

CRYSTALS FOR SOFT X-RAY SPECTROSCOPY

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The techniques necessary for the growth of crystals (organic esters and half esters of long chain alcohols) with large $2d$ spacings, up to 92 Å, for the diffraction of soft X-rays are described. With careful temperature control, thin crystallites of 0.3–1.0 cm by 2–3 cm can be obtained. A simple method for the determination of $2d$ spacings described (tetradecyl hydrogen maleate, 52.3 Å; octadecyl hydrogen maleate 62.5 Å; octadecyl hydrogen succinate, 88.2 Å; dioctadecyl adipate 91.77 Å).

1. Introduction

Crystals, both natural and artificially grown, are widely used as dispersing elements in X-ray spectroscopy, which, as a commercially viable analytical technique spans the X-ray wavelength range 0.2–25 Å. For wavelengths longer than ~ 25 Å, however, crystals are not readily available and gratings or Langmuir–Blodgett [1] soap films have to be used. The former have theoretical advantages in the soft X-ray region and can be fabricated for optimum results in any desired wavelength range. Soap films on the other hand, usually as the lead salts, have only been made with a limited range of effective $2d$ spacings. 70 Å (lead laurate) to 165 Å (lead mellisate) [2–4], the most widely used being lead stearate ($2d \sim 100$ Å). The advantage of the soap film “pseudo-crystals” is that they can be used in exactly the same way as a conventional crystal, either in an X-ray fluorescence spectrometer or in wavelength dispersive analytical attachment to a scanning electron microscope, and do not require the special instrumentation needed for gratings. Soap films do have disadvantages, however; they are fragile and have only modest resolving powers and reflectivities.

The advent of multilayer devices [5,6], in which alternate layers of different materials (e.g. tungsten and carbon) can be built up to produce a diffracting element with any desired $2d$ spacing (typically in the range 30–300 Å) has somewhat

changed the situation. At present, however, whilst these devices have a very high reflectivity, they have rather low resolution (e.g. $E/\Delta E \sim 50$, although higher figures are now being reported [7]. For this reason it was decided to develop techniques for the production of crystals with large $2d$ spacings in the hope that they might combine resolution with reasonable reflectivity. The work of Ruderman and Ness [8], twenty years ago, had indicated that the esters of fatty acids with long chain alcohols produce suitable crystals, and that the $2d$ spacing could be varied by changes in chain length of either the alcohol or the acid. Of the crystals discussed below three have been successfully grown before [8,9] and one of them has been produced commercially [10]. This paper describes the experimental procedures required to grow such organic ester crystals to an area of a few square centimetres, the measurement of their $2d$ spacings and some X-ray spectra obtained with their use.

2. Experimental

Whilst early attempts to grow crystals of long chain alcohols were frustrated by the tendency to spontaneous nucleation, the esters of these alcohols were found to be more tractable [8]. Even so, spontaneous nucleation remains a problem but can be avoided by using very careful temperature control.

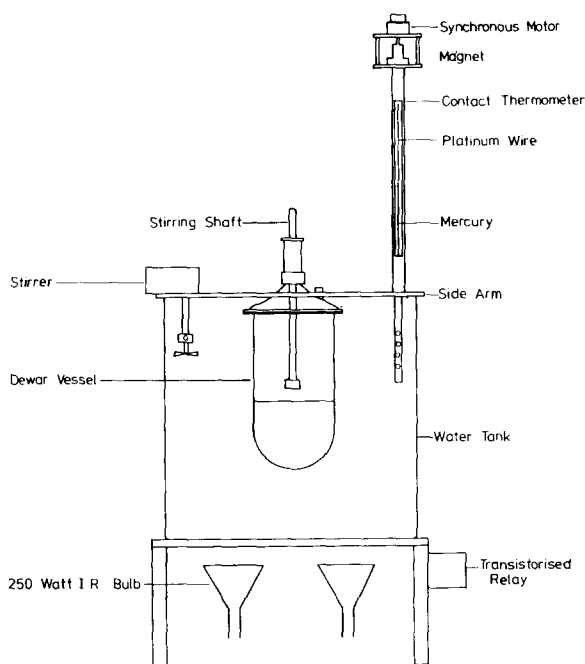


Fig. 1. Crystal growth equipment.

The apparatus is shown in fig. 1. It consists of an inner Dewar vessel which contains the growth solution, and an outer vessel which is a large water bath (20 l). Temperature regulation is achieved using a contact thermometer, with a high switching differential ($1 \times 10^{-3}^{\circ}\text{C}$), in conjunction with a fast switching relay connected to two 250 W bulbs. These lamps enable the heat to be more evenly distributed throughout the bath and the growth solution than can be achieved by other heating sources. The water in the outer bath is kept at a

constant temperature by both pumping and stirring.

