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X-ray multiple diffraction as a probe to determine all the piezoelectric coefficients of a crystal: Rochelle salt case

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Abstract

The x-ray multiple diffraction method, which allows us to determine the piezoelectric coefficients of a single crystal under an external electric field (E), was applied to Rochelle salt (dos Santos *et al* 2001 *J. Phys.: Condens. Matter* **13** 10497) for E parallel to the piezoelectric Y direction. In this work, the theory was extended to consider an observed monoclinic–triclinic distortion under E application into the other two piezoelectric X and Z directions. Renninger scans carried out using the chosen (060) primary reflection have provided the four remaining coefficients through the measurement of the properly chosen secondary peaks. so that all eight piezoelectric coefficients (d_{14} , d_{16} , d_{21} , d_{22} , d_{23} , d_{25} , d_{34} and d_{36}) for Rochelle salt were determined.

1. Introduction

The Rochelle salt crystal ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) shows ferroelectricity in the temperature region between -18 and 24°C in which the crystal is monoclinic (C_2^2)– $P12_11$ with lattice parameters $a = 11.869 \text{ \AA}$, $b = 14.316 \text{ \AA}$, $c = 6.223 \text{ \AA}$ and $\beta = 89.26^\circ$. Outside this temperature range, the crystal presents a paraelectric phase [1, 2], for which the space group is orthorhombic (D_2^3) $P2_12_12$, with lattice parameters $a = 11.880 \text{ \AA}$, $b = 14.298 \text{ \AA}$, $c = 6.223 \text{ \AA}$.

The crystal structure of Rochelle salt was first investigated in 1941 [3]. The investigation of its crystal structure in the ferroelectric phase has shown the importance of the interactions between the O(8) atom and K ions for the ferroelectric activity [4]. Rochelle salt is piezoelectric and therefore it provides different responses to an external stimulus applied to each crystallographic direction. When an electric field is applied parallel to the X piezoelectric axis, the corresponding strain towards the [011] direction appears through d_{14} , the most studied piezoelectric coefficient [5], due to its relationship to the phase transition in this crystal.

Since the piezoelectric effect can occur in all crystallographic directions within the crystal, a very versatile method based on the x-ray multiple diffraction technique was developed

to allow the investigation of the electric field effect in the crystal lattice being the first successful application performed for the non-linear optical organic crystal MNA (meta-nitroaniline) using synchrotron radiation [6]. Next, other applications for MBANP ((-)-2-(alpha-methylbenzylamino)-s-nitropyridine) and Rochelle salt were presented considering the electric field application parallel to the crystal b axis in both cases and the corresponding piezoelectric coefficients, d_{21} , d_{22} , d_{23} and d_{25} , were determined [7, 8].

In this work an extension of the basis of this method can allow it to treat E -induced triclinic distortions in the monoclinic Rochelle salt samples and hence to make it possible to determine all eight piezoelectric coefficients using the x-ray multiple diffraction technique.

2. Theory

The basic non-centrosymmetric property of a piezoelectric material is directly related to the anisotropy of this kind of material. The possibility of obtaining a different response in each crystallographic direction of the material to an applied external stimulus is the basis of the anisotropy.

Application of an external electric field (E_i) to a piezoelectric material causes a strain (ε_{jk}) given by

$$\varepsilon_{ij} = d_{ijk} E_k \quad (1)$$

where d_{ijk} is the piezoelectric coefficient. This is the converse piezoelectric effect.

