Infrared and Dielectrical Properties of SrTiO₃: Nd

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Abstract. Far-infrared reflection spectra and results of dielectric measurements of SrTiO₃ single crystal doped by neodymium are presented in the paper. Dielectric investigations were conducted at temperature range from 25 K to room temperature for the test frequency 1MHz. The numerical analysis of the far-infrared reflection spectra made using a fitting procedure based on factorized form of the dielectric function. The results for SrTiO₃: Nd are compared with those for pure crystal. The lowest-frequency phonon mode is found to be strongly influenced by presence of neodymium ions in SrTiO₃ single crystal.

Introduction

Strontium titanate is one of the crystals with perovskite structure that is of great interest for investigators for more than thirty years [1-6]. First of all, the dielectric properties of nonlinear dielectric (SrTiO₃ is nonlinear dielectric) can be modelled by different means. The crystal growth conditions changes significantly properties of SrTiO₃ crystal. Good optical properties [7] of strontium titanate, large electroluminescence and photochromism and discovery of high temperature superconductivity for separate perovskite are some of the reasons for growing of attention to SrTiO₃ crystal, also.

SrTiO₃ perovskite structure, a cubic crystal structure which is composed of a three-dimensional frame-work of corner-sharing TiO₆ octahedron. The Sr-site cation fills the 12 coordinate cavites formed by the TiO₃ network and is surrounded by the 12 equidistant anions [8].

Several phase transitions (PT) were discovered for SrTiO₃ single crystals under the following temperatures: 10K, 30K, 65K and 105K. The results of some authors do not confirm the existence of all of the transitions [7-11]. The best-known PT and the most studied is the antiferrodistorsion PT of the second order of displacement type at $T_C = (105 \pm 2)$K. Below T_C symmetry of the crystalline lattice of strontium titanate changes from cubic to tetrahedral one.

Strontium titanate was the first material for which it has been demonstrated that the strong increase of static dielectric constant at low temperatures is associated with softening of a long-wavelength transverse optic phonon mode [12,13]. However, despite a strong softening of the polar mode near 0 K, the ferroelectric transition is not observed in pure SrTiO₃ crystals due to the zero quantum fluctuations. Therefore, this compound is regarded as a quantum paraelectric or an incipient ferroelectric. The temperature dependence of static permittivity of SrTiO₃ crystal obeys Curie-Weiss law with transition temperature $T_0 = 35.5$ K. But at low temperatures ($T < 50$ K) permittivity deviates from Curie-Weiss behavior and saturates below 10 K [14].

Early studies of the infrared properties of strontium titanate contributed essentially to the understanding of soft modes in perovskites [15].
In this paper following properties for SrTiO₃:Nd and nominally pure single crystal are studied:
 -Temperature dependence of dielectric permittivity ε_r in the temperature range 25K-300K;
 -IR reflectance spectroscopy at 300K and 80K.

Experiment

Samples. Investigated samples for these experiments were grown by using Verneuil technique. The samples are polished circular disc about 1cm in diameter and approximately 1mm thick. Measurements were conducted for both $SrTiO_3$:Nd and pure $SrTiO_3$ single crystals. The concentration of neodymium ions is $5 \cdot 10^{-3}$ wt% and the concentrations of uncontrolled impurities (Fe-and Cr-ions) are less than 10^{-4}wt%.

The values of these concentrations were reached from EPR and spectral data. The existence of Ti^{3+} ions for all doped and some undoped crystals with different concentrations was observed by using method of valency shift of $K_{\alpha 1}$ X- ray lines [16-17].

