Optical Properties of Li Doped KTaO$_3$
Using Spectroscopic Ellipsometer

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Optical Properties of Li Doped KTaO$_3$ Using Spectroscopic Ellipsometer

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Measurements of complex refractive indices $n^* = n - ik$ are performed on pure KTaO$_3$ and K$_{0.93}$Li$_{0.07}$TaO$_3$ single crystals by using a spectroscopic ellipsometer in temperature range from room temperature to 10 K. At room temperature, experimentally obtained complex dielectric constants $\varepsilon^* = \varepsilon_1 - i\varepsilon_2$ of both crystals are analyzed by the classical Drude model. Temperature dependence of the imaginary part $\varepsilon_2$ of K$_{0.93}$Li$_{0.07}$TaO$_3$ shows a small but distinct change around 70 K. The origin of the anomalous behavior is discussed.

Keywords Quantum paraelectrics; relaxor; ellipsometry; complex refractive index; potassium lithium tantalate

I. Introduction

It is known that KTaO$_3$ (KTO) exhibits specific physical properties particularly at low temperature. One of them is the quantum paraelectricity: The dielectric constant increases toward 3000 with decreasing temperature, but a ferroelectric phase transition does not take place down to near 0K [1]. This phenomenon is thought to be caused by the zero point vibration which prevents the freezing of low-lying TO phonon. External stimuli, e.g., electric field or stress, easily induce the phase transition. It is experimentally confirmed that a small substitution of Li ions into KTO induces the polar state [2, 3, 4]. Concerning the polar state, Toulouse et al. pointed out that Li-doped KTO (KLT or KLT x% with Li molar concentration x) is a relaxor by their measurements of dielectric susceptibilities and neutron diffuse scatterings [5, 6]. We performed second harmonic generation (SHG) microscopic observations of KLT 2.8% and found out that the SH intensities show a history dependence and an extremely slow kinetics under an electric field [7]. These results support that KLT belongs to a relaxor. Additionally, we carried out the same kind of experiments on KLT 7% and confirmed that the polar state evolution also depends on the history which the sample
undergoes. In zero field heating (ZFH) after zero field cooling (ZFC) process, no remarkable SH intensity appears in the whole temperature range. On the contrary, strong SH intensity is generated at low temperature and decreases with increasing temperature in FH after FC process. In FH after ZFC process, weak SH intensity observed at low temperature begins to increase around 80 K, shows a peak at 85 K, and then vanishes at 90 K. These results indicate that KLT 7% is also a relaxor.

Pb(Mg$_{1/3}$ Nb$_{2/3}$) O$_3$ (PMN) is a well known prototype relaxor. Burns et al reported that the refractive index begins to deviate from the linear temperature dependence at a characteristic temperature $T_d$ (Burns temperature) which is much higher than the dielectric peak temperature [8]. They explained that the deviation just below $T_d$ originates from the locally developed polar nano regions (PNRs): The average of squared polarization $<P^2>$ is not zero though $<P>$ vanishes. So the refractive index changes via the second order electro-optic effect.

Another characteristic property of KLT is the occurrence of photocurrent at low temperature, although nominally pure KTO does not exhibit the effect [9]. The appearance of photocurrent in KLT is interpreted by the existence of shallow O$^{2-}$ levels which prevents the recombination of holes and electrons. The relationship between the electronic structure and PNR is also an important issue to be solved.

With these facts in mind, we measure temperature dependences of the complex refractive indices of KTO and KLT7% single crystals by a spectroscopic ellipsometer. As far as we know, few reports exist on the ellipsometric observation with single crystals, in particular, on temperature dependence of it. In this sense, the present study would provide a new approach to the structural phase transitions phenomena accompanied by changes of electronic structure.

II. Experimental

Two single crystals, KTO and KLT7%, were used as specimens. KTO single crystal was grown by the Czochralsky method and KLT7% by a self flux method. The Li concentration of KLT was determined from the empirical relationship between $x$ and electric field-induced transition temperature $T_0 : T_0 = 535(x/100)^{3/2}$ [10]. $T_0$ is defined as the temperature where the SH intensity disappears in ZFH after FC process. We perform the measurements in Geneva University using a spectroscopic ellipsometer, the fundamental wave number of which can be varied from 6000 to 37000 cm$^{-1}$.

An ellipsometer is usually used to measure the thickness and complex refractive indices of thin films and special cares are needed when it is applied to single crystals. One of the most serious problems is the influence of multiple reflections from a back surface. To reduce the effect, we prepare thick samples whose thickness are more than 1 mm and make the back surfaces non-polish. Nevertheless, the treatment is not enough to avoid the back surface reflection perfectly. So we polish the back surface to make the sample in wedge-form in the case of KLT7%.