Here, an orthogonal set of axes $\{X, Y, Z\}$ and two vectors $\vec{r} = \{r_x, r_y, r_z\} \equiv \{r_i\}$ and s , connecting any two points in the crystal, are considered. These two points can be associated with two atoms or even two particular points of the crystalline lattice. When an electric field is applied to the crystal, the relative positions of these points change in such a way that $\vec{r} \rightarrow \vec{r} + \Delta\vec{r}$. The change in the ratio of the $\vec{r}e\theta$ components defines the strain tensor, ε_{ij} . Hence, one can write down

$$\Delta r = \frac{r_i r_j}{r} \varepsilon_{ij} \quad \text{and} \quad \Delta\theta = \frac{1}{\sin\theta} \left[-\frac{r_i s_j + s_i r_j}{rs} + \cos\theta \left\{ \frac{r^2 s_i s_j + s^2 r_i r_j}{(rs)^2} \right\} \right] \varepsilon_{ij}. \quad (2)$$

If the lattice vectors are analysed in a separate way, Δr becomes

$$\Delta a = \frac{a_x a_x}{a} \varepsilon_{xx} + \frac{a_y a_y}{a} \varepsilon_{yy} + \frac{a_z a_z}{a} \varepsilon_{zz} + 2 \frac{a_x a_y}{a} \varepsilon_{xy} + 2 \frac{a_x a_z}{a} \varepsilon_{xz} + 2 \frac{a_y a_z}{a} \varepsilon_{yz}. \quad (3)$$

In the case of the Rochelle salt, a monoclinic single crystal, class 2 [9], the vectors representing the crystallographic axes can be given in an orthogonal frame as

$$\vec{a} = (a_x, a_y, a_z) = (a \sin\beta, 0, a \cos\beta), \quad \vec{b} = (0, b, 0) \quad \text{and} \quad \vec{c} = (0, 0, c). \quad (4)$$

In order to analyse the electric field application in all piezoelectric directions of the Rochelle salt, equation (1) is written in matrix form using the Voigt [10] notation shown below, as

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{zx} \\ 2\varepsilon_{xy} \end{pmatrix} = \begin{pmatrix} 0 & d_{21} & 0 \\ 0 & d_{22} & 0 \\ 0 & d_{23} & 0 \\ d_{14} & 0 & d_{34} \\ 0 & d_{25} & 0 \\ d_{16} & 0 & d_{36} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}. \quad (5)$$

Next, we will describe the relationship between the lattice strains and the direction of application of E :

(a) $\vec{E} = E_x \hat{x}$. In this case, the lattice strains are given by

$$\varepsilon_{yz} = \frac{d_{14}}{2} E_x \quad \text{and} \quad \varepsilon_{xy} = \frac{d_{16}}{2} E_x \quad (6)$$

and considering the lattice parameter variations from equation (2) after the substitution of (4), one obtains

$$\Delta\alpha = -d_{14} E_x \quad \Delta\gamma = -[d_{16} \sin \beta + d_{14} \cos \beta] E_x. \quad (7)$$

(b) $\vec{E} = E_y \hat{y}$. In this case, the lattice distortions are

$$\frac{1}{E_y} \frac{\Delta a}{a} = d_{21} \sin^2 \beta + d_{23} \cos^2 \beta + \frac{d_{25}}{2} \sin(2\beta), \quad (8)$$

$$\frac{1}{E_y} \frac{\Delta b}{b} = d_{22}, \quad (9)$$

$$\frac{1}{E_y} \frac{\Delta c}{c} = d_{23}, \quad (10)$$

and

$$\frac{1}{E_y} \Delta\beta = \frac{1}{2} \sin(2\beta)(d_{21} - d_{23}) - \sin^2(\beta)d_{25}. \quad (11)$$

(c) $\vec{E} = E_z \hat{z}$. Finally, when E_z is applied, the unit cell distortions are

$$\Delta\alpha = -d_{34} E_z \quad \text{and} \quad \Delta\gamma = -[d_{36} \sin \beta + d_{34} \cos \beta] E_z. \quad (12)$$

It should be pointed out that equations (6)–(12) relate the unit cell distortion to the piezoelectric coefficients for a Rochelle salt monoclinic crystal.