Dielectric measurements. Dielectric measurements were conducted for both pure and doped $SrTiO_3$ single crystals. Temperature dependence of dielectric permittivity ε_r in the temperature range 25K-300K for test frequency 1MHz was examined. RLC meter HP4271B was used for these experiment. Cooling of the samples, temperature scanning and temperature control were carried out with Lake Shore Cryotronic equipment. The measurements were obtained under the pressure of 10^{-5} Torr. The relative error in determining the dielectric values was less than 5% and the accuracy of the temperature measurement was less than 1K. The measurements of ε_r were made both for cooling (300K-25K) and heating (25K-300K) cycles. The experimental details were described in [18,19].
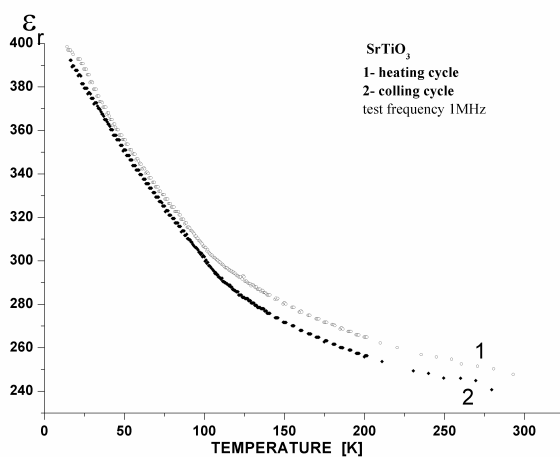

Fig. 1 Temperature dependence of ε_r for pure $SrTiO_3$ sample for heating-1 and cooling-2 cycles; test frequency 1MHz.
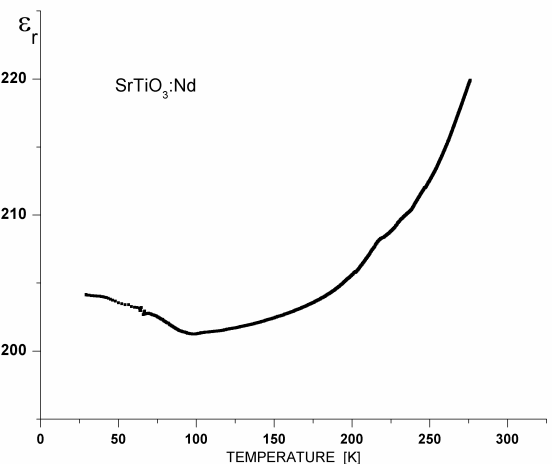
Fig. 2 Temperature dependence of ε_r for $SrTiO_3$:Nd –heating cycle; test frequency 1MHz.

The temperature dependences of dielectric permittivity for pure sample $SrTiO_3$ for frequency 1MHz both for cooling and heating cycles are shown in Fig. 1. A significant difference between these two curves can not be observed. In the other words, the thermal hysteresis in the T-dependence of ε_r is relatively small and does not change sufficiently (decrease 8%−10%) . From 300K to 30K ε_r increases continuously with decreasing of temperature.

Fig. 2 shows the temperature dependence of ε_r for $SrTiO_3$:Nd single crystals. It can be observed that doping with Nd-ions changes the temperature dependence of dielectric permittivity. The value of dielectric permittivity increases with increasing of temperature for whole investigated range.

IR-spectra. Reflectivity spectra were measured with a BOMEM DA-8 spectrometer. Disc shaped pellets were optically polished using diamond paste. The size of the diamond grains was less than 1 μm. A deuterated triglycine sulfate (DTGS) pyro-electric detector was used to cover the wave-number region from 50 to 600 cm^{-1} and a liquid-nitrogen-cooled Hg-Cd-Te detector was used from 500 to 5000 cm^{-1}. Spectra were collected with 2 cm^{-1} resolution. For low-temperature measurements a Janis Super Tran (ST-100) continuous flow cryostat was used. As reference mirror we used an evaporated Au film.

Fitting procedure. The far–infrared spectra of SrTiO$_3$ perovskites have been studied extensively, both the theoretically and experimentally [20,21]. For cubic perovskites, group theory predicts three triply degenerate infrared active modes of F$_{1u}$ symmetry and one optically silent mode of F$_{2u}$ symmetry.

