Electric field induced structural changes in $\alpha - SiO_2$ and $\alpha - AlPO_4$

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In order to understand the atomistic origin of the inverse piezoelectric effect, the changes of integrated intensities of selected Bragg reflection of $\alpha - SiO_2$ and $\alpha - AlPO_4$ were studied, which were induced by an external high electric field of up to $E = \pm 8$ kV/mm. Because the model of the field induced displacement of ionic sublattices against each other fails for the interpretation of experimental data, we propose a model of the inverse piezoelectric effect, which considers the strong covalent bond between Si and O atoms in $\alpha - SiO_2$. Here the main effect of screening the external electric field is a change in the Si-O-Si bonding angles, i.\,e. the rotations of rigid SiO_4 tetrahedra. The same model holds for $\alpha - AlPO_4$, which is an isostructural compound to $\alpha - SiO_2$. For the first time a similar experiment was performed at low temperatures. Between $50\,K \le T \le 300\,K$ the piezoelectric coefficient d_{11} of both substances behaves nearly temperature independent. On the other hand, the field induced change of the intensities increases for decreasing temperature. This can be interpreted by the rotation of tetrahedra, which is partially originated by the temperature decrease and by the external electric field, respectively, accompanied by a field-induced deformation of tetrahedra.

I. INTRODUCTION

The interaction between a crystal and an external electric field is the basis of many fundamental physical phenomena, such as piezoelectricity including the change of unit cell parameters and polarization (change of electron density). Although most of these phenomena are well described and understood on a macroscopic level, relatively little is known about the underlying atomic processes.

Low quartz $\alpha - SiO_2$, trigonal, space group $P3_121$ or $P3_221$ is a well-investigated crystal and widely used for technical applications. $\alpha - AlPO_4$ has the same symmetry as low quartz. Compared to $\alpha - SiO_2$ the unit cell of $\alpha - AlPO_4$ is twice as large in c direction, its unit cell can be derived from $\alpha - SiO_2$ by an alternating replacement of the Si sites by Al and P atoms.

In literature, the explanation of the piezoelectricity of quartz often follows the model introduced by Meissner [1]. He proposed a displacement of the Si_{4+} and O_{2-} ionic sublattices against the external field originating a change in the lattice parameter.

This ionic model is not realistic because the Si-O bond in $\alpha - SiO_2$ is partly quite covalent in nature. Meanwhile one knows that the Si-O bond in $\alpha - SiO_2$ is not purely ionic, it also contains covalent contributions [2-3]. D'Amour et al. [4] and Levien et al. [5] have investigated the high pressure dependence of the $\alpha - SiO_2$ structure and found that the individual Si-O bond lengths and the O-Si-O bond angles changed very little at high external pressure. The main effect is the change in Si-O-Si angles and O-O distances between the different tetrahedra. Generally, one can suppose that the bond angles between the tetrahedra change more than the Si-O bond lengths under influence of any external perturbation. It is well known, that the coordinates of atoms within the unit cell can be reconstructed from X-ray diffraction data. By measuring the electric field induced changes of integrated intensities of Bragg reflections one can investigate the origin of the inverse piezoelectric effect in a crystal.

The influence of a high electric field on the Bragg reflections of $\alpha - SiO_2$ has been studied in a number of works [6-10].

Sometimes huge intensity variations have been observed [6]. In some cases they might be caused by extinction effects and not by the electrostriction [7] because the field may create structural defects and subsequentely a change from the dynamical into the kinematic regime of X-ray diffraction.

As shown in previous experiments [11-12] the electric field of about E<3kV/mm alters the integrated intensity of Bragg reflections in the order of 1% only. Therefore the combination of X-ray diffraction with the electric field modulation technique is suitable for these studies because of the eliminations of experimental fluctuations. Generally, the modulation technique is useful for the study of very small physical effects with high

accuracy. We have applied this method for studying the inverse piezoelectric effect in $\alpha - SiO_2$ and $\alpha - AlPO_4$. For the first time this experiment also was performed at low temperatures.