2.1. Secondary peak position in a Renninger scan

In the multiple diffraction phenomenon, a set of crystallographic planes, normally parallel to the crystal surface, called primary planes (h_p, k_p, ℓ_p), are aligned to diffract the incident beam. By rotation around the primary reciprocal vector, several other planes (h_s, k_s, ℓ_s), called secondary, with arbitrary orientation inside the crystal also diffract simultaneously with the primary reflection. The intensity interaction between the primary and the several secondary reflections is established through the so-called coupling reflection ($h_p - h_s, k_p - k_s, \ell_p - \ell_s$). The plot of the diffracted primary intensity as a function of the rotation angle (ϕ) is the Renninger scan that shows oscillations in the primary intensity as positive (Umweganregung) or negative (Aufhellung) peaks, depending upon whether the interaction between the primary and the secondary beams occurs in a constructive or destructive way, respectively.

The angular position of a multiple diffraction peak corresponding to any (hkl) plane, for a specific wavelength (λ), can be determined in terms of the angle $\phi \pm \phi_0$ (the sign \pm corresponds to the entrance and exit of a secondary reciprocal lattice node of the Ewald sphere). ϕ_0 is the angle between the reference vector and the projection of the secondary vector at the plane perpendicular to the primary vector. The angular position is then given by [11]

$$\cos(\phi^{hkl} \pm \phi_0) = \frac{1}{2} \frac{(H^2 - \vec{H} \cdot \vec{H}_0)}{\sqrt{(1/\lambda^2) - (H_0^2/4)} \sqrt{H^2 - H_p^2}} \quad (13)$$

where \vec{H}_0 is the primary vector, \vec{H} is the secondary vector defined as $\vec{H}_{hkl} = h\vec{a}^* + k\vec{b}^* + \ell\vec{c}^*$, \vec{H}_p is the projection of the secondary vector parallel to the primary one, expressed by $\vec{H}_p = (\vec{H} \cdot \vec{H}_0)(\vec{H}_0/H_0^2)$ and ϕ_0 is obtained from $\cos(\phi_0) = (\vec{H} \cdot \vec{H}_{Ref}) / (\sqrt{H^2 - \vec{H}_p^2} \cdot \sqrt{H_{Ref}^2})$.

3. Analysis of the secondary reflections for $\vec{E} = E_y \hat{y}$

The secondary peak position can be expressed, in the case of $\vec{E} = E_y \hat{y}$ for a monoclinic Rochelle salt ($\alpha = \gamma = 90^\circ \neq \beta$), taking $(h_0 0 0)$ as the primary, as

$$\cos(\phi^{hkl} \pm \phi_0) = \frac{1}{2} \frac{\frac{h(h-h_0)}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2 \sin^2 \beta} - \frac{\ell(2h-h_0) \cos \beta}{ac \sin^2 \beta}}{\sqrt{\frac{1}{\lambda^2} - \frac{h_0^2}{4a^2 \sin^2 \beta}} \sqrt{\frac{\ell^2}{c^2} + \frac{k^2}{b^2}}} = f(a, b, c, \beta). \quad (14)$$

Thus, the differential of this equation gives the relationship between the MD peak position and the E -induced lattice distortion:

$$-\sin(\phi^{hkl} \pm \phi_0) \Delta(\phi^{hkl} \pm \phi_0) = \frac{\partial f}{\partial a} \Big|_{hkl} \Delta a + \frac{\partial f}{\partial b} \Big|_{hkl} \Delta b + \frac{\partial f}{\partial c} \Big|_{hkl} \Delta c + \frac{\partial f}{\partial \beta} \Big|_{hkl} \Delta \beta. \quad (15)$$

Since the $(h00)$ is the chosen primary reflection, the a lattice parameter variation is determined by the differentiation of Bragg's law

$$\frac{\Delta a}{a} = -\cot(\omega_{h00}) \Delta \omega - \cot(\beta) \Delta \beta. \quad (16)$$

Working with equations (8) and (11) and also replacing the result in equation (16) one obtains the d_{21} piezoelectric coefficient:

$$d_{21} = -\frac{\cot(\omega_{h00}) \Delta \omega}{E_y}. \quad (17)$$

The other coefficients are determined by choosing adequate secondary reflections, which are presented next.

