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Abstract

The dehydration of Li$_2$SO$_4$·H$_2$O single crystals at 80°C has been studied by means of both isothermal thermogravimetry at 2.6, 3.6 and 4.6 hPa of water vapor and environmental scanning electron microscope. Thermogravimetric experiments allowed the determination of induction periods. Distributions of these isoconversion induction periods for a large number of single crystals showed that increasing the water vapor pressure produced a longer induction period. Moreover the shape of the distributions of the induction periods over a large number of single crystals changed from one mode at 2.6 hPa to two modes at 3.6 and 4.6 hPa. Using an environmental scanning electron microscope, this result could be attributed to differences in nucleation rates at edges and faces of the single crystals.

Keywords

Induction period, nucleation, water vapor pressure, lithium sulfate monohydrate

1. Introduction

The decomposition reactions of solids, or reactions between a solid and a gas, involve the appearance and growth of nuclei. If the growth process is generally described as the advance of the interface between the reactant and the product, it must be acknowledged that the nucleation process remains really misunderstood. Indeed, it is very difficult to find in the literature some quantitative information about the kinetics of this process. The influence of atmosphere [1-6] and of reactant crystallography [7-8] on the nuclei shape has been put in evidence in the case of the dehydration of copper sulfate pentahydrate. Some authors have also shown that nucleation occurs selectively at the edge of single crystals for the thermal dehydration of magnesium oxalate dihydrate [9] and zinc acetate dihydrate [10], but without quantitative data. Moreover at our knowledge there is no detailed work about induction periods in the field of thermal decomposition of solids, even though the induction time reflects the kinetics of the nucleation process.

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In order to have a better description of the nucleation process, we have chosen the reaction of dehydration of lithium sulfate monohydrate single crystals. This reaction is known to occur in one single-step:

$$Li_2SO_4 \cdot H_2O(s) = Li_2SO_4(s) + H_2O(g) \tag{1}$$

The kinetics of this reaction has been extensively studied on powders [11-15] or single crystals [16-26]. These previous works have shown that the isothermal kinetic curves obtained for powders are sigmoids and various interpretations have been proposed for the kinetic model of transformation. Studies on single crystals led to R_n or A_n laws. For such A_n laws however, the nuclei are supposed to appear in the bulk of the solid phase. If this situation is really encountered in precipitation phenomena in materials, this is not the case in the reactions of decompositions or when solids react with gases. Indeed, the nuclei of the new phase must appear at the surface of the solid particles. Hence, when such reactions lead to sigmoids, A_n laws must not be used to account for the kinetics.

In a previous paper [25], we have presented a kinetic modeling of experimental data obtained with single crystals, based on Mampel's model assumptions [27, 28] and Monte-Carlo calculations. The advantage of such a model was to provide a description of the nucleation and growth processes very near to the physical reality by taking into account the real shape and size of the single crystal, the nuclei appearance at random at its surface, and their inward isotropic growth. From the Monte-Carlo numerical simulations, it was possible to get the values of the areic frequency of nucleation noted γ (in number of nuclei.$m^{-2}.s^{-1}$) and the areic reactivity of growth noted ϕ (in mol.$m^{-2}.s^{-1}$) for each single crystal. We observed that, at same temperature and water vapor pressure, the values of the areic frequency of nucleation varied from a single crystal to another, contrarily to the values of the areic reactivity of growth, showing that the nucleation kinetics depends also of the surface state of the single crystals. This outstanding result, as well as the observation of an induction period on the thermogravimetry curves, led us to investigate more precisely the nucleation process.

This article reports experimental data on the induction periods on a large number of lithium sulfate monohydrate single crystals for three conditions of water vapor pressure: 2.6, 3.6 and 4.6 hPa. In addition, the dehydration reaction has been followed by means of environmental scanning electron microscopy at 3.9 and 5.2 hPa. These in situ observations are discussed in order to interpret the data on the distributions of induction periods, as well as the fluctuating values of the areic frequency of nucleation.

