Acta Cryst. (1987). B43, 502-504

Flash X-ray Studies of the Kinematics of Domain Switching in Gadolinium Molybdate Single Crystals

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(*Received* 28 *November* 1986; *accepted* 6 *July* 1987)

Abstract

The kinematics of domain switching in gadolinium molybdate were used to test the feasibility of studying fast structural changes in crystalline solids by flash X-ray diffraction techniques. Our experiments show the feasibility of detecting the domain switching by flash X-ray diffraction and also indicate the possibility of a quantitative follow-up of the development of the switching process. The switching-time dependence upon the applied electrical field is in good agreement with data reported in the literature, thus proving the reliability of studying these phenomena by flash X-ray diffraction.

Introduction

Investigations of changes in crystal structures induced by an external field are of great theoretical and practical importance. Often these changes are too fast to be followed by conventional X-ray diffraction methods. Therefore, the dynamic properties of such phenomena have usually been explored by indirect techniques (optical, electric, NMR and others). Since these techniques are indirect, translation of the results into structural information is usually based on a number of assumptions and is not always unambiguous. The development of direct methods of investigation of fast phenomena in single crystals, in a manner analogous to conventional X-ray diffraction analysis of static crystalline structures, is still in the initial stages (Izumi, 1975; Izumi, Inada, Nakajima & Khora, 1977; Fujimoto, 1982). Although conventional X-ray diffraction is the most reliable and common technique for the direct determination of structural parameters, it is unsuitable for the investigation of very fast events, as it employs continuous low-intensity X-ray sources, requiring exposure times ranging from seconds to hours. In order to investigate events occurring in a timeframe of the order of nanoseconds, much more powerful X-ray sources are required. Flash X-ray systems, which generate very intense short pulses, afford remarkable opportunities in this regard.

In order to explore these opportunities a flash X-ray diffraction (FXD) system was installed (Lourie, 1983; Green & Rabinovich, 1984; Rabinovich, Lourie & Halfon, 1987). To test this system in real-time experiments, and also to demonstrate one of its possible applications, the kinematics of domain switching in ferroelectric gadolinium molybdate (GMO) single crystals were examined.

Single crystals of ferroelectric materials usually consist of a number of oppositely polarized domains. A sufficiently high electric field, applied along the polar axis of the crystal, causes a polarization of the whole crystal in the direction of the field. When the direction of the applied field is reversed, switching of the ferroic states occurs. The domain switching is usually accompanied by structural changes. In order to enable a time-resolved study of the phenomenon very fast polarity switching of the applied electric field is needed: the field reversal should be considerably faster than the domain switching.

We have chosen gadolinium molybdate (GMO) as the first candidate for testing our FXD system since many aspects of the domain-switching process in GMO have been well studied (Aizu, Kumada, Yumato & Ashida, 1969; Smith & Burns, 1969; Kumada, 1969; Cummins, 1970; Jeitschko, 1972).

Experimental

A detailed description of the flash X-ray system is given elsewhere (Rabinovich, Lourie & Halfon, 1987). The system is based on an HP Fexitron 730/235 Marx-surge pulser delivering a 150 kV, 2 kA, 70 ns pulse and demountable vacuum-discharge X-ray tube designed in this laboratory.

Orthorhombic ferroelectric crystals of $Gd_2(MoO_4)_3$ ($a = 10{\cdot}388$, $b = 10{\cdot}419$, $c = 10{\cdot}701$ Å, space group $Pba2$ at room temperature) display pseudotetragonal symmetry (Jeitschko, 1972). The polar axis of the crystal is directed along **c** and two ferroic states with the spontaneous polarization $\pm P_z$ are possible. As far as the structural changes are concerned, the switching is accompanied by the interchange of the a and b axes of the unit cell (Jeitschko, 1972). As a consequence, the intensities of some reflections should be very sensitive to the crystal polarization. Our calcu-

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0108-7681/87/060502-03$01.50

lations showed that there is, indeed, a significant difference in the magnitudes of the structure factors for some (*hkl*) and (*khl*) reflections, *e.g.*, the reflection (650) is relatively strong as compared to the very weak (560).

In order to follow the kinematics of the domain switching in GMO the following experiments were carried out.