(1) Secondary $(0k0)$

$$\frac{\Delta b}{b} \left(\frac{\partial f}{\partial b} \Big|_{0k0} \right) = \tan(\phi^{0k0} \pm \phi_0) \Delta(\phi^{0k0} \pm \phi_0) - \frac{\Delta a}{a} \frac{\partial f}{\partial a} \Big|_{0k0} - \Delta \beta \frac{\partial f}{\partial \beta} \Big|_{0k0}. \quad (18)$$

(2) Secondary (00ℓ)

$$\frac{\Delta c}{c} \left(\frac{\partial f}{\partial c} \Big|_{00\ell} \right) = \tan(\phi^{00\ell} \pm \phi_0) \Delta(\phi^{00\ell} \pm \phi_0) - \frac{\Delta a}{a} \frac{\partial f}{\partial a} \Big|_{00\ell} - \Delta \beta \frac{\partial f}{\partial \beta} \Big|_{00\ell}. \quad (19)$$

(3) Secondary $(h0\ell)$

$$\Delta \beta \left(\frac{\partial f}{\partial \beta} \Big|_{h0\ell} \right) = \tan(\phi^{h0\ell} \pm \phi_0) \Delta(\phi^{h0\ell} \pm \phi_0) - \frac{\Delta a}{a} \frac{\partial f}{\partial a} \Big|_{h0\ell} - \frac{\Delta c}{c} \frac{\partial f}{\partial c} \Big|_{h0\ell}. \quad (20)$$

4. Analysis of the secondary reflections for $\vec{E} = E_x \hat{x}$ and $E_z \hat{z}$

When the electric field is applied in the $E_x \hat{x}$ and $E_z \hat{z}$ directions it is also necessary to consider that the crystal suffers distortion in the α and γ unit cell angles. In order to take into account this deformation, the crystal is considered as triclinic.

The triclinic lattice parameters can be decomposed into orthogonal axes as shown below:

$$\begin{aligned} \vec{a} &= (a \sin \beta, 0, a \cos \beta), & \vec{c} &= (0, 0, c) & \text{and} \\ \vec{b} &= \left(-b(\cos \alpha \cos \beta - \cos \alpha) \operatorname{cosec} \beta, b \sqrt{\sin^2 \alpha - (\cos \alpha \cos \beta - \cos \gamma)^2 \operatorname{cosec}^2 \beta}, b \cos \alpha \right). \end{aligned} \quad (21)$$

If the $(0k_00)$ is chosen as the primary reflection to keep perpendicular to the y direction, both X and Z directions are used for the application of E . The secondary peak position is

$$\begin{aligned} \cos(\phi^{hkl} \pm \phi_0) &= \frac{\left(c^2h^2 + a^2\ell^2 - 2ach\ell \cos \beta - \frac{\Theta(ack_0 \sin^2 \beta + \Theta)}{\Omega}\right)}{ac \sin \beta \sqrt{(c^2h^2 + a^2\ell^2 - 2ach\ell \cos \beta) \left(\frac{4}{\lambda^2} - \frac{k_0^2 \sin^2 \beta}{4\Omega}\right)}} \\ &= f(a, b, c, \alpha, \beta, \gamma) \end{aligned} \quad (22)$$

being $\Theta = b \cos \alpha (a\ell - ch \cos \beta) + b \cos \gamma (ch - a\ell \cos \beta) - ack \sin^2 \beta$ and $\Omega = b^2 (\cos^2 \alpha + \cos^2 \gamma - \sin^2 \beta - 2 \cos \alpha \cos \beta \cos \gamma)$.

According to the choice of the adequate secondary reflections from the piezoelectric tensor, one can determine the coefficients corresponding to the α and γ unit cell angular distortion.