Fig. 3 presents the reflectance of pure SrTiO$_3$ at temperatures T=300K and T=80K from 50 to 1200 cm^{-1}. There are three broad bands in both the spectra. The first of these bands (TO1-LO1) is located below 160cm^{-1}, the second one (TO2-LO2) at 170cm^{-1} to 500cm^{-1} and the third one (TO3-LO3) at 550cm^{-1} to 800cm^{-1}.
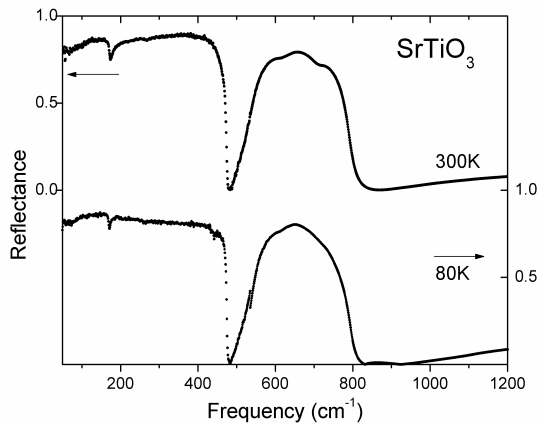

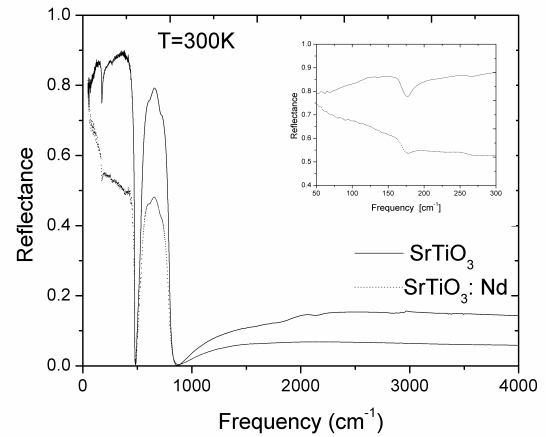Fig. 3 Reflectance of SrTiO$_3$ from 50cm^{-1} do 1200cm^{-1} at 300K and 80 K.

Fig. 4 Reflectance spectra of pure SrTiO$_3$ sample and SrTiO$_3$:Nd from 50cm^{-1} to 4000cm^{-1} at T=300K. The inset shows reflectance spectra from 50cm^{-1} to 300cm^{-1} at T=300K.

The infrared reflection measured for pure strontium titanate agrees reasonably well with previous measurements [21]. Fig. 4 shows the reflectance spectra for both the pure SrTiO$_3$ and doped SrTiO$_3$:Nd single crystals from 50 to 4000cm^{-1} at temperature T=300K. There is significant difference in the shape of reflectance spectra for pure SrTiO$_3$ and SrTiO$_3$:Nd between 50 cm^{-1} and 160cm^{-1}, which might be caused by strongly influence of presence of Nd dopants in SrTiO$_3$ single crystal to the lowest-frequency phonon mode.

Fig. 5 shows reflectance spectra of SrTiO$_3$:Nd at T=300K and T=80K. The reflectance at T=80K is similar to the reflectance spectra for pure crystal.

We have performed a least-squares fit of the reflectivity between 100 and 1200cm^{-1} to the following factorized expression which was proven to be successful for strontium titanate at higher temperatures and for the doped materials [21-23]

$$\varepsilon = \varepsilon_\infty \prod_j \frac{\omega_{jLO}^2 - \omega^2 + i\gamma_{jLO}\omega}{\omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega}, \tag{1}$$

where ω_{jLO}, ω_{jTO}, γ_{jLO} and γ_{jTO} are frequencies and dampings of jth LO and TO modes, respectively; ε_∞ is the dielectric constant at high frequencies.

Fig. 5 Reflectance spectra of SrTiO$_3$:Nd at T=300K and T=80K.

The oscillator strength $\Delta\varepsilon_j$, which represents the contribution of each oscillator to high the dielectric constant from ε_∞ to ε_0 may be deduced from TO-LO splitting via

$$\Delta\varepsilon_i = \frac{\varepsilon_\infty}{\omega_{iTO}^2} \frac{\prod_j (\omega_{jLO}^2 - \omega_{iTO}^2)}{\prod_{j \neq i} (\omega_{jTO}^2 - \omega_{iTO}^2)} \quad . \tag{2}$$

It is generally found that the eigenfrequencies of the higher optical modes exhibit no sizeable variation with temperature.