2. Experimental: material and set-up

Lithium sulfate monohydrate single crystals were grown through slow evaporation of a saturated aqueous solution (using powdered materials (Aldrich 99%) and pure water) at room temperature. Single crystals thus obtained have the typical shape of hexagonal plates, those having a mass higher than 1.9 mg were selected for kinetic measurements. A sample shape is represented in Figure 1 which shows the view of a single crystal by means of scanning electron microscope JEOL JSM6400.
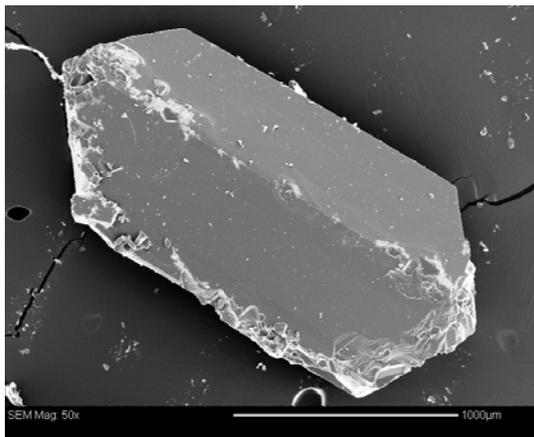

Fig. 1. Scanning electron microscope image of a $Li_2SO_4 \cdot H_2O$ single crystal.

The kinetic curves were obtained by means of isothermal and isobaric thermogravimetry at 80°C, in a water vapor atmosphere. A symmetrical thermobalance was used in static conditions (Setaram MTB 10^{-8}), the water vapor pressure is fixed using a thermoregulated water bath : the temperature fixed the water vapor pressure. After introduction of the sample in the close chamber at room temperature then evacuation up to a vacuum of 0.001 hPa, a pressure of water vapor equal to 123 hPa was established (this value being higher than 93 hPa which is the dehydration equilibrium pressure at 80°C, in order to prevent the sample from dehydration during the heating up to 80°C). When the temperature was stabilized at 80°C, the water pressure was then rapidly decreased to the chosen pressure for the experiment by a short pumping, and then maintained constant during each experiment due to the thermoregulated bath, the total pressure being that of water vapor. The whole apparatus was located in a box heated at 52°C in order to avoid cold points.

The time necessary to decrease the pressure from 123 hPa to the pressure of experiment was about one minute. The origin of the time scale was arbitrarily chosen to be the moment at which the pressure of experiment was reached. This procedure was perfectly reproducible (as shown by repeating several experiments on $Li_2SO_4 \cdot H_2O$ powders).

From thermogravimetric data, fractionnal conversion is calculted as follows:

$$\alpha = \frac{m(t) - m_0}{m_f - m_0} \qquad (2)$$

where m(t) is the sample mass at time t, m_0 the initial sample mass and m_f the final sample mass.

In situ imaging was obtained using an environmental scanning electron microscope (ESEM) FEI/Philips XL30 ESEM FEG. This apparatus allows to examine a single crystal under controlled temperature and controlled water vapor pressure, without metal coating.

3. Results and discussion

Kinetic curves obtained from thermogravimetry showed that an induction period was systematically observed for each single crystal, whatever the water vapor pressure is. Figure 2 represents typical curves of the fractional conversion versus time α(t) for 2.6, 3.6 and 4.6 hPa at 80°C. Induction periods can be distinctly seen in the magnified parts of Figure 2 for all water vapor pressures.
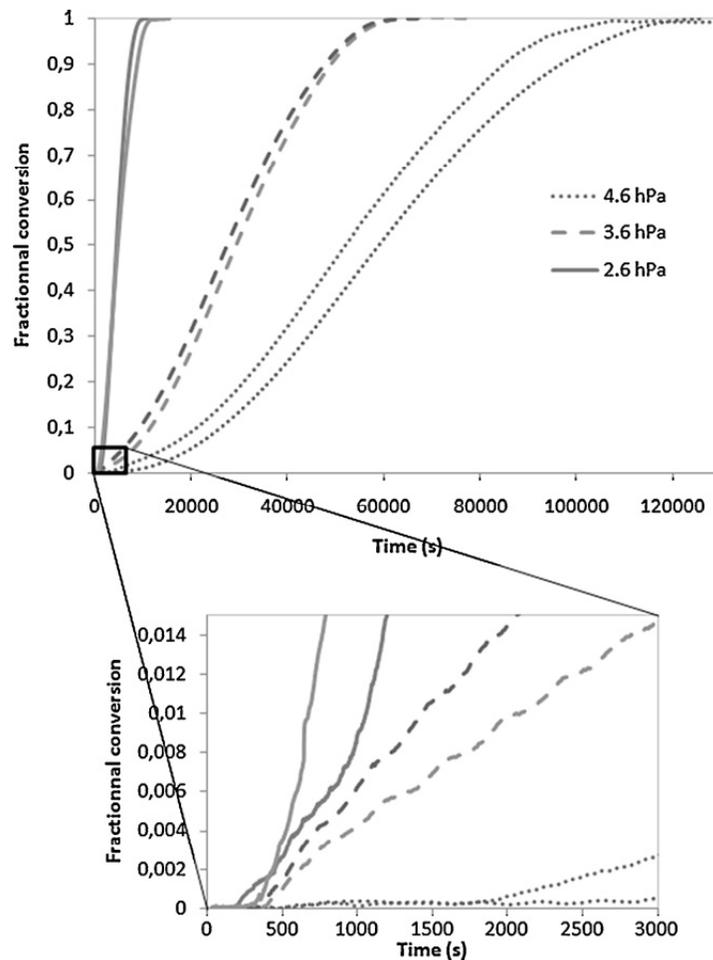

