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Dielectric, spectral and Raman scattering studies of Nd-doped $SrTiO_3$ single crystal

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Abstract

Results of dielectric, spectral and Raman scattering studies of $SrTiO_3$:Nd are reported in the paper, and are compared with one for nominally pure crystal. Dielectric and Raman investigations were conducted at the temperature range from 25 K to room temperature. Analysis of dielectric susceptibility *T*-dependence for test frequency of 1 MHz was conducted. Raman spectra contain broad peak with drastic anomalies at *T*-dependence of intensity around 105 K, indicating the existence of a phase transition (PT). The band gap studies were conducted by analyzing UV–vis spectroscopy. The transmission spectra at 300 K show a linear fit for direct transition.

Keywords: Dielectric response; Light absorption and reflection; Electronic states (localized)

1. Introduction

Strontium titanate is one of the crystals with perovskite structure that is of great interest for investigators for more than 30 years [1,2]. The crystal growth conditions change significantly properties of $SrTiO_3$ crystal [3,4]. Good optical properties [5] of strontium titanate, large electroluminescence and photochromism and discovery of high temperature superconductivity for separate perovskite are some of the reasons for growing attention to $SrTiO_3$ crystal, also.

$SrTiO_3$ perovskite structure, a cubic crystal structure which is composed of a three-dimensional frame-work of corner-sharing TiO_6 octahedron. The Sr-site cation fills the 12 coordinate cavities formed by the TiO_3 network and is surrounded by the 12 equidistant anions [6]. Several phase transitions (PT) were discovered for $SrTiO_3$ single crystals, also [7].

In this paper some properties for $SrTiO_3$:Nd and nominally pure single crystal are studied by: determination of dislocation density by chemical etching, measuring the temperature dependence of dielectric permittivity ε_r in the temperature range 25–300 K, UV–vis-NIR spectroscopy at room temperature and Raman scattering at temperatures below 300 K.

2. Samples and characterization

Investigated samples for these experiments were grown by using Verneuil technique [3]. The concentration of Nd ions is 2×10^{-3} at% and the concentration of uncontrolled impurities (Fe- and Cr-ions) is less than 10^{-4} at%, which obtained from ESR and spectral data. The existence of Ti^{3+} ions for all doped and some undoped crystals with different concentrations were observed by using method of valency shift of VK 1 X-ray lines. This method is described in detail in Ref. [8].

2.1. Chemical etching

The widely known etch-pit technique is very suitable for the study of crystalline solids. Two etchants gave suitable etch-pits for optical investigations. One of these is a mixture of HF (50%):HNO_3:H_2O = 1:2:2 at room temperature after exposure time of 8 min [3] and a mixture of HCl:HNO_3 = 3:1 after exposure of 4 min [9]. Both etchants produced sizable pits with the characteristics shape of the (1 1 1) plane, but better result was obtained by the first etchant. Time exposure was 12 min instead

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of 8 min, 4 min longer than cited in the literature. The microscopic observation of chemically etched (1 1 1) surfaces also revealed other structural characteristics. It was confirmed that $SrTiO_3$:Nd single crystals and low-angle grain boundary crystals were obtained, and no cellular structure and inclusions were observed. The dislocation density is roughly estimated to be in the order of $10^6\,cm^{-2}$. (1 1 1) oriented Nd:$SrTiO_3$ along the close-packed direction of perovskite are important for fundamental studies on the mechanisms of thin film growth and developing new materials [9]. Usually orientation of $SrTiO_3$ is (1 0 0) and (1 1 0), but these directions have the highly anisotropic dislocation arrangements. Namely, $Sr^{2+}Ti^{4+}O_3{}^{2-}$ perovskite oxide can be recognized as the alternate stacking of SrO^+ (A-site) and $TiO_2{}^-$ (B-site) layers [10].

3. Results and discussion

3.1. Dielectric measurement

Dielectric measurements were performed for both $SrTiO_3$:Nd and pure $SrTiO_3$ single crystals. The samples were obtained as small plates of dimension $d \approx 10$ mm, $l = 0.8$–1 mm.

Fig. 1 shows the temperature dependence of reciprocal relative dielectric permitivity ε_r^{-1} for both $SrTiO_3$:Nd and pure single crystals for test frequency of 1 MHz. It is obvious that Nd-doping of $SrTiO_3$ crystal for investigated sample decreases value of dielectric permittivity for hole investigated range of temperatures. It is easy to see the fracture of curve ε_r^{-1} (T) for pure sample under $T = 124$ K. But for $SrTiO_3$:Nd sample one can notice several fractures of curve ε_r^{-1} (T) at following temperatures: 105, 150 and 170 K. In the last case PT can be marked as "expanded" and the break of the curve ε_r^{-1} (T) is not easy to notice.

