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Second Harmonic Generation Study of Field-Induced Changes in the Phase Transition of $K_{1-x}Li_xTaO_3$

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Abstract The phase transition in $K_{1-x}Li_xTaO_3$ with x=0.036 and x=0.063 has been investigated using optical second harmonic generation (SHG). The application of an electric field during cooling and heating shifts the phase transition to higher temperatures and increases the intensity of the frequency doubled light drastically. This can be interpreted as an increased mean size of ordered regions in the low-temperature domain state by the electric field. The shape of the tensor of the nonlinear susceptibility corresponds to a polar tetragonal low temperature symmetry. The temporal dependence of the SHG intensity upon application of an electric field yields an activation energy similar to that for the Li reorientation.

INTRODUCTION

In the incipient ferroelectric $KTaO_3$, small concentrations of impurities like Nb, Na, and Li are known to induce states of polar character at sufficiently low temperatures [1-3]. Because of its claimed dipole-glass behaviour, $K_{1-x}Li_xTaO_3$ (x=0.01..0.1) has gained considerable interest [4,5]. Since it was shown that Li ions occupy off-center positions when replacing K [6], several models for the low-temperature state of $K_{1-x}Li_xTaO_3$ have been suggested.

Dielectric and birefringence measurements on crystals containing 3.5 and 8 % Li, respectively, were interpreted in terms of a distortive phase transition at about 75 K in the case of the 3.5 % sample and of a ferroelectric phase transition at 97 K in the case of the 8 % sample [7]. Nuclear magnetic resonance and dielectric susceptibility data of samples with lower Li concentration indicated that the low-temperature phase exhibits glass-like behaviour [8]. That means that the randomly distributed interacting electric dipoles are freezing at random orientations when the sample is cooled down. Optical second harmonic measurements showed a clearly expressed thermal hysteresis for a 3.6 % sample signalling a first order phase transition [9]. Neutron scattering measurements revealed a temporal variation of the Bragg reflection intensities for a 1.7 % Li sample but no measurable time dependence for a 4 % sample [10]. This suggests a critical concentration below which samples behave glass-like. This critical concentration was found to be approximately 2.2 % by recent birefringence measurements [11,12].

Whereas presently the nature of the low temperature phase seems to be clear — albeit not in every detail — for low concentration samples, it is still discussed controversially for concentrations above 2.2 %. The presently predominant models are that of a dipole glass state up to Li concentrations of 4 % and a polar cluster state at higher concentrations [13,14] and that of a ferroelectric state with more or less long range order [15], which wasrecently interpreted as a random-field induced ferroelectric domain state [11,16], above 2.2 %. Here we present novel experimental results gained by optical second harmonic generation (SHG) measurements on samples with Li concentrations in the above range of interest.

EXPERIMENTAL

Most of the experiments mentioned above probe parameters — as e. g. birefringence — which are proportional to the square of the dielectric or ferroelectric polarization. Because of its third rank tensor behaviour and its coherence properties, optical second harmonic generation, in addition, is sensitive to the direction of the polarization, so being able to investigate e. g. antiparallel ordered dipolar regions. Such 180°-domain arrangements had been proposed for the explanation of Raman measurements [17] in the high concentration regime.

Our SHG experiments were performed on $K_{1-x}Li_xTaO_3$ samples containing 3.6 % and 6.3 % Li , respectively. As fundamental beam served a pulsed Nd:YAG laser (peak power $\approx$ 10 kW, repetition rate 1 kHz), the generated second harmonic light was detected using standard Boxcar techniques. A moderate electric field (up to 400 kV/m) could be applied on the samples perpendicularly to the light beam direction, both being fundamental cubic directions. In a He-cryostat the samples were cooled and heated over the phase transition region with adjustable speed of the temperature variation.

RESULTS and DISCUSSION

A visual inspection of the samples revealed a macroscopic 90°-domain structure below the phase transition, obviously caused by built-in strain fields. This macroscopic domain structure wasn't changed much when electric fields up to 400 kV/m were applied during the cooling procedure. In contrast to this macroscopic domain structure, the intensity of the generated second harmonic light showed a drastic increase with applied electric field. Some of the measured intensity curves are depicted in fig. 1 for the two samples.