The esters were prepared by the reaction of the chosen alcohol with the appropriate acid anhydride. For acid esters the stoichiometric amount of alcohol was added slowly to the molten anhydride. The product was dissolved in hot xylene and the crystals that formed on cooling was washed with ice cold ether. In the case of dioctadecyl adipate the procedure was reversed, the acid being added to the alcohol so that the alcohol was always in excess. A few drops of toluene-sulphuric acid were added as a catalyst. The product was dissolved in hot toluene, dried and cleaned with active charcoal; as before, the solid which formed on cooling was washed thoroughly with ice cold ether.

The compounds that were prepared for this work are listed in table 1, together with melting points, suitable abbreviations and their solubilities in toluene. Toluene proved to be a convenient solvent for crystal growth.

3. Crystal growths

The Dewar vessel was set up with a seed crystal attached to the central stirring shaft as shown in fig. 1. The ester solution was then filtered into this Dewar, past the seed crystal. The solution was gradually cooled and checked for saturation by the introduction of a small seed crystal. When saturation was achieved the solution was slightly warmed (0.05°C) and the stirring shaft lowered into the solution. Cooling this solution slowly at a rate of 0.05°C per day for 20 days with a stirring

Table 1
Compounds prepared for this work

Name	Abbreviation	Formula	MP ($^{\circ}\text{C}$)	Solubility/at 35°C / (g dm^{-3})
Tetradecyl hydrogen maleate	THM	$\text{C}_{14}\text{H}_{29}\text{CO}_2(\text{CH})_2\text{COOH}$	66	430
Octadecyl hydrogen maleate	OHM	$\text{C}_{18}\text{H}_{37}\text{CO}_2(\text{CH})_2\text{COOH}$	78	92.5
Behenyl hydrogen maleate	BHM	$\text{C}_{22}\text{H}_{45}\text{CO}_2(\text{CH})_2\text{COOH}$	84	131
Dodecyl hydrogen succinate	DHS	$\text{C}_{12}\text{H}_{25}\text{CO}_2(\text{CH}_2)_2\text{COOH}$	37	—
Tetradecyl hydrogen succinate	THS	$\text{C}_{14}\text{H}_{29}\text{CO}_2(\text{CH}_2)_2\text{COOH}$	64	—
Octadecyl hydrogen succinate	OHS	$\text{C}_{18}\text{H}_{37}\text{CO}_2(\text{CH}_2)_2\text{COOH}$	72	330
Dioctadecyl adipate	OAD	$[\text{C}_{18}\text{H}_{37}\text{CO}_2\text{CH}_2\text{CH}_2]_2$	64	474

rate of 5 revolutions min^{-1} produced many crystals with dimensions 1–3 cm by 0.3–1.0 cm. At the end of each “growth run” the solution was warmed by a few degrees to avoid adventitious nucleation. Although dioctadecyl adipate crystals were produced as described above, subsequent experiments showed that equally good crystals could be grown without using a seed. Octadecyl and tetradecyl hydrogen maleates, as well as octadecyl hydrogen succinate, were grown in this “seedless” way. The growth of behenyl hydrogen maleate ($2d \sim 74 \text{ \AA}$) crystals was also attempted, but only very small crystallites were produced [8]. Crystals of dodecyl hydrogen succinate were successfully grown but as the $2d$ ($\sim 67 \text{ \AA}$) spacing and other properties were very similar those of to OHM, production was discontinued.

In order to produce a reflecting area suitable for use in a typical commercial wavelength dispersive X-ray fluorescence spectrometer (e.g. Philips PW 1410), i.e. about 2–3 cm by 2 cm, it was necessary to mount a collection of crystallites on a suitable flat surface (e.g. Si 111) as shown in fig. 2.

Subsequent work has shown that the crystals can be equally well mounted directly onto the flat aluminium surface of a spectrometer crystal holder. As the growth habit of the crystals is sheet-like cleavage or cutting was unnecessary. Furthermore the crystals have a reasonable mechanical strength and can be handled easily. Each crystallite was fixed to the silica, or aluminium, surface with a poly acrylamide gel. Being water based, the use of this adhesive avoided damage to the crystals.

These various crystals were used for soft X-ray spectroscopy in a Philips PW 1410 spectrometer. Excitation was by means of a CGR (Compagnie Générale de Radiation) Elent-10 open window gas discharge X-ray tube and detection by a conventional proportional counter fitted with a thin $1 \mu\text{m}$ window.

