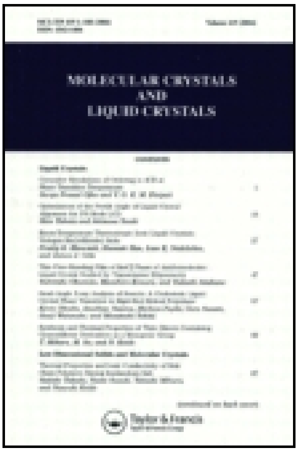

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synchrotron White Radiation Topographic Studies of the X-Ray Induced Solid State Polymerization of Bis(Propio1ato)Tetra-aquozinc(II) Single Crystals

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SYNCHROTRON WHITE RADIATION TOPOGRAPHIC STUDIES OF THE X-RAY INDUCED SOLID STATE POLYMERIZATION OF BIS(PROPIOLATO)TETRA-AQUOZINC(II) SINGLE CRYSTALS

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Abstract *Filtered beam synchrotron white radiation topography* has been used to investigate the role of defects in the x-ray induced, single crystal to amorphous, solid state polymerization reaction of bis(propiolato)tetraaquozinc(II). Images of growth dislocations, which were well defined prior to reaction, were observed to become more and more diffuse as cumulative x-ray exposure increased. This behavior is consistent with existing models for the nucleation of single crystal to amorphous reactions at dislocations, whereby the stress field of the dislocations is relaxed during reaction.

INTRODUCTION

The questions surrounding the influence and role of recognizable lattice defects and other generalized distortion fields in solid state reactions occurring in single crystals have been the subject of an enormous amount of research over a period of many years[1]. Numerous observations of preferential reactivity occurring at dislocations have been documented (for reviews see ref. 1). However, the inability of the techniques most utilized, optical microscopy and transmission electron microscopy (TEM), to monitor the behavior of the bulk defect structure of the crystal during reaction, have prevented clear elucidation of the operative mechanisms. For example, optical studies are limited to transparent specimens or surface studies, and the use of TEM is confined to studies of very thin specimens, in which surface influences may dominate, and which may be difficult to prepare in the case of reactive crystals. The use of TEM is also severely limited by radiation damage and induced beam heating of the specimen, and by the fact that only crystals with relatively large defect densities (for example dislocation densities >> 10^6 cm^{-2}) can be usefully examined owing to the small field of view of the instrument. Such factors have so far, in general, conspired in preventing in situ monitoring of a given volume of the same single crystal by TEM, before, during, and after, solid state reaction[2].

The above restrictions can be avoided by using the various techniques of *x-ray topography* (XRT)[3-6]. These techniques are ideally suited to the study of the influence and role of the bulk state of distortion on local reaction kinetics and mechanisms since they can be used to initially reveal the defect structure and generalized strain distribution in bulk single crystals prior to reaction, and then to monitor these parameters during reaction. The work of Begg et al[7] served both to demonstrate the great potential of XRT for studies of this nature, and to reveal its limitations when used in its conventional mode (i.e., *conventional x-ray topography* (CXRT), or the Lang technique - see ref. 3). The work of Dudley et al[8-12] showed how the use of *synchrotron white radiation topography* (SWRT), employing a filtered beam to inhibit x-ray induced reaction, could effectively eliminate these restrictions.

Enhanced reactivity at dislocations can be the result of many different influences, depending on the material of interest and the nature of the reaction. For example, it has been recognized by several workers that the different stereochemical arrangement of ions or molecular groupings that may be produced in the distortion field of a dislocation may promote preferential reaction[1d], or may act as traps for excitation energy[13]. Dislocations may also become decorated with impurity atoms or molecules, resulting in modified chemical configurations which may be conducive (or prohibitive) to preferential reaction. Beyond this it has been customary to simply regard the dislocation as a high energy site in the lattice and therefore to assign to it the potential for enhanced reactivity. Despite much discussion concerning the detailed mechanism by which the energy associated with a dislocation influences reactivity (e.g., see ref. 1d) no satisfactory approach has yet been postulated.