A clearly expressed hysteresis at the smeared first order phase transition shows up which tends to vanish at higher fields. The phase transition itself is shifted to higher temperatures with increasing electric field. This behaviour is consistent with that measured by birefringence measurements [11]. The low temperature intensity for the 3.6 % sample versus the applied electric field is sketched in fig. 2. An increase by a factor 300 is found

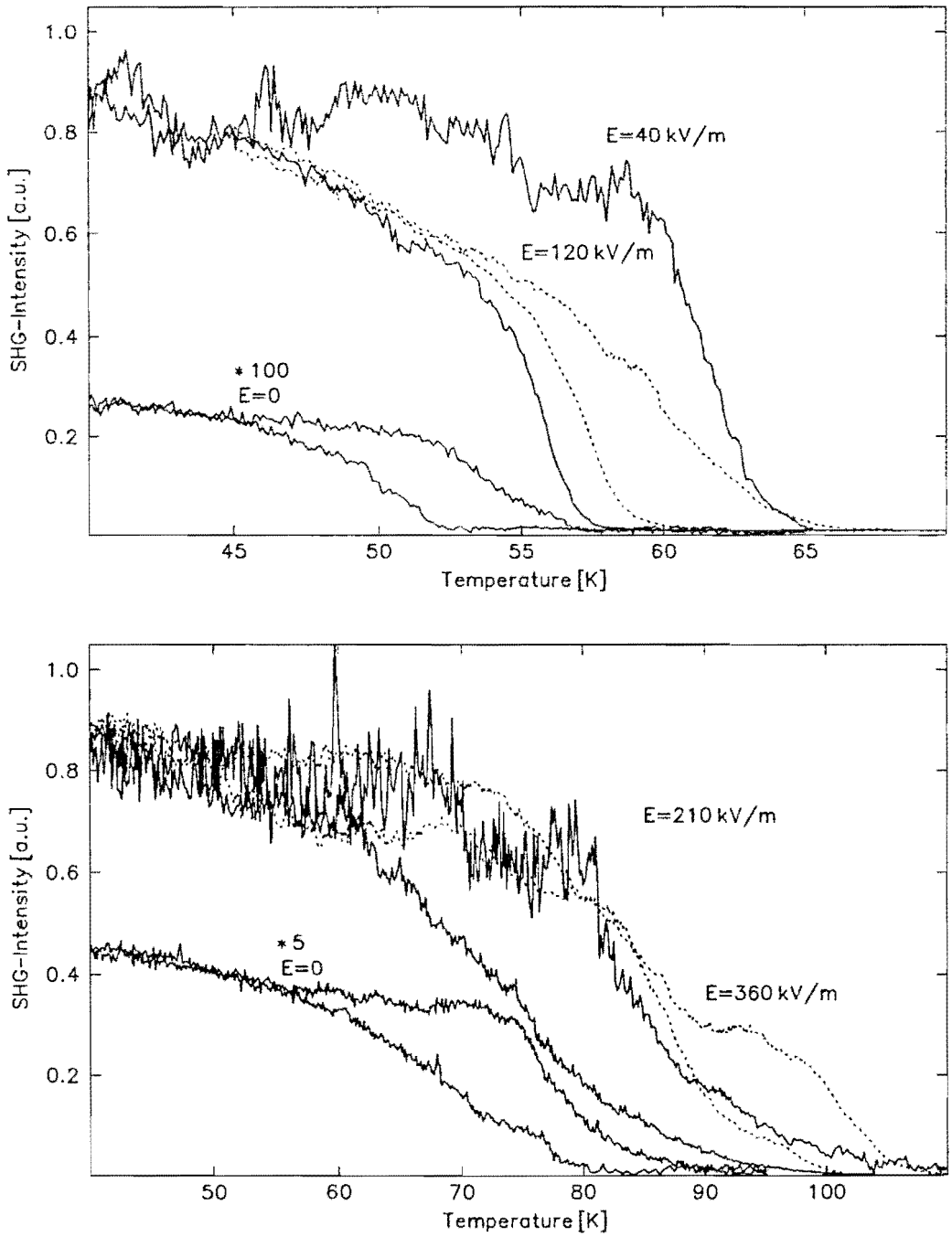

Figure 1: Temperature dependence of the SHG intensity for different electric fields. Upper: 3.6 % Li, lower: 6.3 % Li

for this sample, a similar albeit not so expressed increase by a factor of 10 for the 6.3 % sample. No such increase is found e. g. in birefringence measurements[11]. As birefringence is proportional to the square of the polarization, it can be excluded that the increase in SHG intensity is due to an increase in the absolute value of the local polarization. So the only possible explanation for this growing intensity is an increase of the mean size of ordered regions within the visible domains. For sizes larger than the coherence length for second