Fig. 2. Kinetic curves α(t) for $Li_2SO_4 \cdot H_2O$ single crystals dehydrated at 80°C under three different water vapor pressures: 2.6, 3.6 and 4.6 hPa.

The "theoretical" definition of the induction period is the date of appearance of the first nucleus. Obviously, the thermobalance was not able to detect the mass loss corresponding to one nucleus, and

this "theoretical" induction period is impossible to measure by this way. It was however possible to determine the time necessary for the mass loss to be higher than the noise of the thermobalance (i.e. 0.5 µg) and to get the distribution of these "experimental" induction periods for several tens of single crystals. The drawback of this method was to give "experimental" induction periods which were dependent of the initial mass of the single crystal. Thus we decided to measure the time necessary to reach the fractional conversion α=0.00187, value which was in fact obtained for a mass loss of 0.5 µg for the lightest single crystal (i.e. 1.9 mg). We called this time the "isoconversion" induction period. Figure 3 illustrates the method to determine this isoconversion induction period in the case of a single crystal decomposed at 80°C and 2.6 hPa (the "experimental" induction period is also represented).
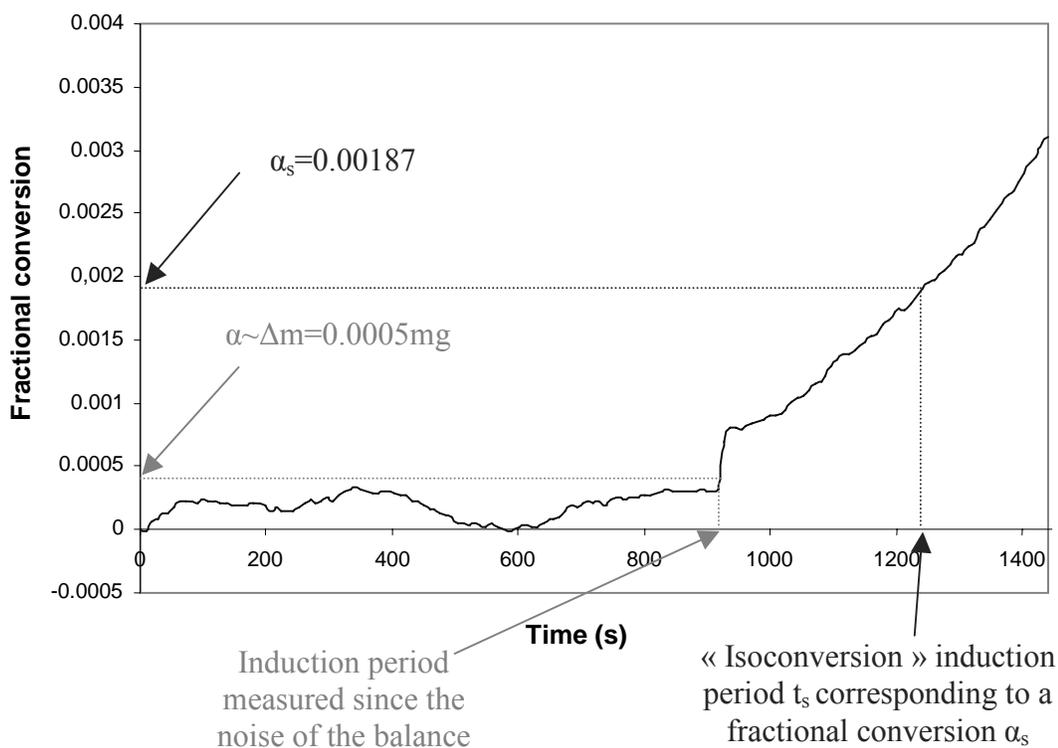

Fig. 3. Experimental induction period and isoconversion induction period determined on a kinetic curve α(t).