Faced with this situation, the solid state chemist can benefit very much from the detailed studies conducted by materials scientists and elasticians regarding the role of dislocations in solid state phase transformations in metals[14-16]. The key lies in recognition of the fact that all solid state reactions (and phase transformations) have one common factor; they are all, by nature, subject to significant degrees of spatial restriction. The volume changes (e.g., per molecule), or lattice parameter changes that inevitably accompany reaction lead to the generation of stresses and distortions in both reactant and product. This fact has long been recognized in the field of phase transformations in metals[17]. In the field of solid state reactivity, it was also recognized on the molecular level by Cohen[18], as embodied in his "reaction cavity concept", although equivalence of the two approaches is not generally recognized.

In the case where reaction occurs homogeneously throughout the bulk of the crystal, the stresses and distortions generated should be relatively homogeneous, i.e., evenly distributed in the crystal, leading to an averaged distortion of the crystal, without the presence of significant strain gradients. The relative significance of these induced stresses is to a certain extent determined by the elastic and plastic properties of the crystal in question. For example, when induced stresses locally exceed the elastic limit, plastic deformation can lead to partial (or full) relaxation of induced stresses. For the case where stresses do not exceed the elastic limit, the relative significance of the induced stresses and distortions can be quantified by computing the free energy associated with the deformations, or the so called "strain energy factors"[17], which are always positive[17], and so always make it more difficult for reactions to occur. They can be thought of as contributing extra thermodynamic potential to the system, possibly adding to any energy barriers to reaction that may exist, thereby influencing kinetics. It is worth noting here that the ready interconversion of chemical and mechanical energy was recognized recently by Basilevsky et al[19].

A potential mechanism by which the magnitude of this strain energy factor can be reduced is via reaction occurring heterogeneously, for example, at dislocation sites, since some of the reaction induced stress can be relaxed via interaction with the strain field of the dislocation. For example, in a single crystal to single crystal reaction, if a lattice dilation is normally required of the matrix (i.e., in the absence of the dislocation) for reaction, reaction might occur more readily in the region of the dislocation distortion field where the lattice is already dilated. In this way the strain energy term can be effectively reduced, and therefore its contribution to the effective barrier to initiation, thereby making reaction more probable. This effect can be quantified by computing a so called elastic interaction term, which simply describes the elastic energy change which occurs when a nucleus forms in the presence of a dislocation[14,15]. On the other hand, if the reaction involves a single crystal to polycrystalline or amorphous transition, preferential reaction at dislocations must, necessarily, eliminate the dislocation from the lattice, since the dislocation can only be defined in the single crystal. Consequently, the stress field of the dislocation must be relaxed, releasing the elastic energy of the dislocation into the crystal as free energy[16]. This free energy release constitutes a negative contribution to the free energy of formation of a "nucleus" of product, and as such can effectively reduce the strain energy factor. This is the driving force for such preferential reaction.

In this paper we report the results of a preliminary investigation of the role of dislocations in the solid state polymerization reaction of bis(propiolato)tetraaquozinc(II). We have previously reported the experiments which led to the "engineering" of this phase as a reactive monomer for solid-state polymerization[20]. The solid-state reaction involves a single crystal to amorphous transition[20], so that any potential preferential reaction at dislocations may be modelled using the above approach originally due to Cahn[16]. In the present study, SWRT, using a filtered beam, is used to test the validity of this model[14], since not only does it render visible the defect content of the crystal prior to reaction, but also it can monitor any changes in defect structure and/or generation of localized strain fields which may accompany reaction. Thus Cahn's prediction of the relaxation of the stress (and related strain) field of the dislocation during reaction can be directly tested, since this relaxation should be accompanied by a gradual diminution of dislocation image contrast during the course of reaction.

RESULTS AND DISCUSSION

Single crystals of bis(propiolato)tetraaquozinc(II)[20] were grown using two different techniques, (a) solvent evaporation (i.e., self-nucleation in aqueous solution), and (b) slow cooling of seeded saturated aqueous solutions. Crystals grown using technique (a) generally had a tabular morphology, with longest dimension parallel to the a-axis, and (010), $(01\bar{1})$