4. Determination of $2d$ spacing

Whilst the $2d$ spacing of a crystal is best measured using standard double crystal techniques, it

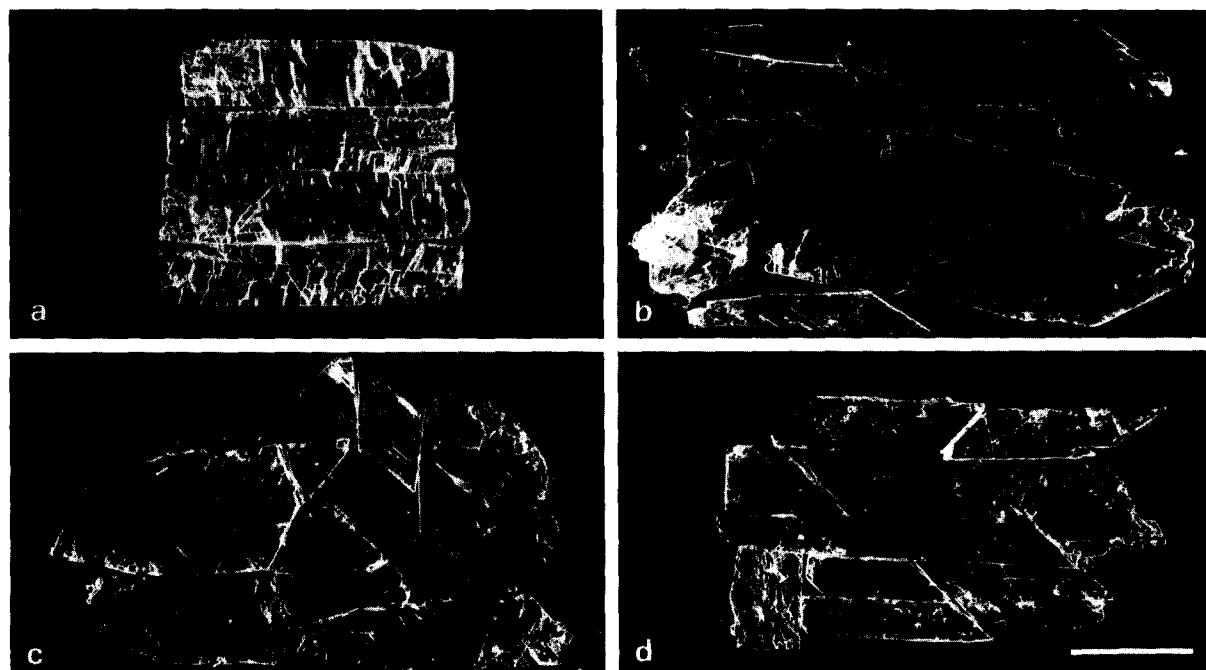


Fig. 2. Crystal mosaics mounted on silicon: (a) OHS octadecyl hydrogen succinate; (b) OHM octadecyl hydrogen maleate; (c) OAO dioctadecyl adipate; (d) THM tetradecyl hydrogen maleate. Marker represents 1 cm.

is possible to determine the $2d$ spacing of a crystal if an approximate value can be estimated; the method is outlined below.

Let $2D$ be the true $2d$ spacing of a crystal and let θ be the angle of reflection for X-ray of wavelength λ , then

$$\lambda = 2D \sin \theta. \quad (1)$$

If the estimated $2d$ value is 2δ and the error 2Δ , then $2D = 2(\delta + \Delta)$. The possibility exists (especially on manually operated spectrometers) that there may be an error in the 2θ dial reading. This may be taken into account as an error x between the correct angle θ and the observed angle ϕ so that $\theta = \phi + x$. Eq. (1) now becomes

$$\lambda = 2(\delta + \Delta) \sin(\phi + x),$$

where Δ and x are both small. Expanding, and ignoring powers of x greater than 1, gives

$$\frac{\lambda}{2\delta \sin \phi} \left[1 + \left(\frac{\Delta}{\delta} \right) \right]^{-1} = 1 + \frac{x}{\tan \phi}.$$

Expanding again, but now ignoring powers of Δ gives

$$(1 + C) \left(1 - \frac{\Delta}{\delta} \right) = 1 + \frac{x}{\tan \phi},$$

where $1 + C = \lambda / 2\delta \sin \phi$. A plot of C versus $(\tan \phi)^{-1}$ should therefore give a straight line of gradient x and intercept (Δ/δ) .

This method will clearly give the best results if data for a wide range of ϕ angles can be calculated. This was done for the OAO crystal using the K $L\eta$ and Mo, Nb and Zr $M\zeta$ lines as standards. The data are given in table 2 and the results presented graphically in fig. 3. (When these calculations were first carried out the Zr $M\zeta$ wavelength given by Bearden [11], 82.04 Å, was used,

which gave a very poor "straight line". Only when the more recent value by Dannhauser and Wiech [12] was used, was a satisfactory result obtained.) The $2d$ spacings of OAO, and other crystals, determined by this method are collected in table 3, and compared, where possible, with previous estimates [8]. The differences of the order of an ångström or more are larger than can be reasonably explained either by experimental error or diffraction effects or even by temperature variation, and is currently being investigated further using a double crystal spectrometer.