II. EFFECT OF AN EXTERNAL ELECTRIC FIELD ON BRAGG REFLECTIONS

When an external electric field is applied to the crystal, two strain effects (external and internal) have to be distinguished. The external piezoelectric effect is described by a third-rank tensor, which for point group $P3_121$ contains eight non-zero tensor components. Due to symmetry two of them, d_{111} and d_{121} are independent from each other. On macroscopic scale the external electric field **E** generates a strain ε_{ij} which is described by

$$\varepsilon_{ij} = d_{ijk}E_k + l_{ijkl}E_kE_l + \ldots \quad (1)$$

where d_{ijk} and l_{ijkl} are the coefficients of the linear electrostriction (inverse piezoelectric effect) and the quadratic electrostriction, respectively.
This external strain changes the unit cell parameters and subsequentely results in an angular shift of the Bragg peaks [10].
In the present case the peak shift for measured reflections is

$$\Delta\theta = -\varepsilon_{ij} \cdot \tan\theta_B \quad (2)$$

where θ_B is the Bragg angle.
The origin of the internal strain is the change of the fractional coordinates of atoms within the unit cell, which alters the integrated intensity of the Bragg reflections. The scattering intensity of a Bragg reflection is related to the structure factor, which for quartz is expressed by

$$F_{hkl}(T,E) = \sum_{i=1}^{3} f_{Si}T_{Si}\exp[2\pi(h(x_i(T)+\Delta x_{Si,i}) + k(y_i(T)+\Delta y_{Si,i}) + l(z_i(T)+\Delta z_{Si,i}))] + \sum_{j=1}^{6} f_OT_O\exp[2\pi(h(x_i(T)+\Delta x_{O,j}) + k(y_i(T)+\Delta y_{O,j}) + l(z_i(T)+\Delta z_{O,j}))]$$

where $f_{Si,O}$ are the complex atomic form factors corrected for anomalous dispersion, x_i, y_i, z_i are the fractional coordinates of atoms within the unit cell, $T_{Si,O}$ are the Debye-Waller factors of Si and O atoms and $\Delta x_i, \Delta y_i, \Delta z_i$ are the changes of the fractional coordinates of the atoms caused by the external electric field.
The measured quantity is the relative change of the integrated intensity $\Delta R/R$ caused by the external electric field E. Assuming kinematic scattering, i. e. weak reflections, and supposing all other quantities of the scattering, as absorption, dispersion ect., are independent of E, $\Delta R/R$ is proportional to the change of the structure factor square written by

$$\frac{\Delta R}{R} = \frac{F_E^2 - F_0^2}{F_0^2} \quad (4)$$

where F_E and F_0 are the structure factors measured with and without field, respectively.
For the evaluation of experimental data we neglect the effect, that the tabulated atomic form factors become changed by the electric field. For free atoms the effect is estimated to be in order of 10^{-5} at E=3kV/mm [11].

In the following we will concentrate us on weak Bragg reflections $F_{hkl} < 8$, where the structure factor is mainly given by the difference of the scattering phases of the Si and O atoms. In this case, kinematic and dynamical scattering theory give the same scattering intensities and extinction effects are negligible. Therefore, the measured intensities are independent from crystal perfection to a large extent. On the other hand, one can show that at present experimental conditions the relative change of the scattering intensity of strong reflections is equal or smaller than the accuracy achievable by the experiment. The uncertainty of structure analysis caused by the restriction to weak reflections has to be compensated by *reasonable* model assumptions.

III. EXPERIMENTS

As samples we have chosen $\alpha - SiO_2$ and $\alpha - AlPO_4$ single crystalline wafers with thickness of about 0.3mm, which were oriented in directions [110] and [100], respectively. The wafers were prepared from synthetic crystals being free from twins and stacking faults. Silver was evaporated as electrodes on both surfaces to prepare a capacitor. Using synchrotron radiation of the beamline D3 at HASYLAB/DESY with $\lambda = 0.76\,\mathring{A}$ a modulation technique [12] was used to record the intensity variations of the 9 Bragg reflections ((440), (550), (660), $(\bar{4}40)$,$(\bar{5}50)$,$(\bar{6}60)$, 500), (800) and (900))

of $\alpha - SiO_2$ and $\alpha - AlPO_4$ for external electric field strengths in the range -8kV/mm<E<8kV/mm. The scattering intensity of a particular Bragg reflection was recorded subsequently into three different channels of a multi-channel analyser. *Umweganregung* was excluded by ψ-scans. For better counting statistics each reflection was measured multiple times. The peak shift $\Delta\theta$ (see eq.2) was deduced from the angular difference of rocking curve maxima measured with and without the applied field.