Table 1 Best fit parameters for SrTiO$_3$ and SrTiO$_3$:Nd at T=300K.

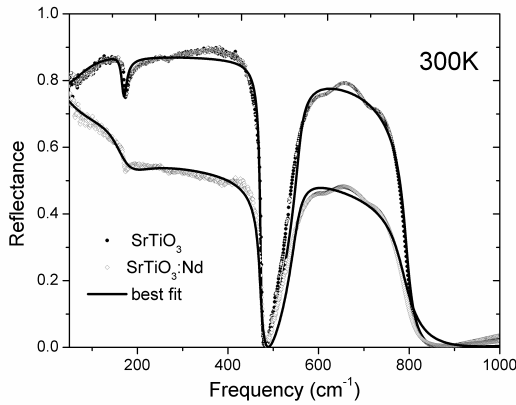|	SrTiO$_3$ 300K	SrTiO$_3$:Nd 300K
$\omega_{TO,1}$	91	95
$\gamma_{TO,1}$	83	310
$\omega_{LO,1}$	169	172
$\gamma_{LO,1}$	12	72
$\Delta\varepsilon_1$	245	130
$\omega_{TO,2}$	173	178
$\gamma_{TO,2}$	20	99
$\omega_{LO,2}$	472	465
$\gamma_{LO,2}$	3	12
$\Delta\varepsilon_2$	13	3
$\omega_{TO,3}$	557	549
$\gamma_{TO,3}$	22	32
$\omega_{LO,3}$	794	772
$\gamma_{LO,3}$	23	57
$\Delta\varepsilon_3$	2	1

Fig. 6 Reflectance of SrTiO$_3$ and SrTiO$_3$:Nd at 300K and 80K. Symbols are measured reflectivity values. Solid lines are calculated using the parameters of Table 1.

The fit was very sensitive to the choice of starting values, often giving unphysical results for some optical functions. For the rest of the parameters, we initially took the 300K values of *Servoin et al.* [23]. In order to obtain satisfactory fit to the reflectivity spectra of SrTiO$_3$:Nd, we use model of dielectric function which consists of a sum a factorized form and a Drude contribution. Fig. 6 shows both IR experimental data and fit curves. Table 1 shows the best fit parameters for SrTiO$_3$ and SrTiO$_3$:Nd at T=300K.

Discussion

In this work we study the effect of Nd-doping on the infrared and dielectric properties of strontium titanate single crystal.

The temperature dependence of dielectric permittivity for investigated Nd-doped $SrTiO_3$ samples deviates from Curie-Weiss behavior. One can see that Nd-doping leads to significant changes in dielectric properties strontium titanate.

From the infra red reflectance spectra it can be seen that the shape of the low- reflectance band is changed with doping. Changing of temperature has a more pronounced effect on the lowest-frequency mode for $SrTiO_3$:Nd than pure $SrTiO_3$ sample.

One of the main factors which significantly affect dielectric properties of strontium titanate single crystals is stoichiometric composition of crystal both with presence of impurities in the crystal structure. Violation of stoichiometry of $SrTiO_3$ samples with respect to titanium, strontium, and first of all, oxygen during crystal growth caused transition of up to 20% of Ti^{4+} ions to the Ti^{3+} state with $3d^1$ configuration. Previous investigation showed the presence of Ti^{3+} ions in most nominally undoped and in almost all impurity $SrTiO_3$ single crystals.

One of the reasons for anomalous behavior dielectric and infrared properties $SrTiO_3$:Nd could be the presence of oxygen vacancies which density is large enough to provide existence of well developed plasmon screening the phonon modes. The possible explanation of the temperature dependence of the reflectance in $SrTiO_3$:Nd will most likely involve electron-phonon coupling, and may be of significance in elucidating the transport properties of $SrTiO_3$:Nd.

However, a clear and unique interpretation of the results could not be given yet. The lattice vibration dynamic properties of these phonon modes, carrier concentrations, mobility, as well as dielectric behavior of these crystals should be study in further investigation.

Acknowledgements

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