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OPTICAL INVESTIGATION OF A Pb_2ScTaO_6 CRYSTAL WITH A ROOM TEMPERATURE PHASE TRANSITION

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The optical properties of a Pb_2ScTaO_6 single crystal are investigated in the room temperature phase transition region. The measured refractometric data are used to determine the average temperature and the interval of the diffuse phase transition $-15 \pm 4^{\circ}C$. The dependence of the crystal's molar polarizability on temperature is determined from the refractometric results.

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1. Introduction

Lead scandium tantalate Pb_2ScTaO_6 (PST) single crystals are ferroelectric relaxors, with a high dielectric constant which changes smoothly with temperature and has a strong frequency dispersion. A diffusive dielectric response with broad maxima, high electrostriction coefficients and switchable pyroelectric-piezoelectric properties are the main characteristics of such ferroelectrics.

PST exhibits the perovskite structure $A(B'_xB''_{1-x})O_3$, where A is Pb^{2+} and B' - B" are the low (Sc^{3+}) and high-(Ta^{5+}) valence cations, respectively. The arrangement of the two B-site cations plays an important role in determining the diffuseness of the ferroelectric phase transition. A structural paraelectric (PE) to ferroelectric (FE) diffuse phase transition between 263 and 298 K has been observed [1]. A PE-FE phase transition accompanied by the creation of ferroelectric domains of ordered Sc^{3+}-Ta^{5+} atoms with sizes from tenths to hundreds of nm, and a change from *Fm3m* (cubic) to *R3m* (rhombohedral) symmetry has been established using TEM and X-ray diffraction [2-3]. The particular PE-FE or disordered-ordered state transition temperature and ordering parameter depend on the growth conditions, the purity of the starting materials and the degree of structural order (the positions of Sc^{3+} and Ta^{5+} atoms in the crystal lattice).

PST crystals find a wide range of applications as capacitor materials, pyroelectric detectors, ultrasonic and modern medical devices, as well as in information storage [4-7]. Furthermore, the diffuse phase transition close to room temperature allows easy PE-FE investigations and analysis of the nature of the physical properties.

In this paper, we report the refractive index (RI) change during the PE-FE transition of a PST crystal. The measured RI data were used to determine the average temperature and the range of the diffuse phase transition. The result was confirmed by reflectance measurements, and by independent reference sources. The refractometric data were used to calculate the variation in the PST molar polarizability during the phase transition, using the Lorenz-Lorentz model. The unit cell restructuring during the PE-FE transition appears to explain the effect.

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2. Experimental details

Optically homogeneous Pb_2ScTaO_6 single crystals were prepared by the high temperature solution growth method in a PbO + PbF_2 + B_2O_3 flux [7]. A crystal prism with a refracting angle of $15.70^{\circ} \pm 0.02^{\circ}$ and a plate with 0.8mm thickness were cut from the mono-crystals.

The RI measurements were carried out by the disappearing diffraction pattern method [8], using the PST prism. The experimental system (Fig. 1) was modified for solids with a high RI n (n>2). A He-Ne laser beam (1) was incident at an angle α on the front face of the PST prism (4). Part of the light refracts into the crystal and leaves it from the second, adjacent to the refractive angle, face. The relative RI for the latter action is $1/n<1$, and thus the outgoing beam could undergo Total Internal Reflection (TIR). If the beam leaves the prism after two refractions, it illuminates the diffraction grating (5) and creates a diffraction pattern, observable on the screen (9). When the angle of incidence α changes toward TIR occurrence, the outgoing ray geometrically approaches the second prism side and its spot on the grating - the corner between (4) and (5). When the TIR condition is satisfied or $\alpha = \alpha_{cr}$, the beam cannot leave the prism, the grating is in shadow and all diffraction orders disappear. Then n can be calculated from the value of α_{cr} [8].

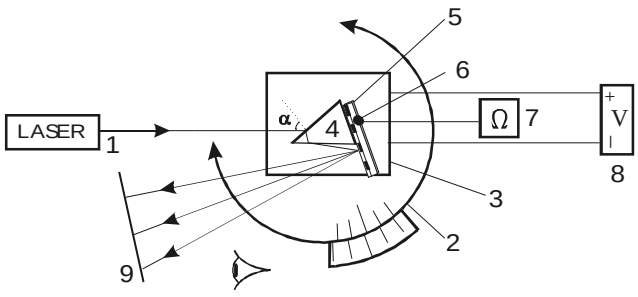

Fig. 1. Experimental system: 1- He-Ne laser, 2- rotary table, 3- Peltier device, 4- PST crystal prism, 5- diffraction grating, 6- thermoelectric sensor, 7- digital multimeter, 8- power supply, 9- screen.