The change of relative intensity Δ R/R (eq.4) was determined after integration of the intensites recorded in different channels. The same experiment was repeated at low temperatures using a wavelength of $\lambda = 0.53\,\mathring{A}$. For this experiment a displex system (APD Cryogenics Inc.) was additionally installed to the Huber 4-circle diffractometer. Here we measured the (440), (660), (500) and (900) reflections of $\alpha - SiO_2$ at temperatures between 50K and 300K.

IV. EXPERIMENTAL RESULTS AND INTERPRETATION OF THE ROOM TEMPERATURE DATA

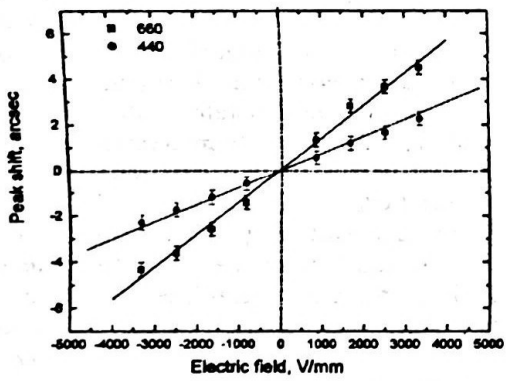

FIG.1 Peak shift of the (440) and (660) Bragg reflection

FIG.1 shows the electric field dependence of the observed peak shifts of the Bragg reflections of $\alpha - AlPO_4$. As for the other Bragg reflections a linear model fits the experimental data fairly well, a contribution of the quadratic electrostriction was not observed. The piezoelectric coefficients of $\alpha - SiO_2$ and $\alpha - AlPO_4$ were determined by least squares analysis of the experimental data points to eq.1 and eq.2 to be d_{111}=2.35(5)10^{-9}mm/V and d_{111}=3.6510^{-9}mm/V, respectively. Both values verify the literature data [13-15]. The field induced intensity variations of the reflections (440) and (660) of $\alpha - SiO_2$ are shown in FIG.2, for example.

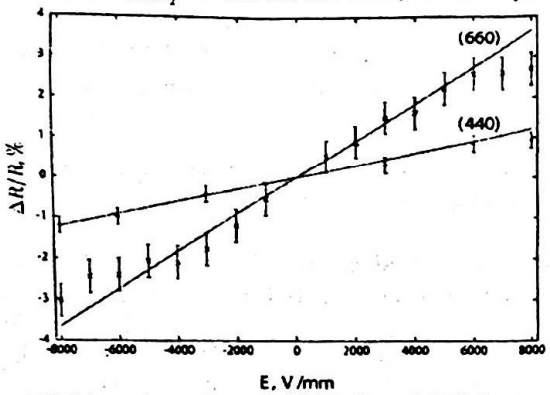

FIG.2 Intensity variations of the (440) and (660) Bragg reflection

As for the other measured reflections we observed an almost linear variation with electric field only up to 6 kV/mm (and not up to 8,kV/mm). As mentioned above, the widely used ionic model for $\alpha - SiO_2$ is not appropriate to explain our data. In the following we used the model of rotating tetrahedra, introduced in [11], but under consideration of a larger number of measured Bragg reflections compared to the previous study. High-resolution X-ray structure analysis has revealed that the Si-O bond in $\alpha - SiO_2$ is partially covalent. The respective charge density map (difference density)[3] emphasizes a charge accumulation between the silicon and oxygen atoms, which makes the bond stiff.

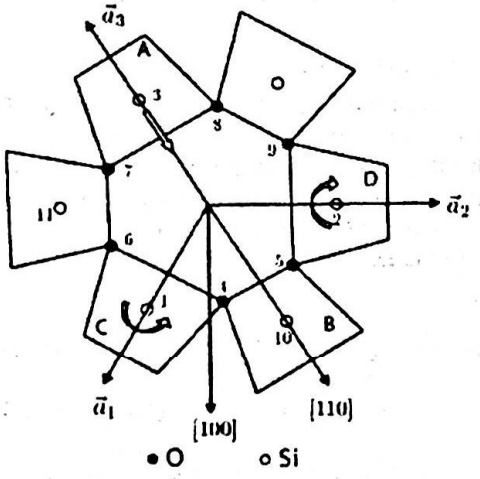

FIG.3 Model of the longitudinal inverse piezoelectric effect in $\alpha - SiO_2$

The O-Si-O angles are very close to those of ideal tetrahedra. Therefore, one can expect that

the field induced deformation of SiO_4 tetrahedra is small. FIG.3 demonstrates our model for the longitudinal inverse piezoelectric effect in $\alpha - SiO_2$. Here the electric field is directed parallel to [110] which corresponds to the direction of maximum longitudinal piezoelectric effect. For the calculation of the (hh0) structure factors in eq.3 one needs to consider changes of the x and y coordinates only. In another experiment the electric field is applied and measured parallel the [100] direction (not shown).