In order to be totally independent of the size of the initial solid (i.e. initial volume and initial surface of the single crystal), it would have been more rigorous to measure the time necessary to reach the value $\frac{V_0}{S_0}\alpha_S$ where V_0 and S_0 are the initial volume and the initial surface of the single crystal. Nevertheless, the use of α_s instead of $\frac{V_0}{S_0}\alpha_S$ introduces an error of about 10 % on the determination of the induction period. As the surface of each single crystal has not been determined, we have chosen to determine the time necessary to reach α_S.

For a group of single crystals dehydrated in the same conditions of temperature and water vapor pressure, we obtained different values of isoconversion induction periods. According to our previous study [25], the kinetics of the growth process was characterized by a constant value of the areic reactivity of growth (ϕ, in mol.m^{-2}.s^{-1}) due to constant temperature and water vapor pressure during the experiment. As a consequence, differences observed in the isoconversion induction periods, for same temperature and pressure conditions, were attributed to differences in the nucleation process, and more precisely in the dates of appearance of the first nucleus.

Of course, this must be related to the dispersion in the values of the areic frequency of nucleation γ which were obtained from our kinetic modeling [25], as previously mentioned in the introduction part. For example, for six single crystals, the values of γ spread out from 1.37 10^3 to 2.97 10^3 nuclei.m^{-2}.s^{-1} (more than a factor 2) whereas those of ϕ did not vary significantly (from 7.32 10^{-5} to 10.08 10^{-5} mol.m^{-2}.s^{-1}) [26].

Using a large number of single crystals, we could represent the distributions of the isoconversion induction periods at 80°C. Figure 4 shows these distributions obtained with three distinct water vapor pressures: 2.6, 3.6 and 4.6 hPa.
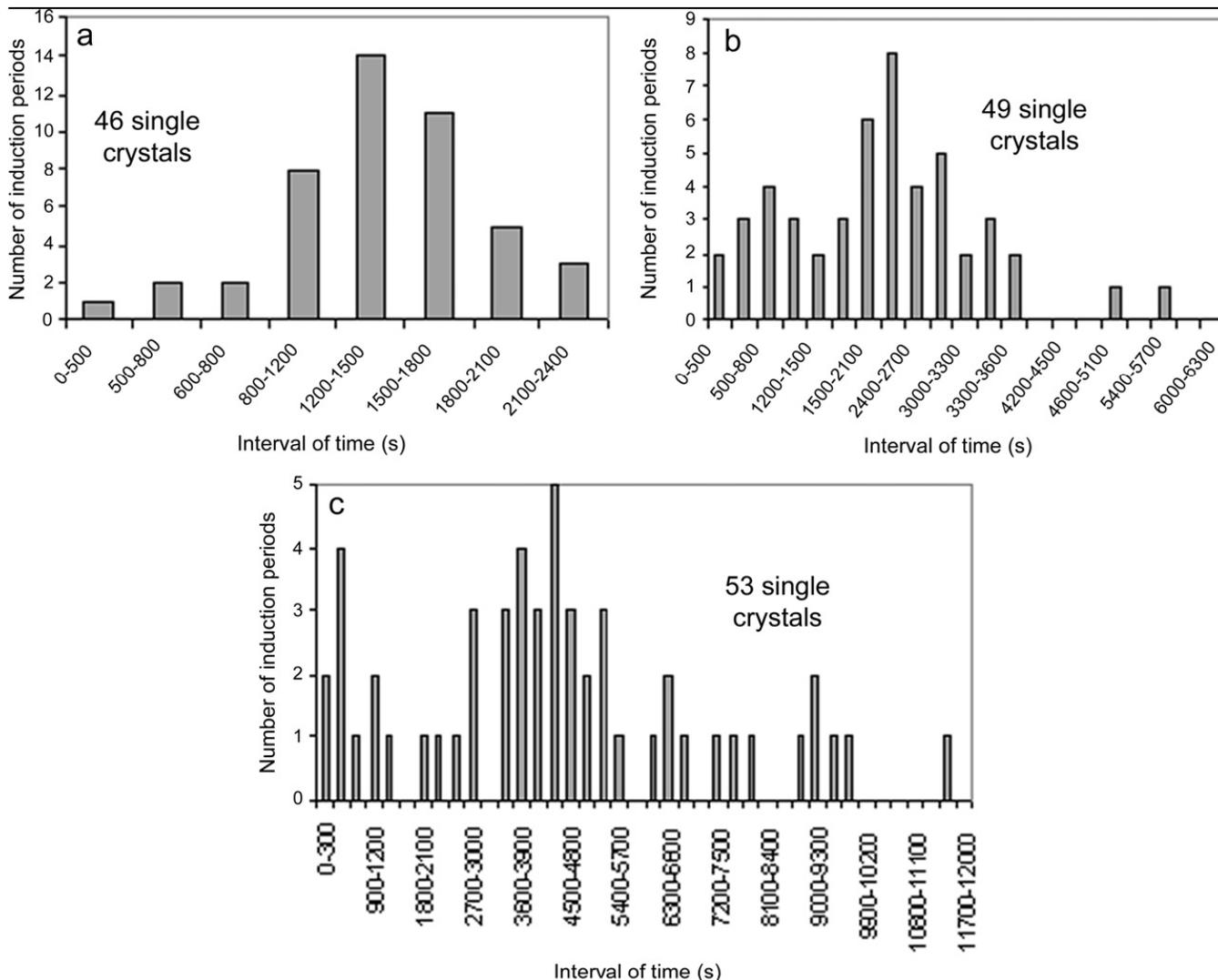
Fig. 4. Distributions of isoconversion induction periods obtained for dehydration of $Li_2SO_4 \cdot H_2O$ single crystals at 80°C and: (a) 2.6hPa, (b) 3.6hPa and (c) 4.6 hPa of water vapor pressure.