The ellipsometer measures the ellipticity $\Psi$ and the phase difference $\Delta$ between S and P reflective waves. From these values, we obtain the real part $n$ and imaginary part $\kappa$ of the complex refractive index [11]

\[
n \sim -\frac{\sin \theta_i \tan \theta_i \cos 2\Psi}{1 + \sin 2\Psi \cos \Delta}, \quad \kappa \sim \tan 2\Psi \sin \Delta
\]  

(1)
where $\theta_i$ is the incident angle. For applying the above relation to our measurements, we do not take the back surface reflection into account, as the influence is sufficiently removed as a result of the above-mentioned treatment.

We first perform the measurement at the room temperature in the range of wave number from 6000 to 37000 cm$^{-1}$ in 500 cm$^{-1}$ step. Second, we choose some wave numbers and measure temperature dependences of $\Psi$ and $\Delta$ at the wave numbers in ZFC and ZFH processes. A special care is paid for the history dependences of $\Psi$ and $\Delta$ since SH intensity of KLT 2.8% strongly depends on the history. So we measure them at the same wave numbers in both ZFC and ZFH processes. After confirming that $\Psi$ and $\Delta$ do not show history dependence, different wave numbers are used for each process. In pure KTO, the measurements are performed with 17 wave numbers (from 6000 to 30000 cm$^{-1}$ and 31000 to 37000 cm$^{-1}$ in 2000 cm$^{-1}$ step). For KLT 7%, 10 wave numbers (from 7000 to 11000 cm$^{-1}$, from 12000 to 20000 cm$^{-1}$ in 2000 cm$^{-1}$ step, and 25000, and 30000 cm$^{-1}$) are chosen.

### III. Results and Discussion

The wave number $K$ (cm$^{-1}$) dependences of $\varepsilon_1$ and $\varepsilon_2$ at room temperature are shown in Fig. 1, where (a) and (b) indicate the results of pure KTO and (c), and (d) those of KLT7%. We calculate $\varepsilon_1$ and $\varepsilon_2$ by using the following relations between the complex dielectric constant and the complex refractive index: $\varepsilon = \varepsilon_1 - i\varepsilon_2$, $n^* = n - i\kappa$ and $\varepsilon = n^2$.

![Figure 1](image)

**Figure 1.** Wave number dependences of complex refractive indices of KTO and KLT7%. (See Color Plate IX)
In Fig. 2, we show the temperature dependences of $\varepsilon_1$ and $\varepsilon_2$ of KTO at some wave numbers. In KTO, as expected, neither $\varepsilon_1$ nor $\varepsilon_2$ shows the anomaly in the whole temperature region. This phenomenon is consistent with the fact that KTO is an incipient ferroelectrics. Fig. 3 shows the temperature dependences of $\varepsilon_1$ and $\varepsilon_2$ of KLT7%. $\varepsilon_1$ increases with decreasing temperature. On the other hand, $\varepsilon_2$ decreases upon cooling, and shows a slight change of inclination around 70 K. First, we fit these experimental results with the Drude-Lorentz model at room temperature

$$\varepsilon = \varepsilon_\infty + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

where $\varepsilon_\infty$, $\omega_p$, $\omega_0$ and $\gamma$ mean high-frequency dielectric constant, plasma frequency, proper frequency and line width, respectively. As the result of fitting, we obtain in pure KTO, $\varepsilon_\infty = 3.03$, $\omega_p = 51302$ cm$^{-1}$, $\omega_0 = 40723$ cm$^{-1}$, $\gamma = 5385.3$, and in KLT 7%, $\varepsilon_\infty = 3.11$, $\omega_p = 50389$ cm$^{-1}$, $\omega_0 = 40029$ cm$^{-1}$, $\gamma = 4430.6$. No significant difference is observed between KTO and KLT 7% at room temperature. At low temperature, it is difficult to fit the data since higher wave number data are needed.

The present experiment reveals that $\varepsilon_2$ of KLT7% shows a slight but distinct change around 70 K ($T^*$). $T^*$ is about 20 K lower than the temperature at which SH intensity appears in FH after ZFC process, and 60 K below $T_d$. The fact indicates that $T^*$ is related neither to the ferroelectric phase transition nor to Burns temperature. On the other hand, the
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photoconductivity of KLT5% is reported to appear around 70 K [9]. Therefore, the change in $\varepsilon_2$ at 70 K may be related to the change in the electronic state and not in the structural one. In fact, our analyses of the present experiments reveal that the plasma frequency changes at $T^*$. We are going to measure $\varepsilon_1$ and $\varepsilon_2$ in higher wave number region to confirm the fact.

In summary, we successfully measure the real and imaginary parts of complex dielectric constant of KTO and KTL7% single crystals by using a spectroscopic ellipsometer. At room temperature, the classical Drude-Lorentz analysis is applied and some optical parameters including plasma frequencies, and proper frequencies are determined for both crystals. The temperature dependences of $\varepsilon_1$ and $\varepsilon_2$ are measured from room temperature to 10 k and a small but distinct change is found around 70 K in $\varepsilon_2$, which is most probably related to the change in the electronic state related to the photoconductivity.

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