Here the calculation of the (h00) structure factors depends on the changes of the x coordinates only. For both directions the external piezoelectric effect is described solely by d_{111} and the number of independent parameters is reduced due to symmetry reasons. Altogether we have determined 9 independent parameters using 9 measured Bragg reflections using eq.3. In detail, we have fitted a straight line through the experimental data points $\Delta R / R(E)$ for each Bragg reflection measured and the respective functional forms are used for the further modelling.

The results of the simulation are shown as solid lines in fig.2. At E=3kV/mm the quality of modelling is estimated by a R-factor of about 0.16 where

$$R = \sum_{hkl}[(\Delta R / R_{model}) - (\Delta R / R_{exp})] / \sum_{hkl}(\Delta R / R_{exp})$$

Due to the restriction to (hk0) reflections the values for Δx_i and Δy_i could be determined from the experiment. The Δz_i values shown were calculated assuming the volume conservation of tetrahedra, i.\,e. the SiO_4 tetrahedra rotate as rigid objects against each other. For the [110] direction the results of modelling are explained in FIG.3. The tetrahedra "A" and "B" both rotate around the $\mathbf{a}_3$ -axis in the same direction and are shifted against each other. The tetrahedron "C" ("D") is rotated clockwise around $\mathbf{a}_1$, ($\mathbf{a}_2$) and is slightly shifted opposite to the electric field direction. The Si-O-Si bonding angles are changed as a consequence of the tetrahedra rotation. At E=3kV/mm the Si_1-O_4-Si_{10} (W_1) and Si_1-O_6-Si_{11} (W_2) bonding angles alter by 0.054deg and 0.020deg, respectively.

The angles between neighbouring tetrahedra decrease linear with increasing the electric field. The specific rotation amounts to (0.011 ± 0.002)deg.m/kV. Up to E≈6kV/mm the agreement between our model calculation and the experiment is fairly good (see FIG.2). At higher electric fields the measured intensity variation is no longer linear. This nonlinearity increases for higher-indexed reflections and may be caused by the increasing contribution of the distortion of tetrahedra, which is neglected in our model. For the [100] direction the fitted Δx_i values are by a factor of five less compared to those obtained for [110]. A specific rotation of tetrahedra was not deduced.

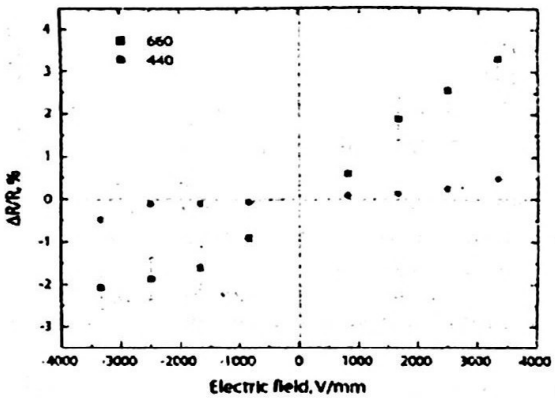

FIG.4 Intensity variations of the (440) and (660) Bragg reflection

The electric field induced intensity variation of the (440) and (660) reflections of $\alpha - AlPO_4$ is shown in FIG.4. For $\alpha - AlPO_4$ we used the same model as for quartz, the distinction of AlO_4 and PO_4 tetrahedra was not possible due to the small number of measured Bragg reflections. Consequently we considered that the rotation of both tetrahedra is same. The results can be explained by Fig.3, again, replacing both Si_1 and Si_3 by Al(P) and Si_2 by P(Al) between $0 \le z \le 1/2$ ($1/2 \le z \le 1$), respectively.

The results of simulation are shown as solid lines in fig.4. The main effect of the structure variation in $\alpha - AlPO_4$ is a change in the Al-O-P bonding angles.

In summary, at room temperature the atomic origin of the piezoelectric effect in quartz-like compounds can be described by the rotation angle between connected nearly rigid tetrahedra.