The isoconversion induction period corresponds to the time of reaction at $\alpha=0.00187$. At this moment, it is obvious that a very large number of nuclei have already appeared and grown. However, the spreading of the distributions over a time scale displayed over 2400s for 2.6 hPa, 6300s for 3.6 hPa and 11700s for 4.6 hPa reflects an important effect of the water vapor pressure on the time required for the formation of the first nucleus.

The most striking feature which comes out from Figure 4a, b and c concerns the change in the shape of the distribution from the lowest to the highest water vapor pressure. The distribution obtained at 2.6 hPa exhibits a maximum for 1200-1500s, and the data are rather well distributed on both sides of this

maximum. For 3.6 and 4.6 hPa, the shape of the distribution is bi-modal since in both cases, two maxima can be distinguished: the first maximum is located before 2000s in both cases; the second one is shifted to longer times when the pressure increases. An explanation for the presence of one or two maxima has been possible due to in situ observations using an environmental scanning electron microscope.

Two in situ experiments were carried out at fixed temperature and water vapor pressure. The micrograph views obtained with the environmental scanning electron microscope are presented on Figure 5 (at 70°C under 3.9 hPa) and Figure 6 (at 70°C under 5.2 hPa).
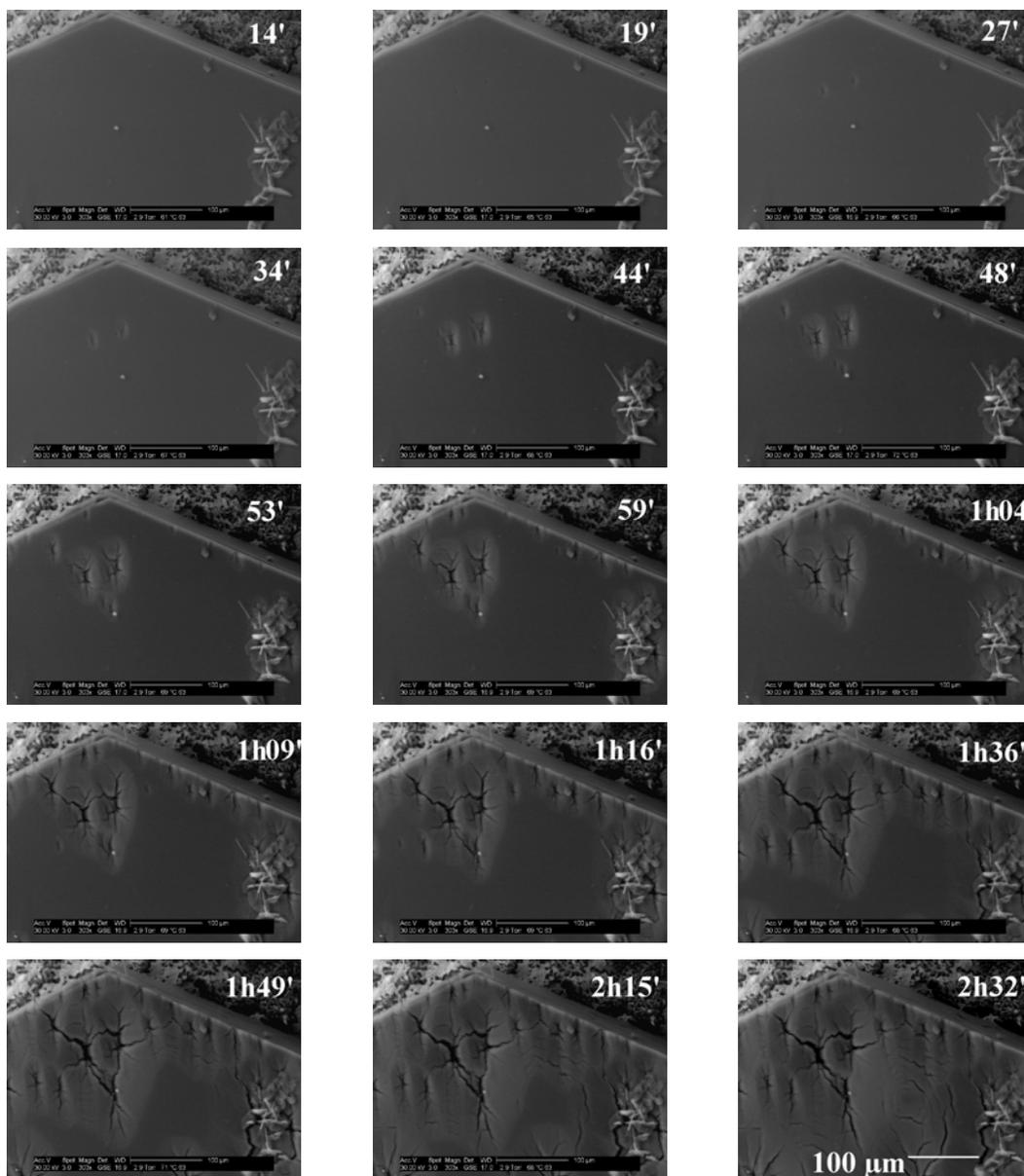
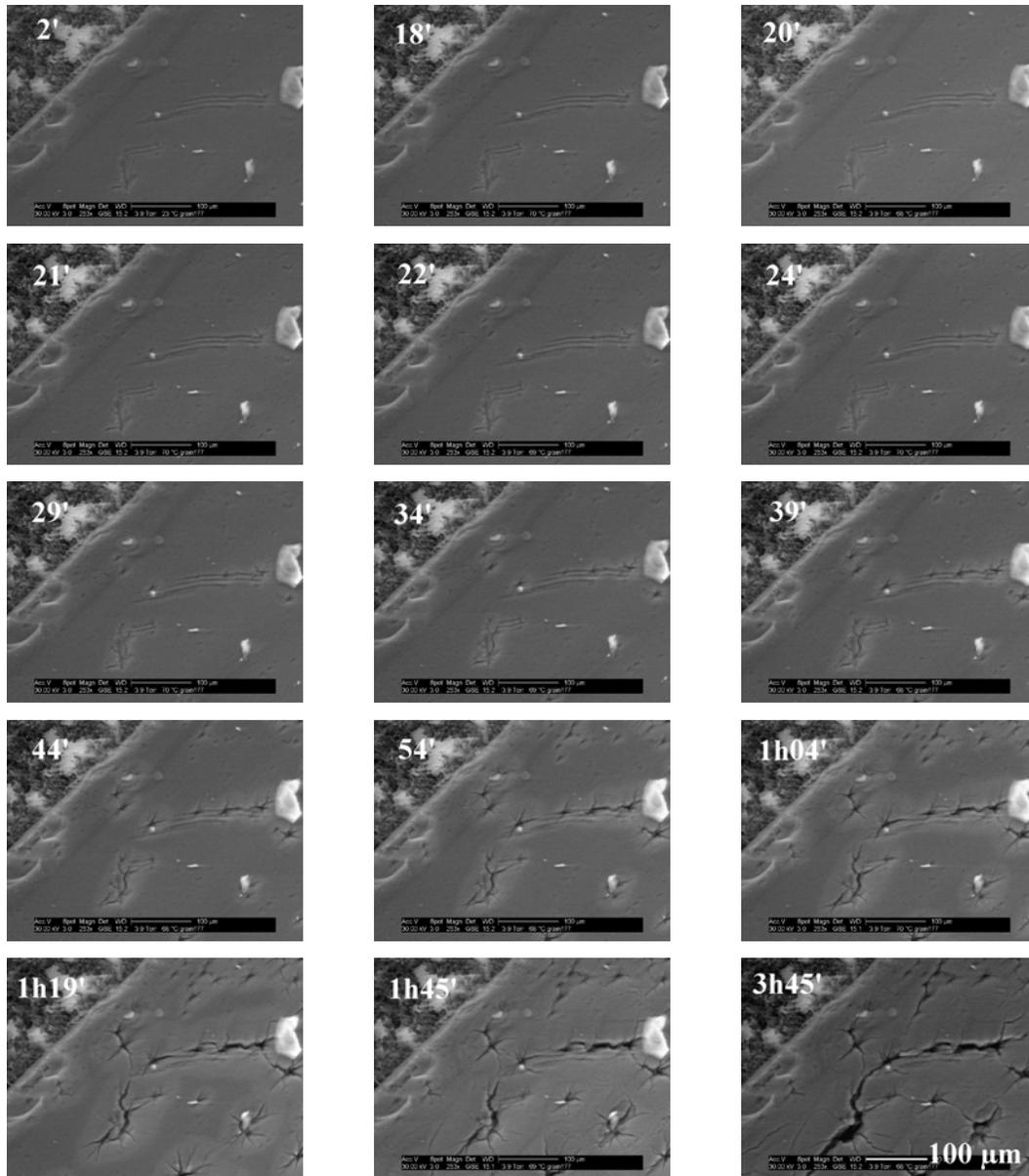