A large single crystal of GMO was cut to a 0·1 mm plate perpendicular to its polar *c* axis. The area of the plate was about 6 mm^2. The plate was polished and coated on both sides with 0·1 μm thick aluminium.

A special crystal holder was constructed. Two flexible metal strips (electrodes) were inserted into a PVC cylinder at a distance of 1 mm to avoid electrical discharge; the free ends of the strips were bent toward each other. The crystal was held between the two bent ends of the electrodes. The holder was inserted into a goniometer head which was then mounted on the Laue camera of the flash X-ray system.

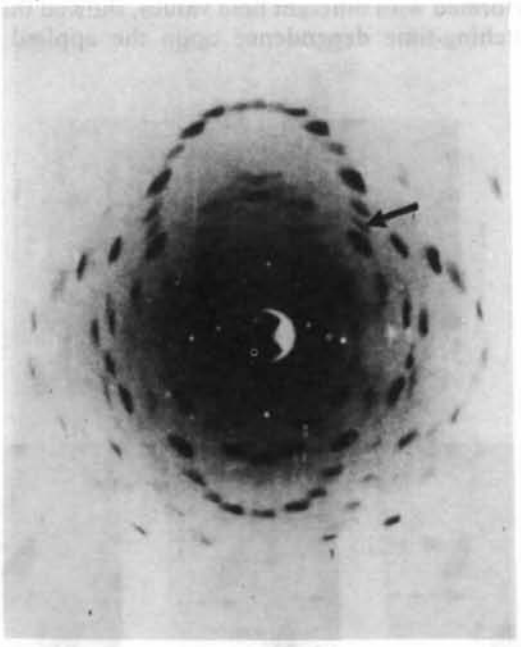
The crystal was oriented so that the two planes (560) and (650) simultaneously diffract and produce spots on the same Laue transmission diffraction photograph. All diffraction patterns for this experiment were photographed on Polaroid 3000 ASA films coupled to fluorescent screens in the cassettes.

A strong electric field (up to 50 kV cm^{-1}) was applied to the crystal electrodes. On reversing the polarity of the field, interchange of intensity of the (560) and (650) reflections was observed. A high-voltage switching circuit was built to allow a fast ($\simeq$50 ns) polarity reversal of the electrodes of the crystal holder. Utilizing this circuit and the delay u .it of the Marx-surge pulser (delay range 1 μs–1 s), a series of diffraction patterns was recorded with increasing delays between the polarity switching event and the firing of the flash X-ray tube. A series of such experiments, with varying field strengths, was performed.

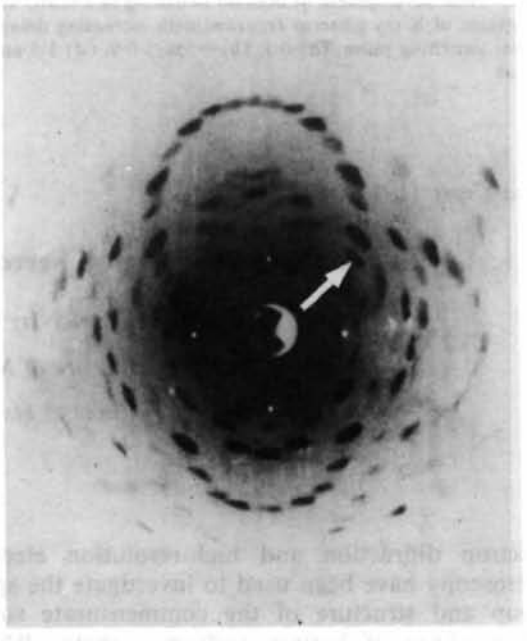
Results and discussion

Fig. 1 shows typical diffraction patterns obtained from a GMO single crystal in the two oppositely polarized states. The two photographs show the diffraction patterns for the same crystal at the same orientation after five flashes of the demountable vacuum-discharge tube with a 2 mm cylindrical molybdenum anode. The position of the reflection (650) was first recorded at the location indicated by the black arrow in Fig. 1(*a*). After the field reversal this reflection was recorded at the location indicated by the white arrow in Fig. 1(*b*) where it replaced the (560) reflection which was too weak to be recorded at the level of exposure used (five flashes). Calculated structure factors (Jeitschko, 1972) for reflections (560), (650) and the very strong (530) are 7, 95 and 504, respectively.

