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Antiferrodisorsion transition and dielectric relaxation in $SrTiO_3-SrMg_{1/3}Nb_{2/3}O_3$

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Dielectric and acoustic studies of solid solutions were carried out $(1-x)SrTiO_3 - xSrMg_{1/3}Nb_{2/3}O_3$. The dependence of the temperature of the antiferrodisorsion phase transition on the concentration x of the second component is obtained. The suppression of dielectricrelaxation at $x \le 0.03$ and temperatures below the temperature of the antiferrodisorsion transition, as well as the coexistence of dielectric relaxation and antiferrodisorsion instability at $0.03 < x \le 0.15$. The reasons for the blurring of the dependence of the relative speed of sound in the transition region and the features of the interaction of antiferrodisorsion instability and the dielectric subsystem are discussed. Keywords: antiferrodisorsion transition, dielectric relaxation, acoustic properties.

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1. Introduction

Among the numerous compounds with the perovskite structure, strontium titanate $SrTiO_3$ has the lowest temperature of the antiferrodisorsion (AFD) phase transition $T_a \approx 105\,K$ [1,2]. The temperatures of T_a for other compounds range from $\sim 1000\,K$ ($SrRuO_3$) to $\sim 2000\,K$ ($CdTiO_3$). For example, for $CaTiO_3$ $T_a \approx 1500\,K$ [3]. As is known, a feature of $SrTiO_3$ is that the ferroelectric transition is not realized up to the lowest temperatures and, accordingly, $SrTiO_3$ is a virtual ferroelectric. It is generally assumed that the ferroelectric phase in strontium titanate is suppressed by quantum fluctuations [2]. However, such a state is unstable, and external influences such as a constant electric field, mechanical pressure, impurities and, in the case of solid solutions, the second ferroelectric active component lead to ferroelectricity (see, for example, [4–8]). Antiferrodisorsion transition (improper ferroelastic transition) from cubic *Pm3m* to tetragonal *I4/mcm* phase along with quantum fluctuations is also considered as a possible cause of suppression of the ferroelectric state in $SrTiO_3$ [9]. The temperature of the T_a AFD transition either increases or decreases depending on the concentration of impurities and/or the second component of the solid solution. So, when introducing ions $A = Ba^{2+}$, Pb^{2+} into the perovskite lattice ABO3, T_a decreases [10], and when $A = Ca^{2+}$ increases [11]. As a rule, the AFD transition is suppressed by the ferroelectric transition when they approach at a temperature of [10,12].

The transition temperature T_a can be close to room temperature, as, for example, in the cases of $SrTiO_3$-Ca^{2+} and $SrTiO_3$-Gd^{3+} [13]. Since the AFD transition in such compositions is realized during the transition from a cubic structure to a tetragonal one, it assumes the existence of ferroelastic domains in the low-temperature phase. The effect of the antiferrodisorsion transition on the ferroelectric transition induced by external influences and/or on the dielectric and elastic properties of strontium titanate is of particular importance, given the active use of nominally pure and doped with impurities $SrTiO_3$ as a nonlinear dielectric material with low losses, as well as a component in the synthesis of ferroelectric ceramics [14]. Strontium titanate is widely used for the manufacture of thin-film capacitors [15,16], electro-optical modulators [17], nonlinear optical devices [18], also in memristors [19,20]. Therefore, the study of the coexistence and mutual influence of antiferrodisorsion and ferroelectric transitions is not only fundamental, but also of practical importance. The dielectric and elastic properties of the system play a key role in such studies. Solid solutions of the system $(1-x)SrTiO_3 - xSrMg_{1/3}Nb_{2/3}O_3$ (STO-SMN), for which previously, the so-called giant dielectric relaxation [21,22] was observed and investigated, were chosen as the object of study.

2. Experiment

Samples of solid solutions were obtained using conventional ceramic technique. The oxides Mg, Ti, Nb, Sc, $SrCO_3$ of high purity (HP) were used and the precursor — columbite ($MgNb_2O$) was synthesized$_6$). Sintering of samples, depending on the composition, was carried out at 1450–1470°C for 1.5 h. An X-ray diffraction study conducted at room temperature showed that the samples with $x \le 0.15$ were single-phase and had a cubic perovskite structure. At a concentration of SMN greater than 0.15, it was not possible to manufacture single-phase samples, which, apparently, is due to the solubility limit of the rhombohedral compound SMN in the STO-SMN system. All samples had a density equal to or greater than 94% relative to the theoretical density of the corresponding compositions. A detailed description of the sample manufacturing technique is published in [21].