Fig. 5. Views of a $Li_2SO_4 \cdot H_2O$ single crystal during dehydration with the environmental scanning electron microscope (T=70°C, P(H_2O)=3.9 hPa).

Fig. 6. Views of a $Li_2SO_4 \cdot H_2O$ single crystal during dehydration with the environmental scanning electron microscope (T=70°C, P(H_2O)=5.2 hPa).

Even if temperature and water vapor pressure are different (but in the same range) for thermogravimetric and microscopic experiments, which does not permit a quantitative analysis, the results of both types of experiments allow to qualitatively discuss the influence of water vapor pressure on the nucleation process during the dehydration.

On Figures 5 and 6 one can see at once a face and an edge of a single crystal. The cracks that can be observed at various times of observations must be considered as the consequence of the growth of the nuclei that were formed earlier in the same area. Indeed the expansion coefficient (proportional to the

ratio of the molar volumes between the final and the initial phases) is equal to 0.78 in the case of the $Li_2SO_4 \cdot H_2O$ dehydration, which involves mechanical stress and thus cracks during the transformation.

At 70°C and 3.9 hPa (Figure 5), even if the first few cracks appear on the face of the single crystal, the cracks observed are much more numerous on the edge than on the face of the single crystal. At 70°C and 5.2 hPa (Figure 6) all the cracks were found to appear on the surface, the edge being unchanged even after more than three hours of reaction. From these observations it could be deduced that the appearance of nuclei on the edges of the single crystal is favored in the case of the lowest vapor pressure (3.9 hPa). Nucleation on the face is observed under both water vapor pressures 3.9 and 5.2 hPa.

From these observations, it is possible to propose an explanation for the shape of the induction periods distribution. The presence of two maxima in the distribution reveals that the nuclei appear statistically according to two distinct rates. Under a pressure of 3.9 hPa, nuclei were observed to appear on both edges and faces. This corresponds to the case of Figures 4b and 4c, respectively under 3.6 and 4.6 hPa. Consequently the two maxima on both distributions can be related to the nucleation on edges and faces. As the pressure increases, the intensity of the first maximum seems to decrease, which is in agreement with the observations of Figure 6: at 5.2 hPa, the majority of nuclei were observed to appear on the face. At a lower pressure, as 2.6 hPa in the case of Figure 4a, the first nuclei are most likely formed on the edges rather than on the faces of the single crystals. Figure 7 represents the various shapes of distributions in a schematic way, from 2.6 hPa up to 5.2 hPa, illustrating both nucleation modes on edges and on faces.