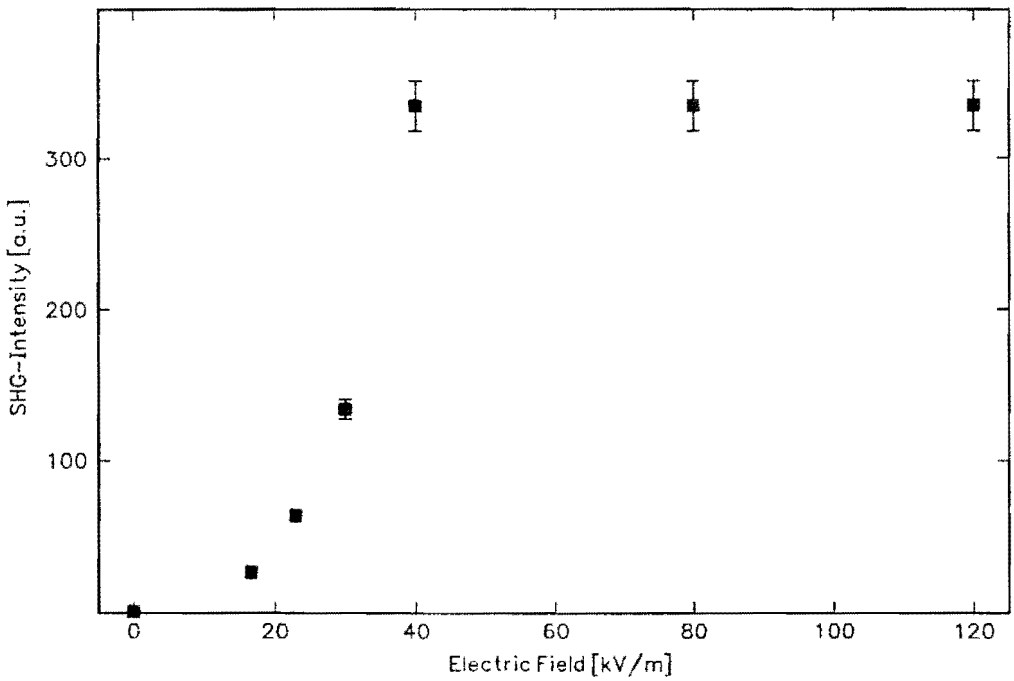

Figure 2: Field dependence of the low temperature SHG intensity for the 3.6 % sample at T = 40 K

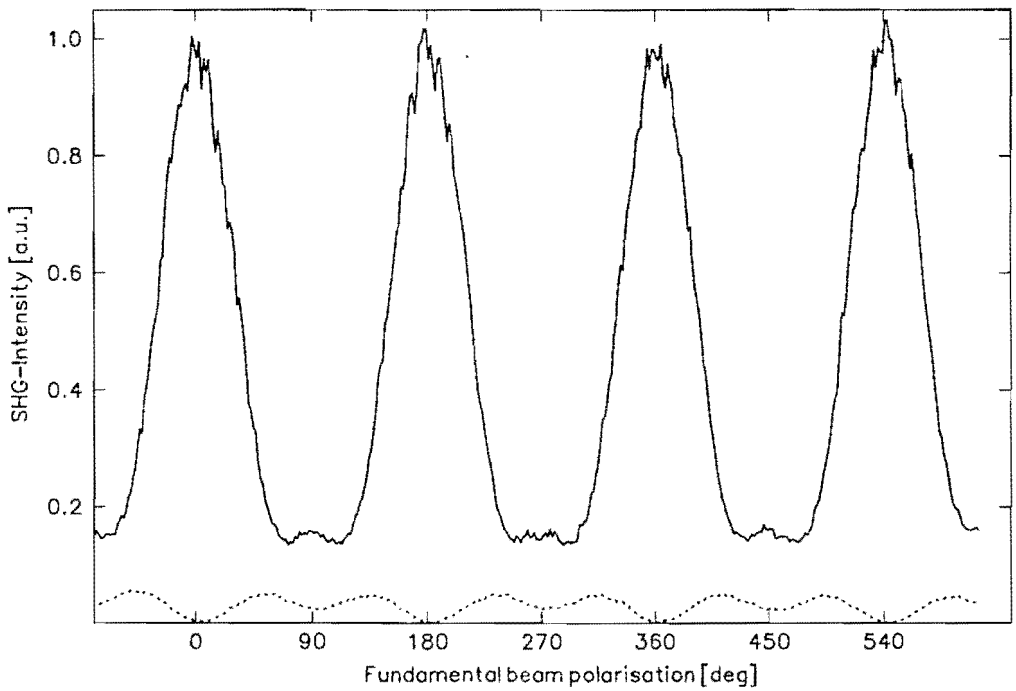

Figure 3: Input polarization dependence of the SHG intensity for output polarized parallel (upper curve) and perpendicular (lower curve) to the applied field (E = 80 kV/m) for the 3.6 % sample

harmonic generation the intensity remains constant.