The time development of the switching process is illustrated in Fig. 2. The photographs are enlargements of the region of the X-ray diffraction pattern where the (560) reflection weakly diffracts before the



(*a*)



(*b*)

Fig. 1. Diffraction pattern from GMO before and after domain switching. (*a*) Before domain switching the (650) reflection is at the upper portion of the pattern (black arrow). (*b*) After domain switching the reflection is lower (white arrow).

polarity switching. They were taken at delay times of 0·1, 0·5, 0·9, 1·5 and 2 ms after the switching pulse (30 kV cm^{-1}). Each photograph is the result of 30 flashes. The gradual build-up of the strong (650) reflection is clearly evident. A series of experiments, performed with different field values, showed that the switching-time dependence upon the applied field was in good agreement with the values reported in the literature (Smith & Burns, 1969); it ranged from about 0·2 ms (at 40 kV cm^{-1}) to 5 ms (at 20 kV cm^{-1}).

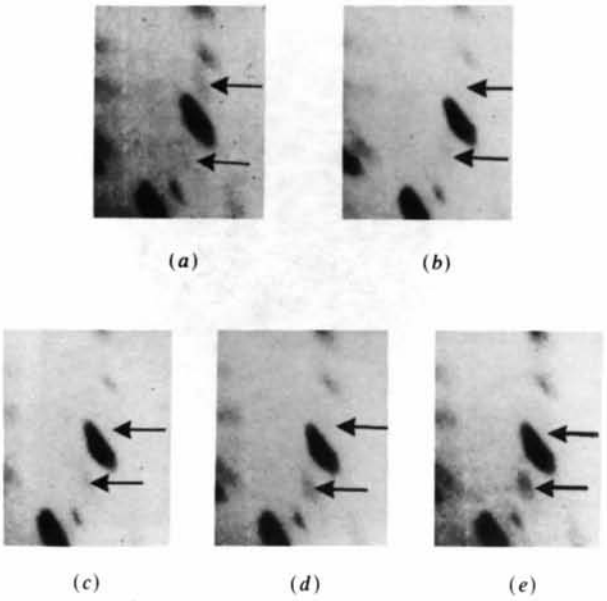


Fig. 2. Time development of domain switching in a GMO crystal. Portions of X-ray patterns recorded with increasing delay time after switching pulse: (*a*) 0·1, (*b*) 0·5, (*c*) 0·9, (*d*) 1·5 and (*e*) 2 ms.

To conclude, the experiments demonstrate that fast structural changes in single crystals can be reliably studied using flash X-ray diffraction techniques.

We thank Dr S. Starobinetz for helpful discussions and suggestions, Dr F. Frolow and Mr Y. Halfon for their contributions to the experimental work. We also would like to thank Mr G. Grimouille of the Centre National d'Etudes des Télécommunications, Paris, France, for providing us with some of the GMO crystals. This work was supported by grant No. 2451/81 from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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Acta Cryst. (1987). B**43**, 504–512

Superlattice Structure of Ferroelectric Barium Sodium Niobate (BNN)

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(*Received* 25 *March* 1985; *accepted* 9 *July* 1987)

Abstract

Electron diffraction and high-resolution electron microscopy have been used to investigate the space group and structure of the commensurate superlattice phase of barium sodium niobate (BNN), $Ba_2NaNb_5BO_{15}$. At room temperature the space group appears to be *Im*2*a* with orthorhombic cell parameters $a = 35{\cdot}18$, $b = 35{\cdot}24$, $c = 7{\cdot}99$ Å. Use of dark-field beam-tilting techniques allow detection of weak symmetry elements and small atomic shifts associated with ordering of Ba and O atoms into pairs of sites which, according to X-ray studies, were assigned split occupancy. Structural models consistent with the above space group were derived and multislice techniques used to calculate the variation of subcell and supercell reflections, as well as the high-resolution images, with crystal thickness and orientation of the incident beam. Ordering of Ba ions, as well as *some* of the O ions, gave model-sensitive characteristics which could be tested by comparison with the experimental results.

0108-7681/87/060504-09$01.50