SHORT COMMUNICATIONS

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The piezoelectric tensor element d_{33} of $KTiOPO_4$ determined by single crystal X-ray diffraction

H. GRAAFSMA,[a]* G. W. J. C. HEUNEN,[a] S. DAHAOUI,[b] A. EL HAOUZI,[b] N. K. HANSEN[b] AND G. MARNIER[c] *at* [a]*European Synchrotron Radiation Facility, Avenue des Martyrs, 38043 Grenoble, France,* [b]*Université Henri Poincaré, Nancy, France, and* [c]*Université de Bourgogne, Dijon, France. E-mail: graafsma@esrf.fr*

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Abstract

The d_{33} piezoelectric constant of $KTiOPO_4$ (potassium titanium orthophosphate, KTP) has been determined for two different samples and at temperatures between 100 and 220 K, using high-resolution X-ray diffraction of a single crystal in an electric field. The observed value of $15(2) \times 10^{-12}$ m V^{-1} is between the two values of 10.4 and 25.8×10^{-12} mV^{-1} found in the literature. The value of d_{33} is shown to be constant over the temperature range 100–220 K and no anomaly was observed at the conductor–insulator transition at 150 K. The results obtained are believed to be sample-independent, since the same value was obtained for two different crystals, measured at different sources.

1. Introduction

The study of the influence of an external electric field on the atomic structure of piezoelectric crystals has long been limited to feasibility studies of selected cases (Fujimoto, 1982; Ståhl, Kvick & Abrahams, 1990; Paturle, Graafsma, Sheu, Coppens & Becker, 1991; Graafsma *et al.*, 1992). With the development of third-generation synchrotron sources combined with the development of new high count-rate detectors (Graafsma, Thorander, Heunen & Morse, 1996), it is now possible to perform more complete diffraction studies in a reasonable time, of the order of days rather than months. This opens the way to study either a series of isostructural compounds or one compound under different conditions, such as temperature, voltage and frequency of the applied electric field, to obtain a better understanding of the origin of piezoelectricity on an atomic level.

Here we describe the results of a first study performed at the Materials Science Beamline of the European Synchrotron Radiation Facility on $KTiOPO_4$ (KTP) under an external electric field. Only the results obtained from the peak shifts, related to the changes in unit-cell dimensions, are given. The effect on the peak shape, related to the changes in mosaicity and domain structure, as well as on the integrated intensity, related to the changes in interatomic distances, will be discussed in a later paper.

The interest in crystalline KTP stems mainly from its pronounced non-linear optical properties and especially from its applications for second harmonic generation of near IR laser light. It is also a quasi one-dimensional ionic conductor above 150 K (Yanovskii & Voronkova, 1980; Khodjaoui, 1993) due to the high mobility of the potassium ions. A detailed analysis of the electron density distribution was carried out (Hansen, Protas & Marnier, 1991) and has been followed up by diffraction experiments at several temperatures between 10 and 1100 K (Dahaoui, 1996).

Two publications have appeared in which the full piezoelectric tensor is given. However, the two results show large discrepancies for almost all elements. For the piezoelectric constant d_{33}, Sil'vestrova, Maslov & Pisarevskii (1992) determined a value of 25.8×10^{-12} m V^{-1}, whereas Chu, Bierlein & Hunsperger (1992) obtained a value of 10.4×10^{-12} m V^{-1}. Similar differences are found for d_{31} and d_{32}, with the value of Chu *et al.* always being lower. Both groups performed the measurements at room temperature and used the direct piezoelectric effect, but, unfortunately, give no indication of the precision of their results.

2. Experimental

KTP crystallizes in the orthorhombic space group $Pna2_1$, with room-temperature cell parameters: $a = 12.814(6)$, $b = 6.404(2)$ and $c = 10.616(5)$ Å. Large single crystals, grown from a flux (Marnier, 1986), were used. From these, rectangular plates were cut perpendicular to the crystallographic c axis. Thin aluminum electrodes were sputtered onto the extended faces. Two samples, originating from different batches, were used in the present experiment. Sample (1) with dimensions $5 \times 5 \times 0.44$ mm was not polished after cutting. Sample (2) with dimensions $4 \times 4 \times 0.33$ mm had an optical quality polishing after cutting. For both samples the dimensions of the electrodes were *ca* 1 mm less than the extended faces, in order to prevent through-air electric discharge. The electrodes were connected to the high voltage cables by a small amount of Ag paste.

The d_{33} piezoelectric tensor element can readily be determined by diffraction of monochromatic X-rays from a crystal in an external electric field (Paturle, Graafsma, Sheu, Coppens & Becker, 1991). We have measured the influence of an external electric field parallel to **c** on the $00l$ reflections, for the two different samples of KTP.

In all measurements a voltage was applied in the form of a three-step square wave with a frequency of 33 Hz and the detection synchronized on three counting chains (Paturle, Graafsma, Sheu, Coppens & Becker, 1991). The amplitude of the voltage was varied between 500 and 2000 V.

Two series of measurements were carried out. For the first sample the measurements were carried out at the Materials Science Beamline of the European Synchrotron Radiation Facility (Kvick & Wulff, 1992), using a wavelength of 0.564 Å. The temperature dependence of the d_{33} constant was measured on the second crystal, on a rotating anode source (Mo $K\alpha$ radiation), with a high-resolution diffraction set-up. In both cases the crystal was cooled by a nitrogen gas stream. It is to be noted that by using high-energy synchrotron radiation we were able to reach very high resolution. Furthermore, the very high

Table 1. *The d_{33} value ($\times 10^{-12}$ m V^{-1}) of KTP at various temperatures and voltages*

Crystal (1)										
100 K/3.4 × 10^6 V m^{-1}	15 (2)									
Crystal (2)		3.0 × 10^6 V m^{-1}			4.5 × 10^6 V m^{-1}			6.0 × 10^6 V m^{-1}		
100 K		16 (2)			16 (2)			17 (2)		
Crystal (2)	100 K	120 K	140 K	150 K	153 K	157 K	166 K	180 K	200 K	220 K
4.5 × 10^6 V m^{-1}	15	18	16	16	16	17	17	17	13	18

flux was needed in order to investigate the changes in integrated intensity induced by the electric field.