In a simple model [19] the intensity could be assumed to be proportional to the square of the mean size of ordered regions. This allows to estimate the region size to be about 0.2 μm and 1 μm for the 3.6 and 6.3 % samples, respectively, when cooled down under zero electric field. Similar sizes had been derived from Raman scattering results [18].

Measurements in the low temperature phase (cooled under applied electric field) with fixed second harmonic light polarization under rotation of the polarization of the fundamental beam revealed a characteristic dependence depicted in fig. 3. This measured angular dependence is consistent with a polar tetragonal low temperature symmetry where the intensities should behave according to

$$I_{2\omega,\parallel}(\varphi) \propto I_\omega^2\{d_{31}^2 \sin^4\varphi + d_{33}^2 \cos^4\varphi + V d_{15}^2 \sin^2 2\varphi\}$$

$$I_{2\omega,\perp}(\varphi) \propto I_\omega^2\{V d_{31}^2 \cos^4\varphi + V d_{33}^2 \sin^4\varphi + d_{15}^2 \sin^2 2\varphi\}$$

for second harmonic polarization parallel and perpendicular to the direction of an applied electric field (φ: angle between fundamental beam polarization and applied electric field, d_{il}: elements of the tensor of the nonlinear susceptibility, V: ratio factor for the contribution of 'unpoled' regions). The measured curves can be exactly fitted by these dependencies, the relative sizes of the d_{ij} derived from the fit are $d_{15} \approx d_{31} = 0.4 \cdot d_{33}$.

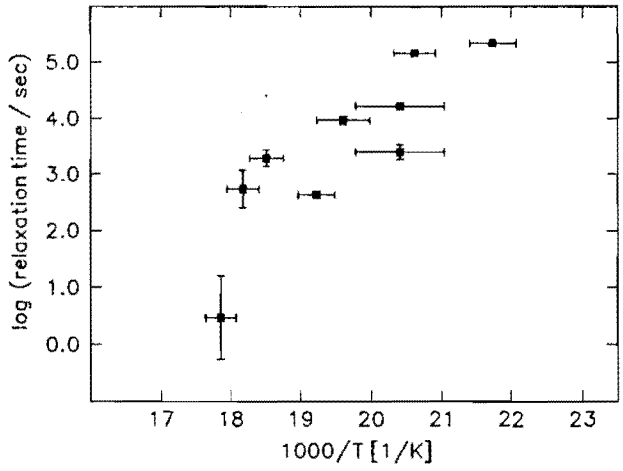

Figure 4: Temperature dependence of the polarization relaxation time in $K_{1-x}Li_xTaO_3$ containing 3.6 % Li.

To get more information concerning the dynamics, field switching experiments were performed at different temperatures. In these experiments, the sample was cooled down under zero electric field from temperatures far above the phase transition region, the temperature then was kept constant, an electric field of about 80 kV/m was switched on, and the temporal development of the second harmonic intensity was measured. Far below the zero field phase transition temperature, no temporal intensity change could be measured, which indicates that at these temperatures the polarization configuration is frozen. At higher temperatures up to the nonzero field phase transition temperature, an exponential-

like temporal intensity increase was found. The characteristic time constants are shown in fig. 4. In a small temperature region an Arrhenius-like behaviour with an activation energy of about 0.1 eV can be stated. This activation energy is very close to that for reorientation of single Li dipoles[8,20] which clearly indicates that the polarization relaxation is dominated by the dipole dynamics of the Li impurities.

CONCLUSION

Optical second harmonic generation measurements show that the low temperature phase of $K_{1-x}Li_xTaO_3$ ($x \geq 3.6$ %) exhibits a strain-induced domain structure. These visible 90° domains consist of polarized regions aligned in antiparallel directions. With zero applied field, the mean size of these regions is about 0.2 μm for 3.6 % and 1 μm for 6.3 % Li content. The local symmetry of the polarized regions is tetragonal, the activation energy for polarization relaxation corresponds to that for Li reorientation. Both facts allow the conclusion that the polarized regions are clusters of polarized matrix[21] surrounding parallel orientated Li dipoles. Applying an electric field during the phase transition increases the mean cluster size at least up to sizes larger than the coherence length for SHG.

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