The samples for dielectric measurements had a diameter of 8 mm and a thickness of 1 mm. As electrodes, a silver paste was used, fired into the samples at a temperature of 500°C. Measurements of the permittivity spectra in the range of 10 Hz−1 MHz were carried out using a PSM 1735 analyzer. The amplitude of the alternating electric field was 1 V/cm. The velocity of the longitudinal acoustic wave as a function of temperature was measured using the ultrasonic pulse-echo method method (installation „PHONON-N") at a frequency of 10 MHz. Sound attenuation measurements at room temperature were carried out at a frequency of 20 MHz. Resonant plates of lithium niobate Y + 36° of the cut were used as converters. These measurements were carried out on ceramic bars with a size of $8 \times 5 \times 5\,\mathrm{mm}^3$.

3. Experimental results and discussion

Anomalies of the sound velocity V and, accordingly, the relative velocity V_r were found in the form of a step in samples of nominally pure strontium titanate (Fig. 1) and in compositions $(1-x)$STO $-\, x$SMN with $x = 0.01$, 0.03, 0.05, 0.1 and 0.15 (Fig. 1–4), characteristic of the AFD transition from cubic to tetragonal phase (see, for example, [10–12]).

The relative velocity of sound V_r is defined as the ratio of velocity at a given temperature V to velocity V_o at the initial measurement temperature. The same figures show the dependences of the real part of the dielectric constant measured at frequencies from 10 Hz to 1 MHz.

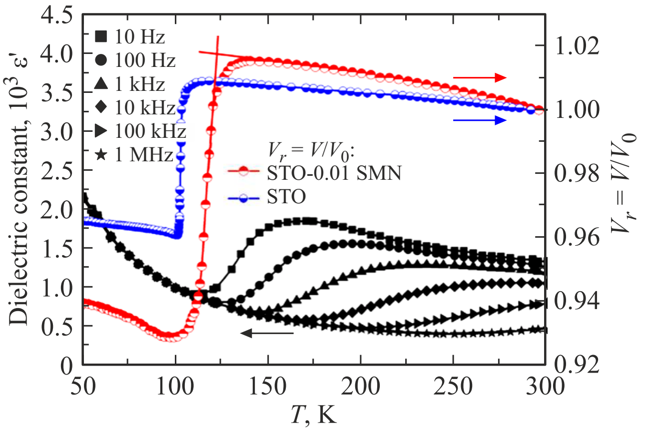

Figure 1. Dependences of relative sound velocity V_r on temperature for $(1-x)$STO$-x$SMN ($x = 0$ and 0.01), as well as the dielectric constant of ε', measured at different frequencies, for $x = 0.01$.

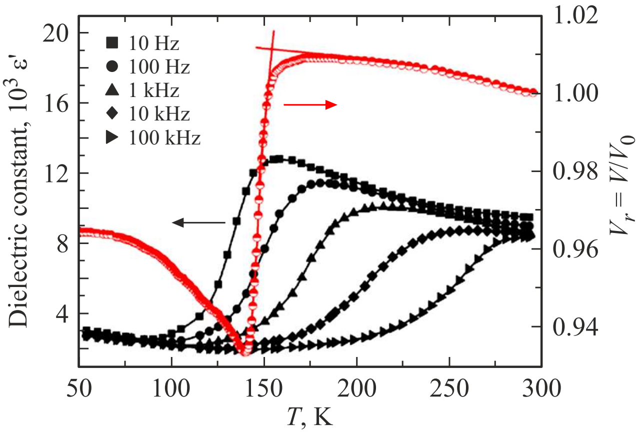

Figure 2. Dependence of the relative velocity of sound V_r on temperature and the real part of the permittivity ε' measured at different frequencies for a solid solution $SrTiO_3-0.03SrMg_{1/3}Nb_{2/3}O_3$.

