A ‘soft electronic band’ and the negative thermooptic effect in strontium titanate

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Abstract. The optical functions of strontium titanate (SrTiO$_3$) (STO) single crystals were determined with spectroscopic ellipsometry in the 1–6 eV spectral region and the 4.2–300 K temperature region. On approaching the band gap edge, the optical absorption shows Urbach tail behavior followed by the onset of indirect optical transitions starting at $\sim$3.2 eV and extending up to $\sim$3.68 eV; then direct transitions are very well seen. The refractive index and its temperature and spectral dependences were obtained. In the visible region, the refractive index rises on cooling (negative thermooptic effect) down to 50 K, saturating at lower temperatures. The energy of indirect interband optical transitions increases on cooling up to 3.23 eV at 100 K. The observed magnitude $\partial E/\partial T = -1.7 \times 10^{-4}$ eV K$^{-1}$ is typical of ionic crystals. Surprisingly, the absorption edge in the region of the lowest direct interband optical transitions 3.7–4 eV shifts to lower energies on cooling. It is concluded that the presence of this ‘soft electronic band’ together with the rise in absorption intensity at 4.8 eV is responsible for the increase of refractive index on cooling, elucidating the origin of the negative proper thermooptics in STO.
1. Introduction

Strontium titanate (SrTiO$_3$) (STO) is a very popular and thoroughly studied model that is representative of the family of ABO$_3$ oxides and related materials [1]. At room temperature (RT) it adopts the cubic $O_h^1$ perovskite-type structure. At $T_C \approx 105$ K, it undergoes a second order antiferrodistorsive (AFD) cubic–tetragonal $O_h^1 \rightarrow D_{4h}^{18}$ structural transition with condensation of the $R_{25}$ mode [2, 3]. The dielectric permittivity strongly rises on cooling, the lowest TO$_1$ phonon mode softens (incipient ferroelectricity) and the STO paraelectric central inversion phase nearly loses stability. However, in the low-temperature region of dominating quantum statistics, the ferroelectric instability is inhibited and the paraelectric phase is maintained due to quantum mechanical effects (quantum paraelectricity) [4, 5]. Owing to the unique and abundant properties of STO, a variety of the basic phenomena of solid state physics, phase transitions and ferroelectricity have been recognized during STO studies. Therefore, gaining better knowledge about this topical model material is extremely important and so STO continues to be the subject of active research. Surprisingly, there are still some basic properties of STO that have been studied only scantily and their nature remains unclear. In this paper, we focus our attention on elucidating the nature of such a relatively unusual and unclear phenomenon—the negative thermooptic effect (TOE) in STO, which has been recognized by Pisarev et al [6].

The temperature dependence of the refractive index (the TOE) of STO has been studied at temperatures above RT in [7, 8] and in more detail within the wide temperature range of 20–900 K in [6], [9]–[12]. It is known [13]–[16] that in mechanically non-clamped crystals without phase transitions, the changes of the dielectric permittivity tensors, which control the changes of the principal values of the refractive index $\delta n_i$, are connected with changes of $B_{ij}$ as $\delta n_i = -(n_i^3/2)\delta n_{ij}$, and the form of the expression depends on the actual crystal symmetry. In the case of cubic crystals, the formula for variation of the refractive index can be written as

$$\Delta B_{ij} = (\mu_{ij} + p_{ijkl}\alpha_{kl})\Delta T,$$

where $\mu_{ij}$ is the thermooptical tensor of the mechanically clamped crystal, which describes temperature-dependent changes of the refraction at constant crystal size, $\alpha_{kl}$ is the thermal expansion coefficient, and $p_{ijkl}$ is the photoelastic coefficient—components of the tensor that determine, in the general case, the increment of $B_{ij}$ under mechanical deformation. Changes of the principal values of the refractive index $\delta n_i$, are connected with changes of $B_{ij}$ as $\delta n_i = -(n_i^3/2)\delta B_{ij}$, and the form of the expression depends on the actual crystal symmetry. In the case of cubic crystals, the formula for variation of the refractive index can be written as