One can see that nucleation on the edges is faster than on the faces: this is not so surprising since defects (at the atomic scale) are expected to be much more numerous on the edges than on the faces, and also because atoms or molecules situated on the edges are known to be energetically more reactive than those on faces.

Nevertheless, our results seem to indicate that the water vapor pressure had an inhibiting effect when the nucleation takes place on the edges. Moreover, nucleation taking place on the faces seems to be delayed when water vapor pressure is increased. These results suggest that kinetics of nucleation on the edges and on the faces of the single crystals are different. Thus it seems that the mechanisms of nucleation should be different, which appears obvious if one considers that the formation of a nucleus may involve the following steps (a nucleation mechanism can be write by analogy with the classical nucleation theory [29, 30]):

(a) appearance of defects on the surface (here: H_2O vacant sites),

(b) surface diffusion of these defects,

(c) defect aggregates formation up to a critical size.

In the present study, the defects, that are thought to be water molecules vacancies, are expected to have rates of appearance which take different values if exposed to different water vapor pressures, and if one considers edges or crystallographic planes. A microscopic model involving steps (a) to (c) has been developed in order to attempt to calculate distributions of the dates of appearance of the first nucleus [31]. This work indicates that the frequency of defect formation on the surface is responsible for the position of the maximum of the distribution, which confirms our interpretation.
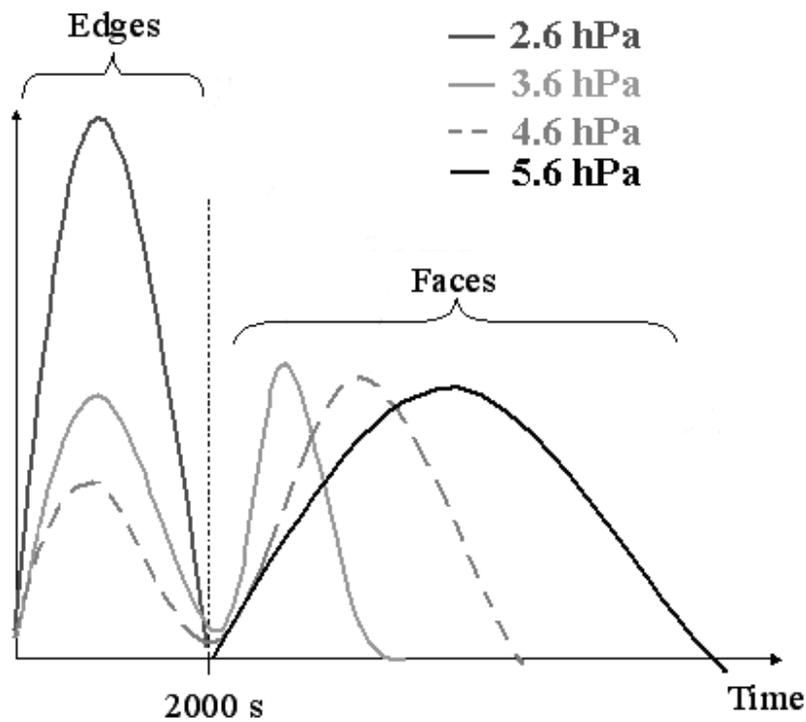

Fig. 7. Scheme of the isoconversion induction periods distributions for different water vapor pressures at 80°C.

4. Conclusion

Isothermal and isobaric thermogravimetry was used to follow the dehydration of a large number of $Li_2SO_4 \cdot H_2O$ single crystals. For each of them, an induction period was determined for a conversion α_s equal to 0.00187. This isoconversion induction period was found to vary from a single crystal to another so that distributions could be represented for experiments performed at 80°C and under 2.6, 3.6 and 4.6 hPa of water vapor. The shapes of these distributions were analyzed and discussed according to previous

results on the values of the areic frequency of nucleation and to in situ observations of cracks appearing at the edges and/or faces of the single crystals.

It could be concluded that two modes of nucleation process have to be considered, according to the appearance of the nuclei on the edges and on the faces of the single crystals. If nucleation on the edges is faster than on the faces, we noted that when the water vapor pressure is increased, nucleation on the edges no longer takes place, and the nucleation on faces is delayed.

Acknowledgments

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