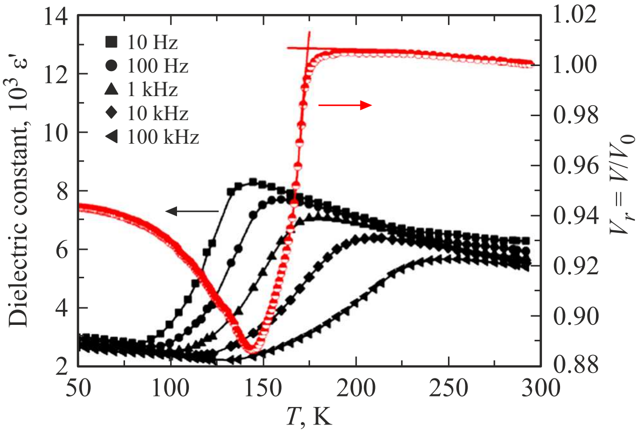

Figure 3. Dependence of the relative velocity of sound V_r on temperature and the real part of the permittivity ε' measured at different frequencies for a solid solution $SrTiO_3-0.05SrMg_{1/3}Nb_{2/3}O_3$.

The temperature of the AFD transition T_a was determined as the intersection point of straight lines of extrapolations of the dependence of V_r on the temperature at high temperatures and the lines of the greatest slope of the anomaly in the form of a step (straight lines in Fig. 1–3 for $0 \leq x \leq 0.05$).

The totality of the results of acoustic and dielectric measurements showed that for compositions with $x \leq 0.03$, dielectric relaxation occurs only above the AFD junction, already in the cubic phase (Fig. 1, 2). A solid solution with $x = 0.05$ demonstrates relaxation occurring in the region of the antiferrodisorsion transition (Fig. 3). There is an increase in T_a with an increase in the concentration of x (Fig. 5, box), which qualitatively corresponds to the data of the work [23], in which the shear modulus measurements were carried out at frequencies in the region of 25 Hz.

In the case of the highest concentrations ($x = 0.1$ and 0.15) relaxation also occurs in the transition region,

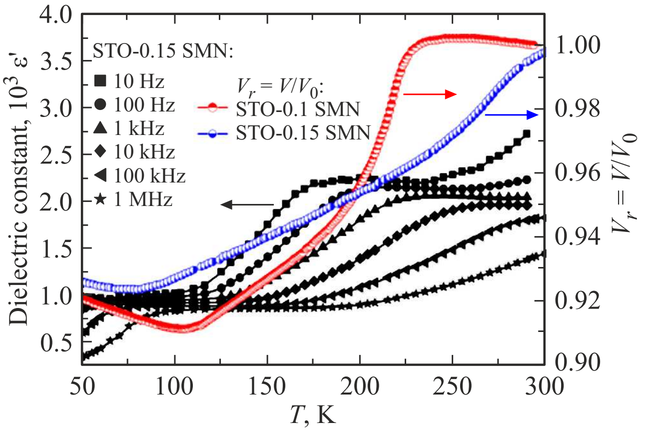

Figure 4. Dependence of V_r on temperature for $(1-x)$STO$-x$SMN ($x = 0.1$ and 0.15), as well as the dielectric constant of ε', measured at different frequencies, for $x = 0.15$.

but the kind of dependences of the sound velocity V_r on temperature changes significantly (Fig. 4). This is no longer the traditional step for the AFD transition dependence of the velocity on temperature, but such a dependence $V_r(T)$, which is rather characteristic of diffused phase transition (relaxors) [12,24].

A feature of the behavior of relaxors is that the velocity of the ultrasonic wave gradually decreases with a decrease in temperature, reaches a minimum at a certain temperature $T_{\min}$, and then begins to increase again. The softening of the elastic constant $C(T)$ and the corresponding decrease in velocity V (as is known, $C = \rho V^2$) is explained by the appearance of polar regions (PNRs) with local ferroelectric polarization in the paraelectric matrix P_{loc}, the influence of which is estimated as $\delta C = \rho(\delta V)^2 \propto -g^2\langle P_{\mathrm{loc}}\rangle^2$, where g — electrostriction coefficient [24,25]. By analogy, it can be assumed that local defects — dielectric dipoles in the strontium titanate lattice, characterized by high polarizability, lead to the observed blurring and the form $V_r(T)$ in the case of the STO-SMN system under consideration.