and $(0\overline{2}\overline{1})$ forming the main habit faces. Crystals grown using technique (b) using seeds grown by technique (a) generally developed a slightly different morphology, with the longest dimension still parallel to the a-axis, but with $(02\overline{1})$ appearing as an additional habit face. Topographic images recorded using SWRT from crystals grown using method (a) are shown in Figure 1. The main features include growth dislocation images and growth sector boundary images. Since the crystals are x-ray sensitive, selective filtering of the incident beam is necessary to minimize beam induced reaction. This selective filtering, achieved through interposing a 5 mm sheet of Al in the incident beam, removes the more highly absorbed wavelength components in the beam which are the most efficient in inducing reaction. It also smooths out the profile of energy absorbed as a function of depth, which may lead to inhomogeneous reaction as a function of depth, and to the associated generation of inhomogeneous distortion fields. Repeated exposure in the filtered beam, does, however, eventually induce reaction, as indicated by the accompanying color changes in the crystal. Thus, the behavior of dislocations during X-ray induced reaction can be studied in a controlled fashion.

Figure 2 shows a series of details from filtered beam topographs recorded from a crystal grown from slow cooling of a seeded saturated aqueous solution. Note the increase in the diffuseness of the dislocation images. This increase in diffuseness can be attributed to the relaxation of the dislocation strain fields caused by reaction occurring preferentially at dislocations. Thus the predictions of the Cahn model appear to be borne out by the results of this preliminary study.

Finally, we note that in the solid-state polymerization of the isomorphous bis(propiolato)tetraaquocobalt(II) complex, cracking of the crystal develops along the [100] direction[21]. The observed cracks *in the Co complex* coincidentally are parallel to the images of the growth dislocations which appear along the long dimension of the *isomorphous zinc complex* on the topographs shown in Figures 1 and 2. At this stage it is too early to confirm a definitive relationship between the macroscopic and microscopic observations, but future study will focus on this possible relationship.

CONCLUSIONS

1. Bis(propiolato)tetraaquozinc(II) crystals of a quality suitable for X-ray topographic study can be grown by either solvent evaporation or seeded slow cooling.

2. SWRT employing a filtered beam can be usefully used to characterize these crystals and to investigate the role of defects in their solid state polymerization reactions.

3. Images of growth dislocations on topographs recorded using filtered beam SWRT are seen to become more and more diffuse as a function of x-ray exposure. This is consistent with the predictions of the Cahn model for dislocation nucleation whereby the stress field