The rotation angle scales with the amount of the piezoelectric coefficient.

V. EXPERIMENTAL RESULTS AND INTERPRETATION AT LOW TEMPERATURES

The temperature dependence of selected Bragg reflections was studied at constant electric field strength of E=3kV/mm and temperatures between 50K and 300K.

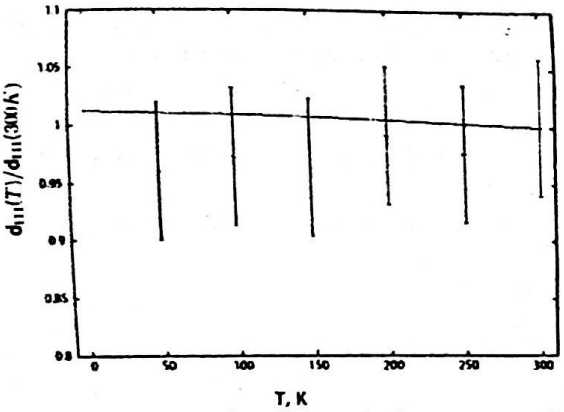

FIG.5 Temperature dependence of the experimentally determined piezoelectric coefficient of $\alpha - SiO_2$ compared with a theoreticalprediction

FIG.5 shows the temperature dependence of the experimentally determined piezoelectric coefficient of $\alpha - SiO_2$ compared with a theoretical prediction [16]. Considering the experimental uncertainty the experimental piezoelectric coefficient is constant within the temperature range of measurement. The theoretical calculation performed in terms of lattice dynamics predicts a small increase of d_{111} in the same direction [16]. Unfortunately no other experiment or calculation is known for comparison. FIG.6 shows the relative intensity variation of the (660) reflection of $\alpha - SiO_2$ as a function of temperature.

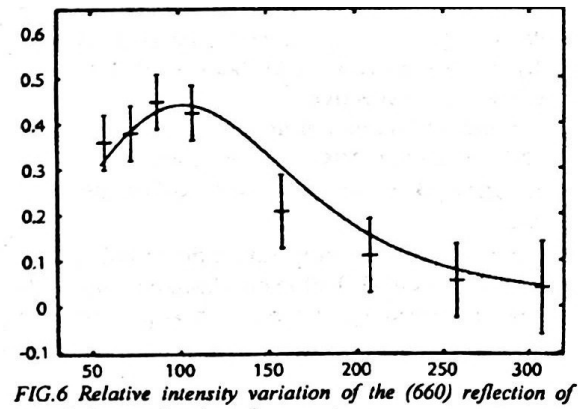

FIG.6 Relative intensity variation of the (660) reflection of $\alpha - SiO_2$ as a function of temperature

The internal strain effect increases for decreasing temperature.

This behaviour is no more a simple function of the tetrahedra rotation but depends on further parameters. The temperature dependence of the Debye-Waller factors alone cannot be responsible for the experimental finding because they affect F_E and F_0 in eq.3 equally. Moreover, as found by Le Page et al.[17] the SiO_4 tetrahedra do rotate already without an external electric field decreasing the temperature. Below 90K Lager et al.[18] have indicated an increase of the tetrahedral deformation. Both findings are essential for the explanation of the electric field dependence. In order to cancel the external strain the deformation of tetrahedra just has to compensate the polarization charge induced by the rotation of tetrahedra. That means an increasing rotation due to the electric field is compensated by a tetrahedron deformation. Another mechanism of cancelation could appear if the effective ionic charge alters with temperature. Unfortunately our experiment is not very sensitive to the change of the ionic charges. The solid lines in fig.6 were calculated using the temperature dependence of both the Debye Waller factors and the fractional coordinates from literature[17-18] and an additional atomic displacement caused by the electric field.

Compared to room temperature the tetrahedra "A" and "B" in fig.3 are rotated opposite to each other while the E-field always induces a rotation of both tetrahedra in the same direction. Between 300K and 90K the Si_1-O_4-Si_{10} bonding angle alters by 0.76deg due to the temperature effect [17] and by 0.094deg due to the electric field. At temperatures below 90K, where the intensity variation of quartz decreases with decreasing temperature we considered a small tetrahedra distortion in addition following the suggestion from [18]. The measured intensity variation can be interpreted by a temperature and an electric field dependent rotation of tetrahedra accompanied by an E-field induced deformation of tetrahedra

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