3. Results

Fig. 1 shows the shift ($\Delta\theta$) as a function of $\tan\theta$ for crystal (1) at 100 K, 3.4 × 10^6 V m^{-1} and 33 Hz for the 00l reflections with l = 20, 22, 24, 26, 28, 30, 32 and 36, measured with synchrotron radiation. The 0034 reflection was influenced by multiple scattering and thus was not included in the data treatment. The shifts were determined by an algorithm based on the linear Pearson correlation coefficient between two shifted profiles. The change in profile shape due to the applied electric field is very small, as confirmed by the large correlation coefficient between the two profiles at maximum overlap. All reflections and their Friedel equivalents have been measured between 10 and 30 times, with merged data presented in Fig. 1. The solid line gives a linear fit to the data points (Paturle, Graafsma, Sheu, Coppens & Becker, 1991). The slope of the curve gives a value of 15 (2) × 10^{-12} m V^{-1} for the piezoelectric constant d_{33}, between the values of 10.4 × 10^{-12} m V^{-1} obtained by Chu, Bierlein & Hunsperger (1992) and 25.8 × 10^{-12} m V^{-1} obtained by Sil'vestrova, Maslov & Pisarevskii (1992).

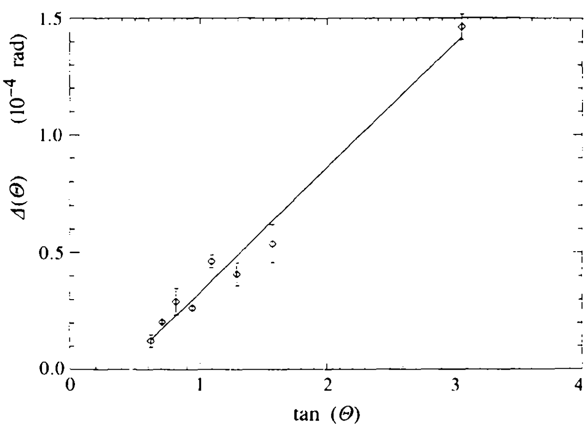

Fig. 1. Electric-field-induced peak shift for the 00l reflections as a function of $\tan\theta$, l = 20, 22, 24, 26, 28, 30, 32 and 36.

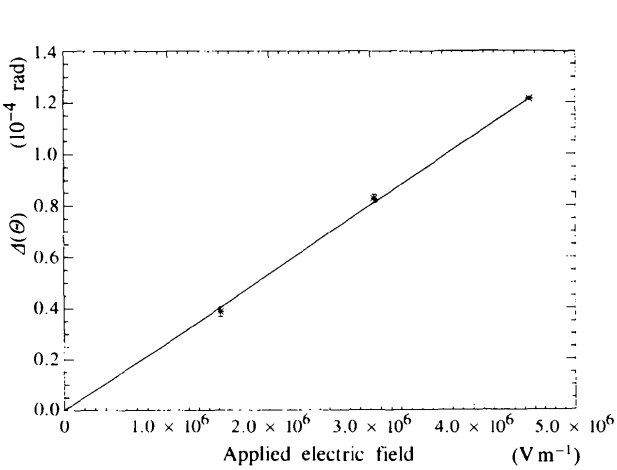

Fig. 2. Induced peak shift for the l = 36 reflection for crystal (2) at 100 K as a function of applied electric field.

Fig. 2 shows the peak shift ($\Delta\theta$) l = 36 as a function of applied electric field for crystal (2) at 100 K, showing the expected linear behaviour (Paturle, Graafsma, Sheu, Coppens & Becker, 1991).

Since the quoted literature values for the d_{33} piezoelectric constant are obtained at room temperature, we also measured the temperature dependence of d_{33}. Piezoelectric tensor elements are, in principle, temperature dependent and show, in certain cases, large anomalies around phase transitions, *e.g.* d_{36} of KH_2PO_4 (KDP). A high-resolution rotating anode set-up with Mo $K\alpha_1$ radiation was used to determine the temperature dependence of the d_{33} value. The measurements were performed on crystal (2) with 6.7 × 10^6 V m^{-1} and 33 Hz. No anomaly in the d_{33} value is observed, which is related to the fact that the transition at 150 K does not involve a change in symmetry.

Table 1 shows a summary of the d_{33} value obtained for different crystals and under different experimental conditions.

A least-squares fit of a line to the temperature data gave a temperature dependence of d_{33} of 0.001 (0.01) × 10^{-12} m V^{-1} K^{-1}.

4. Conclusions

We have determined the d_{33} piezoelectric tensor element of KTP between 100 and 220 K using X-ray diffraction of a single crystal in an external electric field. The value 15 (2) × 10^{-12} m V^{-1} was reproduced using two different samples and at various voltages, and is thus believed to be sample-, temperature- and voltage-independent. No anomaly in the d_{33} tensor element is observed at the insulator to conductor transition at 150 K. This transition, however, does not involve a change in symmetry, as is the case with KDP at 123 K where the d_{36} tensor shows a large anomaly. Further analysis of the induced changes in peak shapes and integrated intensities is under way and will be published in a subsequent paper.

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