Even so, and without a detailed knowledge of the crystal structure of the esters, it is possible to estimate the effect upon the $2d$ spacing of changing the nature of the acid. In the former case the addition of two carbon atoms increases the $2d$ spacing by about 5 Å, whilst going from maleic acid to succinic gives an increase of about 25 Å. Thus octyl hydrogen maleate is predicted to have a $2d$ spacing of about 37 Å (which would be useful for N K α) but of course these calculations do not indicate the melting point of the ester, or if a solid at room temperature, whether it could easily be crystallised.

5. Applications of ester crystals

Using crystals with $2d$ spacings of up to 90 Å it is possible to detect K radiation from elements with atomic numbers (Z) greater than 5 (boron), L radiation from elements with Z greater than 15 (phosphorus), and M radiation from elements whose Z exceeds 38 (strontium). Such crystals can therefore be used to extend the range of X-ray fluorescence analysis to the lightest elements. But this can also be done with multilayer devices. The

Table 2
Data for OAO crystal

Element	Line	Wavelength (Å)	2ϕ (deg)	$(\tan \phi)^{-1}$	$\lambda / 92.0 \sin \phi$	$C \times 10^3$
K	L ℓ	47.74	61.25	1.6892	1.01864	18.64
Mo	M ζ	64.39	87.65	1.0417	1.01073	10.73
Nb	M ζ	72.22	102.30	0.8049	1.00797	7.97
Zr	M ζ	81.75	124.45	0.5266	1.00429	4.29

Values of $2d$ are 91.83 Å (rounded off to 91.80 ± 0.05 Å).

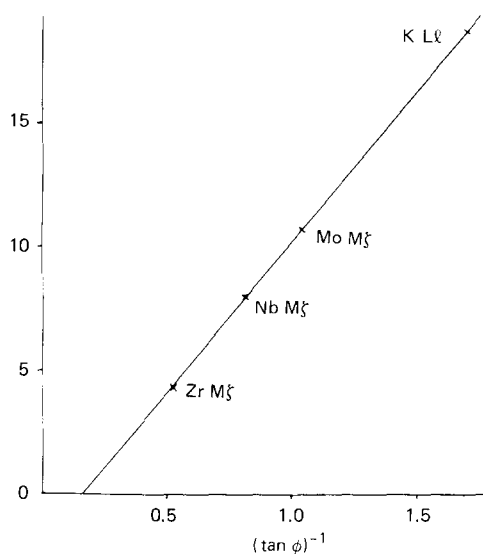


Fig. 3. Plot of $100C$ versus $(\tan \phi)^{-1}$ for four soft X-ray calibration lines (see text).

advantage of the range of ester crystals described in this paper is their much greater resolving power and the availability of a variety of $2d$ spacings. It is therefore possible to select to particular crystal

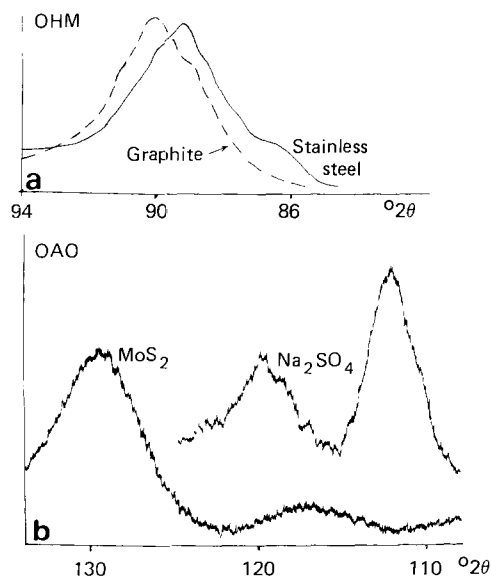


Fig. 4. (a) Carbon K spectra from graphite and steel. (b) sulphur L spectra from sodium sulphate and molybdenum disulphide.

Table 3
 $2d$ spacings (in Å) for OAO

Crystal	Previously reported value	This work
THM	—	52.3
OHM	63.5	62.5
OHS	96.9	88.2
OAO	93.8	91.8

for the best dispersion of the characteristic X-rays from any element. By way of example fig. 4 shows typical carbon (K) and sulphur (L) spectra to demonstrate how the high resolution enable "chemical effects" to be easily observed. As these effects can be related to valency, oxidation state, etc., the use of ester crystals in long wavelength X-ray spectroscopy greatly enhances the potential of this technique in analysis.

6. Conclusions

When reasonable care is taken, organic ester and half-ester crystals can be grown which can act as diffracting elements for soft X-rays by virtue of their large $2d$ spacings. Such crystals are robust and are characterised by good resolving power and reflectivity.

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