(1) *Secondary* $(0kk)$

$$\frac{\Delta \alpha}{f} \left(\frac{\partial f}{\partial \alpha} \Big|_{0kk} \right) = \tan(\phi^{0kk} \pm \phi_0) \Delta(\phi^{0kk} \pm \phi_0) - \frac{\Delta \gamma}{f} \frac{\partial f}{\partial \gamma} \Big|_{0kk}. \quad (23)$$

(2) *Secondary* $(hh0)$

$$\frac{\Delta \gamma}{f} \left(\frac{\partial f}{\partial \gamma} \Big|_{hh0} \right) = \tan(\phi^{hh0} \pm \phi_0) \Delta(\phi^{hh0} \pm \phi_0) - \frac{\Delta \alpha}{f} \frac{\partial f}{\partial \alpha} \Big|_{hh0}. \quad (24)$$

All Rochelle salt piezoelectric coefficients can be obtained by substituting the above-determined unit cell parameter variation into equations (7)–(12).

5. Experimental details

Rochelle salt samples were cut with dimensions of $5 \times 2.5 \times 1.5 \text{ mm}^3$ (the x-ray beam reaches the narrower sample face) and the electric field is applied in the X , Y and Z directions. E is generated by a DC variable source with low current. The electric contacts are established through conducting sponges kindly provided by SGL Carbon Group, Meitingen, Alemanha. They are put in between the metal plates and the larger sample face to avoid mechanical strain and to provide a uniform E within the sample.

Renninger scans were carried out in a specially developed geometry with a long pipe collimator (1.75 m) adapted on a single-crystal diffractometer. The obtained divergences are $\delta_v = 107 \text{ arc s}$ in the vertical plane and $\delta_h = 149 \text{ arc s}$ in the horizontal plane. The $\text{Cu K}\alpha_1$ radiation was used in the Renninger scans whereas $\text{Cu K}\beta$ was used in the rocking curves. All measurements were performed using step sizes of 0.0008° and 0.005° in the ω and ϕ axes, respectively. The (060) reflection was chosen as primary for the Renninger scans.

5.1. Results

The experiments in which the electric field was applied parallel to the y axis, i.e. the $[010]$ direction of the Rochelle salt sample, were already described in detail in [7]. Here, just the important points and results will be presented for the better understanding of the readers. The effect of E was looked for in the crystallographic directions $[100]$, $[010]$, $[001]$ and $[101]$, as predicted by the matrix notation equation (5). The magnitude of the effect in each direction is proportional to the corresponding converse piezoelectric coefficient. The sample was kept at $T = 22^\circ \text{C}$ (ferroelectric phase) and, for each value of E , rocking curves and Renninger scans were measured for the primary and secondary reflections previously chosen. The variation in the peak positions as a function of E were transformed into unit cell distortions through

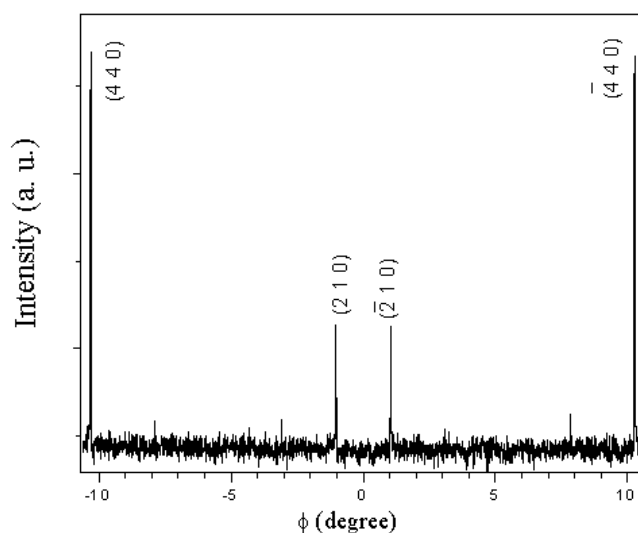


Figure 1. Portion around the $\phi = 0^\circ$ symmetry mirror of the (060) Renninger scan of the orthorhombic Rochelle salt. The secondary reflection (440) allows to obtain the d_{16} and d_{36} coefficients.

equations (8)–(11) and (17). Thus, the piezoelectric coefficients for $\vec{E} = E_y \hat{y}$ were determined as $d_{21} = 7.0(6) \times 10^{-10} \text{ C N}^{-1}$; $d_{22} = 2.2(9) \times 10^{-9} \text{ C N}^{-1}$; $d_{23} = 2.1(9) \times 10^{-9} \text{ C N}^{-1}$ and $d_{25} = 3.7(8) \times 10^{-11} \text{ C N}^{-1}$.