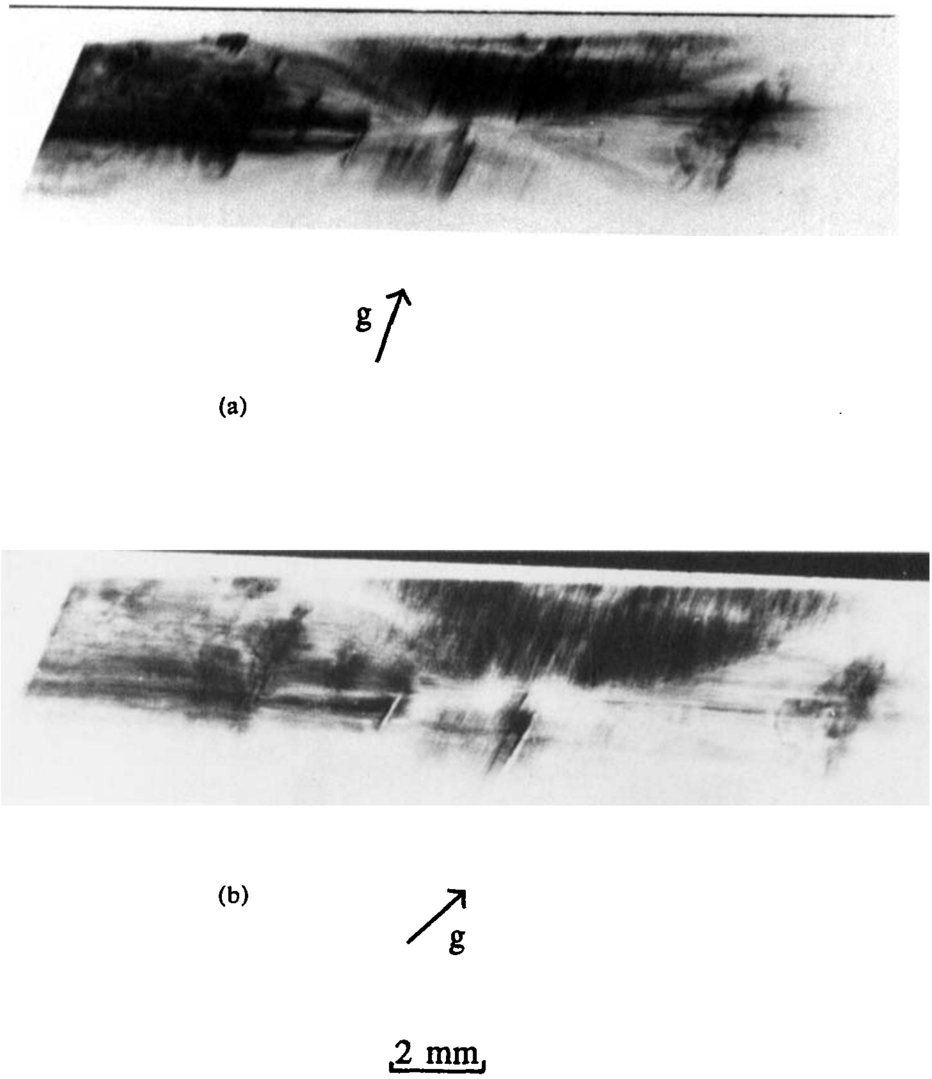

Figure 1. Filtered synchrotron white radiation topographs recorded from a crystal grown using solvent evaporation, (a) (crystal F, g=103, λ=0.41 Å, incident beam direction, I_o approximately perpendicular to (010)), and (b) (crystal F, g=101, λ=0.97 Å, I_o approximately perpendicular to (010)). Note growth dislocations parallel to the long and short dimensions of the crystal, and growth sector boundaries along the "diagonals" of the crystal.