$$\Delta(\delta n(T)) = -n_i^3/2(\mu + (p_{11} + 2p_{12})\alpha)\Delta T.$$

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The second term in equation (1) defines the change in the refractive index caused by the photoelastic effect due to thermal expansion (photoelastic contribution). The term $\mu_{ij} \Delta T$ defines the temperature-dependent variation of the refraction because of isochoric electron–phonon interaction, which is not connected with thermal expansion, and therefore it can be considered as a ‘proper’ thermooptical contribution. Further investigating the thermooptical mechanism of the temperature changes of the refractive index, we should take this effect into account. It should be mentioned that in the literature the term ‘thermooptical’ is sometimes used for denoting the total (photoelastic and ‘proper’ thermooptical) contributions to $\Delta n(T)$. Analysis of the literature and our experimental data shows that the photoelastic coefficients $p_{ijkl}$ as a rule have sufficiently weaker temperature dependence in comparison with $\mu_{ij}$ and $\alpha_{kl}$ [13, 17]. Comparison of the temperature dependences of the refractive index and thermal expansion has been carried out for CaF$_2$, KBr, NaBr, KCl, NaCl and KI crystals with a dominant photoelastic contribution in a wide temperature region, 100–450 K [18]–[21]. It was shown that $\Delta n(T)$ varies in proportion to thermal expansion, and the proportionality coefficient corresponds to that calculated from the data on photoelastic constants. We have analyzed the experimental data of [22] for BaF$_2$, CdF$_2$, NaF and came to the same conclusion. So, the photoelastic contribution to the temperature-dependent changes of the refraction of light can be calculated from independent measurements of photoelastic coefficients at RT and thermal expansion. As a rule, (at positive values of $p_{ijkl}$) this mechanism leads to reduction of the refractive index with increasing temperature. For dielectrics, to which class the materials considered here belong, temperature variations $\Delta n(T)$ are mainly caused by the thermooptical effect connected to the $\mu_{ij}$ tensor. In contrast to the photoelastic contribution $\Delta n(T)$, the thermooptical contribution cannot be determined experimentally from independent experiments. The latter can be obtained only as the difference between a measured full change of $\Delta n(T)$ and the photoelastic contribution. Calculation of the temperature dependence of the thermooptical contribution $\Delta n^{\text{TO}}(T)$ to variation of the refractive index is the main problem for the full $\Delta n(T)$ approximation. The first serious attempt at a microscopic calculation of $\Delta n^{\text{TO}}(T)$ was undertaken in [15] using the temperature dependence of the dispersion parameters of the Sellmeier-type one-oscillator formula expressed via the Debye–Waller factor. However, in that work, the value of $(dn/dT)^{\text{TO}}$ was calculated only at RT, although quite satisfactory agreement with experimental results for a series of semiconductors, in which TOE plays a dominant role in the $\delta n_i(T)$ dependence, was obtained. Pisarev et al [6], based on their own measurements of the temperature dependence of the refractive index in STO and photoelastic tensor values [23], showed that ‘proper’ TOE in STO is negative and of large magnitude. According to the Kramers–Kronig relationship, the magnitude of the refractive index in the transmission region is controlled by the main resonances of the imaginary part of the dielectric permittivity. Temperature variations of the refractive index are determined by the temperature changes of these resonances, particularly due to isochoric electron–phonon interaction. In most cases, temperature shifts of the main resonances correspond to the temperature shift of the optical forbidden gap, i.e. the respective direct and indirect transitions; this is shown in our work.

Such a large negative proper TOE in STO needs a special explanation. As was argued in [6], one can think of a possible role of phonons’ contribution to electron–phonon interactions as responsible for TOE. Indeed, in STO, the strongest temperature changes in the phonon spectrum occur in the low-frequency region of $\omega < 100 \text{ cm}^{-1}$, due to softness of the TO$_1$ mode $\omega_{\text{TO1}}$ (soft mode). The other five modes remain hard. However, since the TO$_1$ mode softens on cooling, it
should lead to a decrease of the refractive index. This disagrees with experiment and leads to the conclusion that only electronic contributions control the negative TOE in STO [6]. Moreover, according to [24], the energy of the band edge optical transitions in STO increases on cooling, promoting a decrease of the refractive index. Therefore, Pisarev et al [6] suggested the presence of an internal ‘soft electronic band’ whose energy decreases on cooling. Nevertheless, such a soft electronic band has never been observed to date. Inspired by this long-term challenge, we have undertaken spectral ellipsometric studies of the optical properties of STO in wide spectral and temperature regions in order to elucidate the nature of the negative TO effect. Besides, in our opinion, there is an obvious lack of detailed data on temperature evolutions of the interband and near band-edge transitions in STO. Most of the available results have been obtained by the spectrophotometric technique (see e.g. [25]–[30]). Since these studies were hampered by the necessity of using a set of equivalent quality specimens of different thicknesses, it is very difficult to obtain detailed and reliable data in the region of direct optical transitions and large values of the absorption coefficients. Hence, the spectral ellipsometry technique appears to be quite suitable.