In order to determine the other Rochelle salt piezoelectric coefficients, one has to apply E parallel to the Z direction and look for its effect in the [011] and [110] crystallographic directions.

Prior to the application of E , (060) Renninger scans were performed to allow the determination of the symmetry mirrors as well as to choose the adequate secondary reflections to provide the coefficients associated with the E applied in the Z direction.

Figure 1 shows the region around the $\phi = 0^\circ$ symmetry mirror of the Renninger scan for the (060) primary reflection. The (440) secondary reflection that appears in this figure was used to determine the d_{36} coefficient.

For each value of E , a (060) rocking curve and Renninger scans for the (440), $(\bar{4}40)$ and (022) secondary reflections were measured. As expected, several of the rocking curves provided the same (060) peak position for all E values since the d_{32} coefficient must be zero for a monoclinic crystal. On the other hand, the shift in the (440) and (022) secondary peak positions, which are related to the α and γ angular distortion, can give us d_{34} and d_{36} through equation (12). Figure 2 shows the corresponding distortions as a function of E and the obtained values are: $d_{34} = 8.2(3) \times 10^{-11} \text{ C N}^{-1}$ and $d_{36} = 1.23(7) \times 10^{-11} \text{ C N}^{-1}$. Again, the d_{36} coefficient measured by the multiple diffraction method is very close to the $1.168 \times 10^{-11} \text{ C N}^{-1}$ value published in the literature [12] which also supports the method.

In the last measurements using Rochelle salt, E was applied parallel to the piezoelectric X direction and the (060) primary reflection was also chosen to keep the scan in the $\vec{a} \times \vec{c}$ plane for this monoclinic crystal. Therefore, only one symmetry mirror at each 180° in ϕ is obtained in the whole Renninger scan. The (022) secondary reflection is used in the determination of the d_{14} coefficient since it has awakened the interest of several authors due to its variation with temperature [5]. This anomalous behaviour can be associated with the spontaneous polarization of the material, which is temperature-dependent.

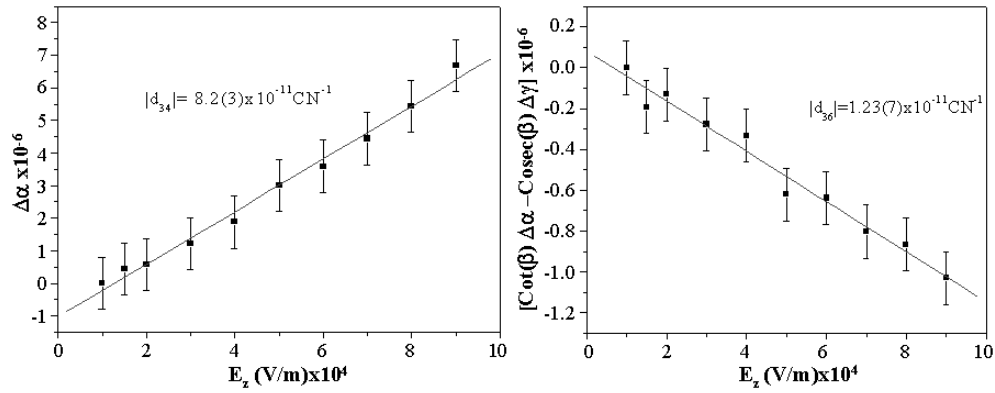


Figure 2. Rochelle salt lattice strain obtained from the (000)(060)(440) and (000)(060)(022) secondary peak shifts as a function of the electric field (E_z) providing the d_{34} and d_{36} piezoelectric coefficients.

