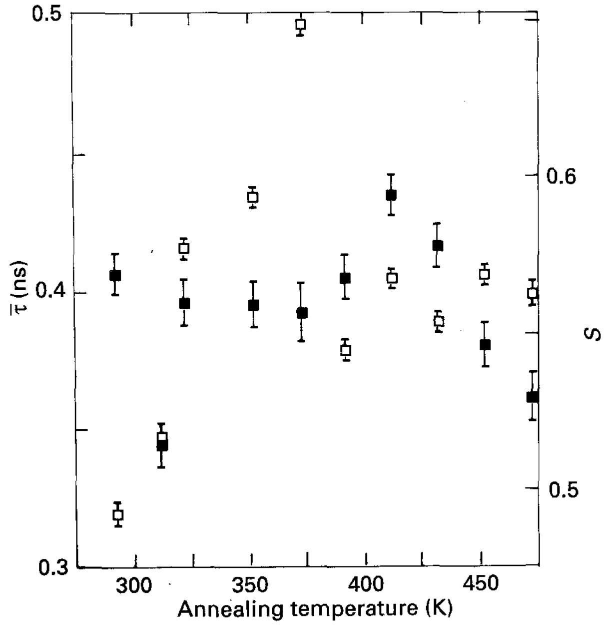

Figure 5 (□) Average positron lifetime, $\bar{\tau}$ and (■) *S* parameter from the Doppler curve, for samples of Figs 3 and 4.

It is observed that the intermediate lifetime, τ_2, oscillates around 0.330 ns for all samples, except for specimens annealed at 373 K. Somewhat larger deviations are noticed in τ_3, between 0.800 and 0.900 ns. However, the intensities show a peculiar behaviour: for specimens annealed at temperatures over 313 K it is practically true that $I_3 = 3I_1$, not considering again samples at 373 K. This effect is characteristic of the existence of positronium. This scheme disappears in samples annealed at temperatures lower than 323 K, where the relation $I_3 = 3I_1$ breaks down, although lifetimes remain with nearly the same values. It is therefore plausible to consider that in the intermediate component τ_2, besides a free positron state, there is also included a bound positron state, and this component would be a mixture of both. However, a four-component analysis fails to converge. Nevertheless, a free two-component analysis with a good fit, in RT samples which are evidently the specimens with the lowest amount of positronium, about 10% because $10\% \simeq I_3 + I_3/3$, gives lifetimes of 0.199 and 0.421 ns with $I_2 = 63\%$, resulting in an average lifetime of 0.338 ns. This indicates the existence of a positron bound state, highly populated, with a lifetime twice the value of the supposed free positron lifetime. It is not likely that this state had its origin in positrons bound to water molecules, because I_2 remains practically constant until 473 K, where all water molecules have disappeared. Possibly, this complex state is associated with positrons bound to SO_4^{2-} ions, and it will persist at all temperatures.

It must be remarked here that in recent work on triglycine sulphate [14] a free two-component analysis of positron lifetime spectra gives lifetimes of $\sim$0.240 and $\sim$0.500 ns, with $I_2 = 20\%$ and an average lifetime of around 0.300 ns. When the spectra are analysed in three components by fixing τ_1 at 0.100 ns, an intermediate lifetime $\tau_2 \simeq 0.300$ ns is obtained [15]. These and other results have led us to consider the existence of the above-mentioned bound state positron–sulphate ion.

There are not many positron studies on sulphate crystals. To our knowledge, the first work was on various salts dissolved in water [16] which need not be considered here. Later, there are results for lifetimes of some ionic compounds, particularly several sulphates [17], namely Na_2SO_4, K_2SO_4, $MgSO_4 \cdot 7H_2O$ and $Na_2SO_4 \cdot 10H_2O$. The samples were multicrystalline powders pressed in the form of pellets and the lifetime spectra have a main component with $\tau_1 \simeq 0.300$ ns and a second one with τ_2 around 1.5 ns and I_2 between 3 and 6%, which may be associated with the aggregated character of the specimens. Finally, in the lifetime spectra of $CaSO_4$ [18] it was found that $\tau_1 = 0.379$ ns and $\tau_2 = 2.230$ ns, with $I_2 = 3.6\%$. Effectively, in samples of gypsum, for virgin RT samples the average lifetime $\bar{\tau}$ is around 320 ps, and in gypsum annealed at 473 K, where it is supposed that all water has escaped, a value of $\bar{\tau} = 0.398$ ns is obtained, as shown in Fig. 5, in agreement with the values from the above references.

Concerning positronium, it is observed in Fig. 4 how it increases up to $20\% \simeq I_3 + I_1 \simeq I_3 + I_3/3$ at 323 K, and remains roughly constant during the whole dehydration process, if samples annealed at 373 K (and perhaps at 473 K) are excluded. This increase of the positronium yield must be related to the distortion of the crystalline structure and the free volume originated in the channels along the [1 0 1] direction that water molecules create at the beginning of their diffusion to the outside of the crystal [10]. From this point of view, it is interesting to consider the analysis of Fig. 5, where the average lifetime $\bar{\tau}$ and parameter S are represented as a function of the annealing temperature. It is observed here that the almost monotonous behaviour of lifetimes and intensities of Figs 3 and 4 has disappeared.

Values of $\bar{\tau}$ and S in RT virgin samples change drastically for samples annealed only at 313 K: there is a slight increase of $\bar{\tau}$ and a large drop of S. This change indicates the onset of the first transition. Although the first escape of water molecules is not visible until 323–353 K because of the milky appearance of the samples and the consequent increases of $\bar{\tau}$ and S, S remains constant until 373 K, where $\bar{\tau}$ reaches a maximum and the summit of this transition, gypsum–bassanite, is attained. There is immediately a tendency of the system to stabilization, which is evident through the decrease of $\bar{\tau}$, but another maximum is reached at 413 K, this time of S, probably indicating the disappearance of the last molecules of water. It is worth remarking that this clear-cut variation denoting the second phase transition, bassanite–anhydrite, is not explicitly observed in the lifetimes and intensities of Figs 3 and 4. In fact, this maximum of S must be associated with the situation in which all water molecules have disappeared and the channels are still open, i.e. the crystalline structure has not yet relaxed. Relaxation is not achieved before 473 K, as established by the decrease of S and the stability of $\bar{\tau}$.

4. Conclusions

Although the low-temperature products of gypsum dehydration, bassanite and anhydrite, have non-centrosymmetric crystallographic point groups, they do not show any piezo- or pyroelectric property. The absence of ferroelectric hysteresis loops and piezoelectric resonances, low values of the dielectric constant and insignificant readings of the Berlincourt meter are all characteristics of a linear dielectric material. Even the decrease of the dielectric constant with temperature does not suggest any transition at low temperature. Actually, it seems that the water molecules of gypsum are the main contributors to the low polarizability of these materials.

Positron lifetime spectra are well analysed as three components, showing the existence of positronium, which increases from 10% in gypsum to $\sim$20% in bassanite and anhydrite. The intermediate component is probably a mixture of free positrons and a complex positron bound state which may be the sulphate ion plus the positron. This seems to be the case in the few positron studies on sulphates carried out until now. The free positron lifetime is around 0.200 ns and the bound state turns out to have twice this value. Lifetimes and intensities show a certain sensitivity to the phase transitions. However, the average lifetime and the S parameter from the Doppler curve give a clear description of the reaction of positrons to the structural changes of the system.

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