The PST prism was fixed on a scaled rotary table (2) with 1 arc.min. resolution, which is used to measure the critical angle. The RI uncertainty dn depends on the errors in the critical and the refracting angles. According to [8] it is $dn = 1\text{x}10^{-3}$. The metal diffraction grating (5) was mounted on the short prism side with the stripes forwards, by thermo-conductive paste. A Pl thermo-resistive sensor (6) with 0.4 Ω/K sensitivity, deeply dug into the grating's substrate, and an ohmmeter (7) with 0.1Ω accuracy were used to measure the temperature. A Peltier device (3) with feedback from (6) was pasted below the crystal, to change and sustain its temperature with $\pm$ 0.3°C accuracy. The PST reflectance from the plate's surface was recorded by a Cary 5E. PST UV-VIS-IR spectrophotometer. The temperature was controlled and measured from its rear side, in a similar way to that used in the refractometric setup.

3. Results and discussion

During a temperature scan from 0 to 40°C, it was observed that the value of the TIR angle floats, i.e. the RI of the crystal changes. The PST RI changed sharply by $2\text{x}10^{-2}$ within the 11 to19°C range, while the RI temperature coefficient was an order of magnitude lower outside this interval. Thus, the average temperature and the region of the diffuse phase transition could be determined to be 15 $\pm$ 4°C, which agrees with the reference observations [1].

It's interesting to analyze the RI change at the transition. According to the Lorenz-Lorentz model, the observed RI jump is related to a change in the crystal's molar polarizability A_p:

$$A_p = \frac{\mu}{\rho}\frac{n^2-1}{n^2+2}, \tag{1}$$

where μ and ρ are the molar mass and the density, respectively [9]. The dependence of A_p on the reciprocal absolute temperature *1/T*, calculated from the measured refractometric data, is presented in Fig. 2. The error in A_p is also shown . The dependence $A_p = A_p(1/T)$ is linear, as could be expected according to the Debye model [9].

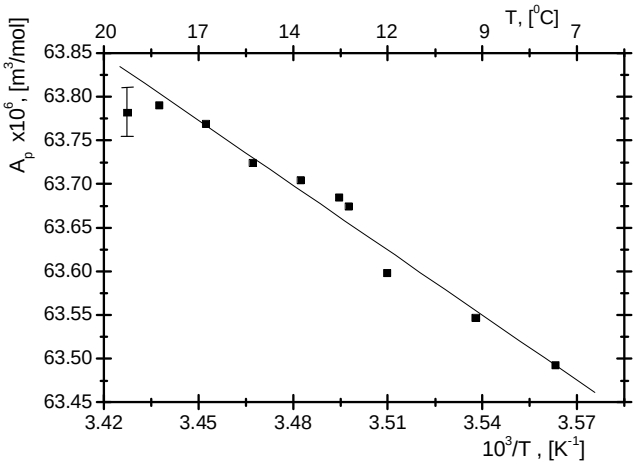

Fig. 2. PST molar polarizability as a function of the reciprocal temperature.

The presence of the phase transition and changes in the PST RI should be accompanied by changes in the crystal's absorption, i.e. transmittance and reflectance. Measurements of the PST reflectance, in conjunction with the RI data, can be used to calculate the absorption index of the material, which is the imaginary part of the complex RI. Both the refractive and absorption indices permit the determination of the dielectric permittivity of the PST crystal, which is essential for applications of PST as an electro-capacitive material, an electrostriction actuator, etc. The PST reflectance spectra R(λ), measured in the temperature interval 10 to 27°C, are shown in Fig. 3. A significant reflectance change can be observed at 15°C, confirming the previously determined average transition temperature. Here, the change with temperature was sharper and the transition range was more difficult to determine. The reflectance *R* of an absorbing dielectric medium attenuates with increasing absorption index κ and with decreasing refractive index *n*. Noting that the relative reflectance change is $dR/R \sim 3$, which is much greater than $dn/n = 0.01$, one can conclude that the change *dR* is mostly related to the change in the PST absorption index .

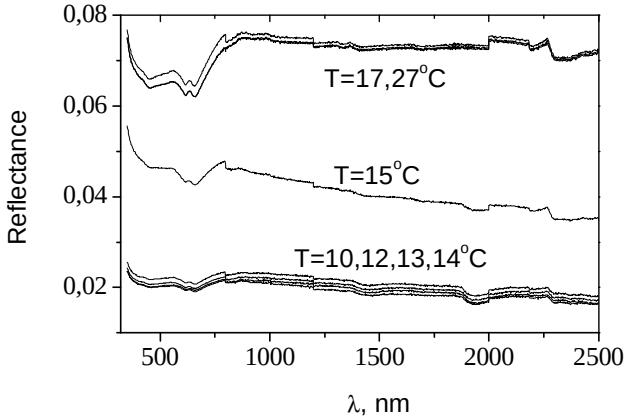

Fig. 3. Reflectance spectra at different temperatures.

3. Conclusions

This work proves the applicability of RI measurements to investigate phase transitions in solid-state matter. The average temperature and range of the PST transition are determined to be $15 \pm 4^{\circ}C$, in agreement with the reflection measurements and data reported in the literature. The variation of the PST molar polarizability during the PE-FE transition has also been considered.

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