

on the type of electrolyte and the voltage for oxidation applied. For both electrolytes, the film thickness increased with the voltage applied.

The concentration of the electrolyte produced minor shifts in color, negligible enough to establish a relation between color and thickness of the film for each electrolyte as a way to have a quick method to determine thickness.

The films produced at low voltages were homogeneous, with low roughness and amorphous. At higher voltages, sparks discharges were observed and porous films, with a degree of crystallinity, were produced. The voltage for spark discharge depended on the electrolyte.

Using H<sub>2</sub>SO<sub>4</sub> 1M as electrolyte, the films produced were compact, homogeneous and no crystalline phases of TiO<sub>2</sub> were detected up to 60V. From 70V to 80V, the films were porous and crystalline with the anatase phase formed, and above 80V, the rutile phase was formed. As the concentration of electrolyte increased, the conductivity increased and the homogeneous/amorphous to porous/crystalline transition was produced at lower voltages.

In the case of the H<sub>3</sub>PO<sub>4</sub> 1M electrolyte, there were no spark discharges or crystalline phases up to a voltage of 100V, which was the highest voltage used.

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### Evaluation of polychromators for angle-wavelength dispersive X-ray reflectometry

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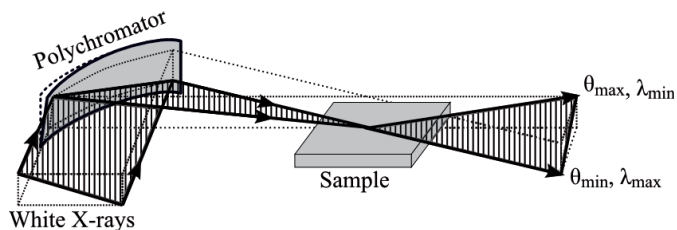
We are developing a method for time-resolved measurements of the specular X-ray reflectivity [1], [2], [3]. In this method, a convergent X-ray beam with a one-to-one correspondence between angle and X-ray energy impinges onto the sample (Figure). The incident beam has a range of specular angles  $\theta$  and wavelengths  $\lambda$ . The reflected X-rays are detected with a two-dimensional detector. The reflectivity curve in the range  $q_{min}=4\pi\sin\theta_{min}/\lambda_{max}$  to  $q_{max}=4\pi\sin\theta_{max}/\lambda_{min}$  can be measured in a single detector exposure, with no need to scan the sample, incident beam, or detector.

A key element of the reflectometer is the polychromator that produces the convergent X-ray beam. It consists of a Si crystal curved in two dimensions so that the Bragg angle and the angle to the horizontal plane change continuously with the position on the crystal. The curvature is adjusted to focus the incident white X-rays onto the sample.

In this report, different methods for bending the Si crystal to the desired shape are compared. They were evaluated using visible laser light. Size and shape of the reflected laser beam were recorded with a CCD camera at different distances from the focus. Finite-element simulations of the bending were done as well.

In the first method for bending the Si crystal, the crystal is fixed at two opposite edges. The crystal is bent by moving the edges independently. This method has the advantage that the curvature of the crystal can be adjusted during the experiment, but it is difficult to produce small focus sizes. In the second method, a Si crystal is pressed

to a copper support that was machined to the desired shape. Alignment is comparatively simple and small focus sizes are easier to achieve.



Setup for the X-ray reflectometry measurements.

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### The five twin laws of gypsum. A theoretical analysis on interfaces of the growth contact twin

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All the twin laws of gypsum belong to the [010] zone, which is not an important one from the morphological point of view, as it ensues from the fact that the [010] direction does not correspond to a periodic bond chain (PBC), in the sense of Hartman-Perdok.

Our research starts from the experimental observation that the five twin laws of gypsum can be divided in two groups: to the first one belong the 100 and  $\bar{1}01$  laws, both characterized by a high occurrence frequency, while to the second and less important group belong the 20 $\bar{1}$ , 001 and the 101 twin laws. Concerning both the natural and the solution grown crystals, the  $\bar{1}01$  penetration twins have by far the highest occurrence frequency, while the  $\bar{1}01$  contact twins were never observed; the 100 penetration twins are more frequently observed than the 100 contact twins, for every supersaturation value.

We considered the contact twins only and attempted at calculating the twin energy for each twin law, starting from suitable unrelaxed profiles of each twin interface and evaluating the convergence of the twin energy values once the interface was allowed to relax. Hence, we were able to model both the amount and the extent of the perturbations occurring at atomic level, for each twinned interface, and compare with the relaxed and untwinned one.

The most probable contact twin law results to be 100, the corresponding twin energy being 13 erg cm<sup>-2</sup>. The twin energy of  $\bar{1}01$  and 001 laws is higher by an order of magnitude, being 145 and 255 erg cm<sup>-2</sup>, respectively. For the remaining laws the twin energy value is even more higher and the convergence is hard to obtain.

This should change our mind on the interpretation on the genetic mechanism of gypsum twins:

- the only "true" contact twin is 100, all other twins being related to penetration mechanism;
- the morphological confusion between 100 and  $\bar{1}01$  laws can be experimentally avoided by the control of the optical extinction, according to the Cody's hypothesis;