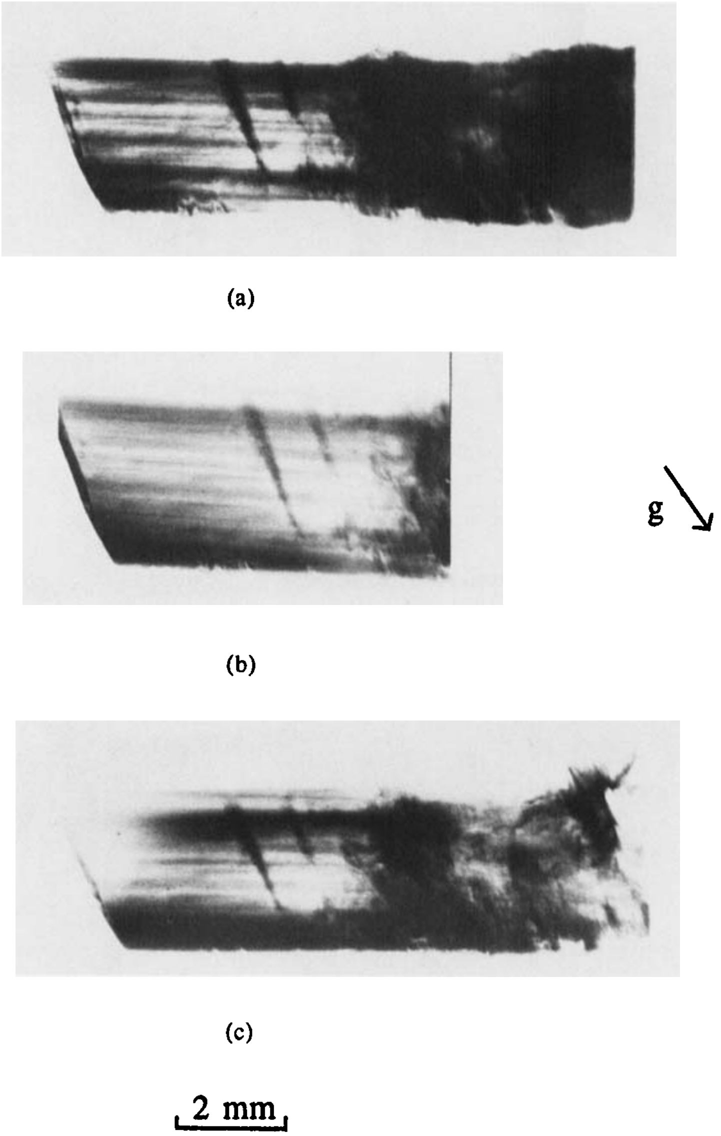

Figure 2. Details from a sequence of filtered synchrotron white radiation topographs recorded from crystal E, g=$\bar{1}1\bar{2}$, λ=0.4 Å with cumulative exposure times of (a) 60, (b) 120 and (c) 155 sec. The left half of the crystal including the seed (dark area on right) is shown. Note the increase in the diffuseness of the images of the growth dislocations which propagate from the seed towards the ($\bar{1}01$) growth face. These appear as horizontal lines which progressively lose definition from (a) to (c).

of a dislocation is relaxed due to reaction occurring preferentially at dislocation sites.

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REFERENCES

1. Representative review articles of the role of defects and other generalized distortion fields in solid state reactions include;- (a) J. M. Thomas, Adv. in Catalysis, 19, 293, (1969), (b) J. M. Thomas, E. L. Evans and J. O. Williams, Proc. R. Soc. Lond., A331, 417, (1972), (c) W. Jones and J. Thomas, Prog. Solid St. Chem., 12, 101, (1979), (d) D. B. Sheen and J. N. Sherwood, Chem. in Brit., p. 535, June, (1986).
2. W. Jones, private communication.
3. Many techniques fall under the general title of "X-ray Topography"; They can be usefully divided into two main regimes, (a) those utilizing radiation from conventional sources, or "conventional techniques", such as the Lang technique (referred to in the text as "Conventional X-ray Topography" (CXRT), and (b) those utilizing synchrotron radiation sources, or "synchrotron techniques", such as "Synchrotron White Radiation Topography" (SWRT). General reviews on the various techniques can be found in references 4 and 5.
4. B. K. Tanner, "X-ray Diffraction Topography", Pergamon, (1976).
5. "The Characterization of Crystal Growth Defects by X-ray Methods", NATO-ASI Series B: Physics, Vol. 63, Plenum, NY, (1980).
6. T. Tuomi, K. Naukkarinen and P. Rabe, Phys. Stat. Sol., (a) 25, 93, (1974).
7. I. Begg, P. J. Halfpenny, R. M. Hooper, R. S. Narang, K. J. Roberts and J. N. Sherwood, Proc. R. Soc. Lond., A386, 431, (1983).
8. M. Dudley, J. N. Sherwood, D. Bloor and D. J. Ando, J. Mater. Sci. Letts., 1, 479, (1982).
9. M. Dudley, J. N. Sherwood, D. Bloor and D. J. Ando, Mol. Cryst. Liq. Cryst., 93, 223, (1983).
10. M. Dudley, J. N. Sherwood, D. Bloor and D. J. Ando, in "Polydiacetylenes", NATO-ASI Series E, Applied Sciences - No 102, R. R. Chance and D. Bloor (EDS), M. Nijhoff Publishers, Dordrecht, NL, (1985).
11. M. Dudley, J. N. Sherwood and D. Bloor, Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, 54, 426, (1986).
12. M. Dudley, Mat. Res. Symp. Proc., 143, 253, (1989).
13. M. D. Cohen, Z. Ludmer, J. M. Thomas and J. O. Williams, Proc. R. Soc. Lond., A324, 459, (1971).
14. D. M. Barnett, Scripta Met., 5, 261, (1971).
15. R. Gomez-Ramirez and G. M. Pound, Metall. Trans., 4, 1563, (1973).
16. J. W. Cahn, Acta Met., 5, 169, (1957).
17. J. W. Christian, "Theory of Transformations in Metals and Alloys;- Part I, Equilibrium and General Kinetic Theory", 2nd Edn. pp. 198, 460, Pergamon, (1981).
18. M. D. Cohen, Angew. Chem. Internat. Edit., 14, 386, (1975).
19. M. V. Basilevsky, G. N. Gerasimov and S. I. Petrochenko, Chem. Phys., 97, 331, (1985).
20. C. A. Booth, B. M. Foxman, and J. D. Jaufmann, in Crystallographically Ordered Polymers; D. J. Sandman, ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; pp 95-105.
21. R. B. Sandor, Ph. D. thesis, Brandeis University, 1988.