2. Experimental

Nominally pure, strain-free high-quality top seed solution grown STO single crystals were supplied by the University of Osnabrueck. Ellipsometric spectra were collected with a J A Woollam variable-angle spectroscopic ellipsometer, assembled with a continuous flow Janis UHV cryostat system operating in the 1200–200 nm (1–6 eV) spectral range. The refractive index at the wavelength $\lambda = 600$ nm (2.1 eV) was measured in the temperature range 4.2–300 K. To avoid the problems connected with AFD-phase transition, symmetry changes, domain formation and related effects, optical constant spectra in the region 2.5–6 eV were measured in the cubic phase only (300–110 K). Experimental specimens were prepared as optically polished \{100\} oriented platelets $6 \times 6 \times 2$ mm$^3$ in size. The resulting surface roughness was $\lesssim 2$ nm. To eliminate the depolarizing effects of back-surface reflection, the back surface of specimens was mechanically roughened. The ellipsometric spectra were analyzed with the WVASE32 software package. For optical constants calculations, a generalized multioscillator model was used. Surface roughness was also taken into account as a Bruggeman effective medium [31]–[33] assuming 50% voids and 50% STO.

3. Results and discussion

Conventionally, interband optical spectra experiments are treated on the basis of classical theoretical calculations (e.g. [34]–[36]) and later ones (e.g. [37, 38]). It was established that the upper valence band (VB) for the bulk STO is quite flat, with the top at the M and R points of the Brillouin zone (BZ), and almost perfectly flat upper VB between these points. The bottom of the lowest conduction band (CB) lies at the $\Gamma$ point, with energy very close to the X point. The dispersion curve between these $\Gamma$ and X points is very flat. The upper VB consists of O 2p atomic orbitals with a small admixture of d-orbitals of Ti atoms, whereas the CB bottom consists essentially of Ti d$e$ orbitals. The orbital contribution from Sr atoms is negligible in this energy range. The Sr orbitals make a significant contribution to the DOS only at high energies in the CB. Figure 1 shows the resulting complex index of refraction ($n^* = n + ik$) of STO crystals as determined from the spectroscopic ellipsometry measurements at RT.
Figure 1. The complex index of refraction for the bulk STO determined from spectroscopic ellipsometry measurements.

Figure 2. Spectral dependence of the absorption coefficient of STO crystals, calculated by using $a = (4\pi k)/\lambda$.

The obtained value of the real part of the refractive index at 2.06 eV (600 nm) is 2.38. It agrees well with both the reflectance spectra of Cardona [39] and the ellipsometric results of Zollner [37]. It is seen that refraction in the visible region is controlled by three refractive index maxima located at 3.88 eV (320 nm), 4.10 eV (302 nm) and 4.66 eV (266 nm). This is very similar to the observation of Cardona [39], who reported and classified unresolved reflectivity maxima $A_1$ at 4.00 eV and $A_2$ at 4.86 eV, and attributed them to $X_4/X_5 \rightarrow X_3$ and $X_5' \rightarrow X_5$ direct band gap transitions, respectively.

Figure 2 shows the absorption coefficient spectrum determined from the ellipsometry measurements using the conventional formula $a = (4\pi k)/\lambda$. In the main features the absorption...
Figure 3. Temperature dependence of the refractive index in STO crystals ($\lambda = 600$ nm).