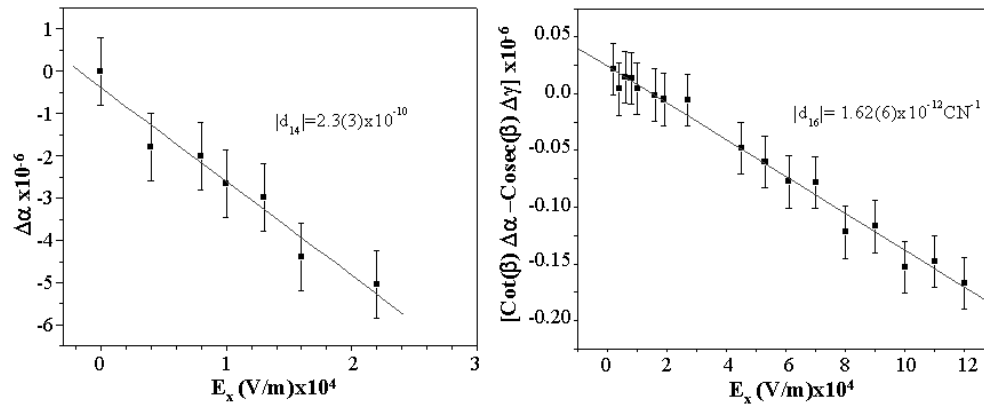


Figure 3. Rochelle salt lattice strain obtained from the (000)(060)(440) and (000)(060)(022) secondary peak shifts as a function of the electric field (E_x) providing the d_{14} and d_{16} piezoelectric coefficients.

$$\begin{array}{c}
 \begin{array}{cccccc}
 & [100] & [010] & [001] & [011] & [101] & [110] \\
 \mathbf{E}_x & \left(\begin{array}{cccccc}
 0 & 0 & 0 & 23(3) & 0 & 0.162(6) \\
 70(6) & 220(90) & 210(90) & 0 & 3.7(8) & 0 \\
 0 & 0 & 0 & 78.2(3) & 0 & 1.23(7)
 \end{array} \right) \\
 \mathbf{E}_y \\
 \mathbf{E}_z
 \end{array}
 \end{array}
 \times 10^{-11} N/C$$

Figure 4. Rochelle salt piezoelectric tensor with the coefficients obtained by the x-ray multiple diffraction method.

The result for $d_{14} = 2.3(3) \times 10^{-10} \text{ C N}^{-1}$ and $d_{16} = 1.62(6) \times 10^{-12} \text{ C N}^{-1}$ coefficients obtained from the α and γ angular distortions as a function of E applied towards the X direction comes from figure 3.

In figure 4 all piezoelectric coefficients for Rochelle salt obtained by the x-ray multiple diffraction method are shown in a matrix form for better visualization.

6. Conclusions

In this work, the successful application of the x-ray multiple diffraction method to study E -induced structural deformation in a Rochelle salt crystal is presented. As result, the four remaining piezoelectric coefficients needed for this material to complete the piezoelectric tensor (eight coefficients) were determined.

The great advantage of this method lies in:

- (i) its versatility to measure rocking curves and Renninger scans for each E value using the same geometry;
- (ii) the possibility of obtaining three-dimensional information on the lattice analysed;
- (iii) its high sensitivity to detect very small E -induced lattice distortions.

These special features of the multiple diffraction method allow one to choose three adequately cut samples and to use them in order to determine all the piezoelectric coefficients of a crystal. Therefore, these coefficients are all obtained under the same experimental conditions whereas, in a two-beam diffraction case, one would need to analyse eight samples, each one cut in a chosen crystallographic direction to allow for the application of a electric field.

It has been considered that Rochelle salt suffers triclinic deformation under application of E . Then some modifications to the multiple diffraction theory have to be done, particularly for the distortion of the α and γ angles, to obtain all the required piezoelectric coefficients.

The results obtained in this work show that the multiple diffraction technique acts as a precise probe to study the effect of an external electric field in crystals. In fact, it allows for the determination of all piezoelectric coefficients of any piezoelectric crystal as well as the analysis of E -induced phase transitions in single crystals.

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