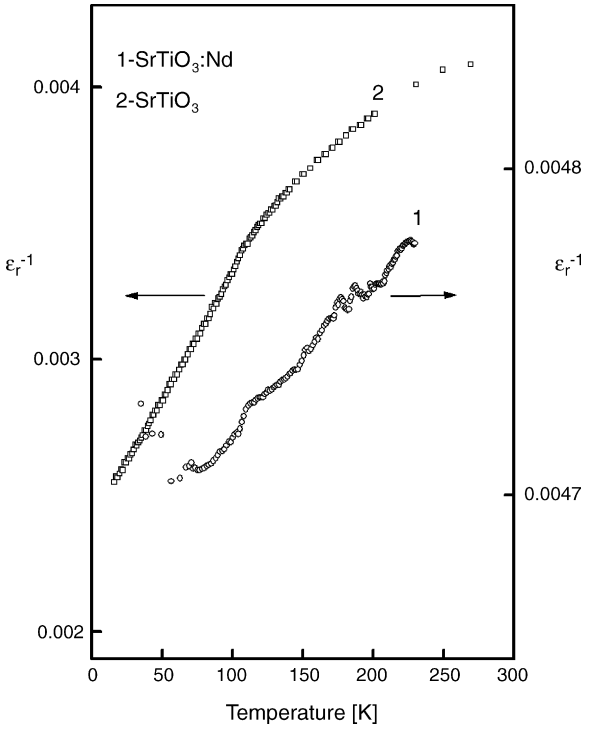

Fig. 1. Temperature dependence of ε_r^{-1} for $SrTiO_3$:Nd single crystal-1 and pure $SrTiO_3$ single crystal-2; test frequency 1 MHz.

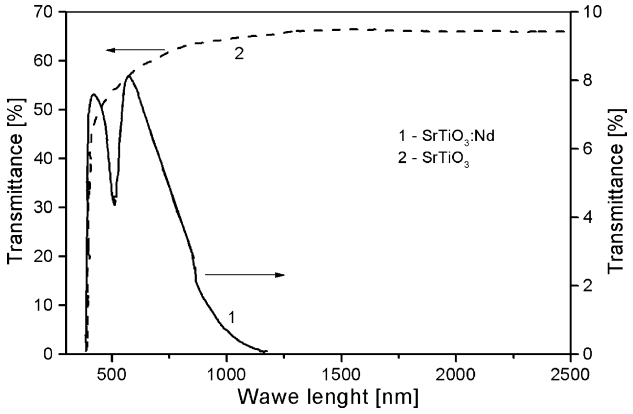

Fig. 2. Transmittance spectra for $SrTiO_3$:Nd single crystal-1 and pure $SrTiO_3$ single crystal-2.

The temperature dependence of dielectric permittivity for investigated pure and Nd-doped $SrTiO_3$ samples are in good accordance with Currie–Weiss law. The values of dielectric susceptibility are lower for $SrTiO_3$:Nd than for pure $SrTiO_3$ sample for whole investigated range of temperatures. The Currie constant C is minimum for pure $SrTiO_3$ sample under $T = 124$ K. In the case of Nd-doped $SrTiO_3$ sample C did not change significantly for investigated temperature range. The thermal hysteresis for both pure and doped samples is less than 10% for whole temperature region.

3.2. Spectral studies

Spectral investigations were conducted for the range 350–2500 nm at room temperature. Spectrophotometer Perkin-Elmer model Lambda 9 was used. Fig. 2 shows transmittance spectra for both $SrTiO_3$:Nd and pure $SrTiO_3$ single crystals.

The edge of fundamental absorption is near 395 nm for both, pure and Nd-doped crystal. Band gap of the fundamental absorption E_g was determined by extrapolating the straight line portion of the α^2E^2 versus E plot to $\alpha = 0$ [7]. The absorption coefficient α was calculated from the transmittance data. Band gap of the fundamental absorption is 3.15 eV for both doped and pure sample. Narrow absorption band at 514 nm of $SrTiO_3$:Nd crystal, which is registered in the other RE doped $SrTiO_3$ crystals [11], should be noticed.

3.3. Raman spectroscopy

The Raman spectra were excited by the 488 and 514.5 nm lines of an argon laser (the average power was about 100 mW) in the back-scattering geometry. We used a Jobin Yvon model U-1000 monochromator, with a conventional photocounting system. The samples were held in a closed-cycle cryostat, equipped with a low-temperature controller and evacuated by a turbopump.