spectrum agrees well with those reported by Cardona [39]. However, the absorption coefficient spectra could not be determined with sufficient accuracy below 3.2 eV, where the obvious presence of the long Urbach-like exponential absorption tail near the absorption edge is seen. This exponential tail spreads with the absorption coefficient rising up to $\sim 100$ cm$^{-1}$ (e.g. Zollner [37]), followed by a region of indirect transitions at higher energies. The value of the lowest indirect band gap, determined as the intercept of the linear fit line to a plot of $\alpha^{1/2}$ versus energy for the absorption coefficient in the range of $1600$ cm$^{-1} < \alpha < 9100$ cm$^{-1}$ (where a linear fit works well), was found to be $E_i = 3.198$ eV. This agrees well with indirect transition values reported in [30, 37] and is close to those in [24, 25, 38]. Taking into account these experiments and calculations [34]–[38] we attribute the indirect optical absorption edge of STO to the $R_{15'} \rightarrow \Gamma_{25'}$ transitions. Detailed analysis shows the possibility of another indirect transition with energy 3.64 eV, which also agrees with the results in [24] and can be attributed to the deeper $M_{51} \rightarrow \Gamma_{52'}$ indirect transition. At higher energies, up to about 5 eV, the absorption coefficient obeys the relationship $\alpha h\nu^2 \sim h\nu - E_d$ evidencing direct optical transitions with energies 3.75, 3.81, 3.9 and 4.34 eV. They can be tentatively attributed to direct gaps between the $\Gamma$ (as in [24, 37, 38]) and $X$ (as in [24, 39]) points of the BZ. A shoulder at $\sim 4.8$ eV and the broad absorption at higher energies are consistent with $A_2$ and $A_3$ reflectivity spectral maxima [39]. They can be due to direct interband optical transitions in $X$ and/or $M$ points of the BZ. Thus, our results at RT agree well with the experimental and theoretical works available on STO crystals and supplement them, proving the correctness of the obtained data.

Figure 3 presents the temperature dependence of the refractive index for STO single crystals taken at $\lambda = 600$ nm. In agreement with [6, 39] the value of the refractive index rises linearly, on cooling, to 2.424 at 50 K and saturates at the lowest temperatures. As in [6], only a faint feature of refractive index behavior can be seen in the region of the AFD structural phase transition. Figure 4 presents the absorption coefficient spectra taken at different temperatures and the temperature dependence of the indirect band gap energy calculated from ellipsometric data. Respective temperature dependences of the indirect and direct (tentatively $\Gamma \rightarrow \Gamma$ [38]) transition energies are shown in figures 5(a) and (b).
Figure 4. Absorption coefficient spectra of STO at different temperatures.

Figure 5. Temperature dependences of the indirect (a) and direct (b) optical transitions calculated from ellipsometric data.

It is seen that the energy of indirect transitions increases, on cooling, to 3.23 eV at 100 K, with a value of the thermal coefficient $\partial E/\partial T = -1.7 \times 10^{-4}$ eV K$^{-1}$ that is typical of crystals.

Surprisingly, the edge of the stronger lowest direct interband optical transitions 3.7–4 eV shifts to lower energies on cooling, manifesting behavior that can be expected of a ‘soft electronic band’. Such an observation of the anomalous sign of the temperature dependence of the energy gap in STO disagrees with the results $[19]$ obtained by the two-photon spectroscopy technique. At the same time, the same result for the upper portion of the absorption coefficient has already been mentioned in $[28]$. So, we suggest that the presence of this ‘soft electronic band’ together with the increasing intensity of the $2p \rightarrow d\epsilon$ interband transitions in the region of 5 eV is responsible for the increase of the refractive index on cooling, i.e. negative proper TOE in STO.
4. Conclusions

In this work, the results of a detailed spectral ellipsometric study of the STO optical properties in wide spectral and temperature regions are reported. New results regarding features of band edge and near band edge indirect and direct fundamental optical transitions were obtained and updated. The temperature dependence of the refractive index in the visible region was determined from direct ellipsometric measurements (earlier, the thermooptical behavior of STO was known from temperature changes of the refractive index [6]). It was shown that whereas the indirect transitions lowest in energy shift to higher energies on cooling, the energy of the stronger direct optical transitions in the region of 3.7–4.0 eV shifts to the opposite side, to lower energies, and these transitions can be treated as the ‘soft electronic band’ predicted in [6]. It is concluded that the presence of this ‘soft electronic band’ together with increasing absorption band intensity at 4.8 eV results in the increase of the refractive index on cooling, elucidating the origin of the negative proper thermooptics in STO, as recognized in [6]. The microscopic nature of such anomalous behavior deserves further investigation and is being studied. It should also be mentioned that analogous behavior (negative thermooptic effect) has been observed by us also in rutile TiO₂, KTaO₃, which are incipient ferroelectrics like STO.

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