A possible type of such dipoles is a variant of the local charge created by an impurity in place of the host ion in combination with compensation due to oxygen vacancy. Considering the electrostatic interaction, the configuration in which impurity ions and bound vacancies are the closest neighbors is the most favorable. In this case, these are complexes $[\mathrm{Mg}_{\mathrm{Ti}}^{+2}-V_{\mathrm{O}}]$ [21]. It is the thermally activated reorientation of such dipoles due to the jump of oxygen vacancies (or, more precisely, oxygen ions jumping through oxygen vacancies) that is assumed to be the cause of the observed Debye dielectric relaxation (with activation energy $U = 0.22-0.3$ eV and $\tau_0 = 10^{-11}-10^{-12}$ s). The strong polarizability of the strontium titanate lattice, associated with the existence of a soft ferroelectric mode, can lead to the fact that dipoles polarize the lattice in the immediate area around them, forming polar regions [26]. The interaction of polar regions with the elastic subsystem through electrostriction, the magnitude of which in strontium titanate is quite large [27], can have, like relaxors, effect on the velocity of sound.

It can also be assumed that the resulting dipoles have not only dipole moments capable of creating local polarization in such a highly polarizable lattice as in strontium titanate, but are also elastic dipoles [28]. This assumption is supported by the increase in the attenuation coefficient of ultrasound α with an increase in the concentration of SMN with a maximum value for $x = 0.15$ (Fig. 5). For small concentrations of SMN, at temperatures below T_a, dielectric relaxation is suppressed due to the interaction of polar regions (due to electrostriction interaction) and/or elastic dipoles with ferroelastic domains existing in the AFD phase. At temperatures above T_a, such interaction disappears, and relaxation is clearly manifested in the form of the so-called „giant relaxation“ (Fig. 2). The relatively low activation energy observed for concentrations with $x \leq 0.03$ contributes to the suppression of relaxation. The dependence of the activation energy on the concentration x obtained by processing the permittivity spectra is shown in Fig. 5. With an increase in the activation energy, the dipoles become more stable and already at concentrations 0.05–0.15, in the region „of the step“ T_a, dielectric relaxation occurs (Fig. 3, 4). Thus, the coexistence of antiferrodisorsion instability in the transition region and dielectric relaxation caused by dipoles is observed in the STO-SMN. system.

It is also known that lattice defects usually cause deformation of the nearest crystal regions. In the case of $\mathrm{SrTiO_3}$, this is a change in the rotation angle φ around the cubic axis of alternating octahedra $\mathrm{TiO_6}$ in local regions, that is, a local change in the secondary order parameter that determines its AFD (improper ferroelastic) transition [2]. This circumstance is probably another reason for the blurring of the dependence of the velocity of sound

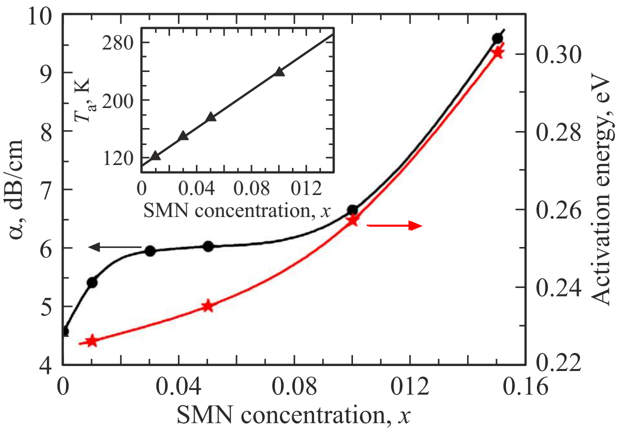

Figure 5. Dependence of the sound attenuation coefficient α and the activation energy U on the concentration of the second component x of the solid solution $(1-x)\mathrm{SrTiO_3}-x\mathrm{SrMg_{1/3}Nb_{2/3}O_3}$. In the insert: the temperature of the antiferrodisorsion junction T_a depending on the concentration x.

on temperature due to the interaction of the ultrasonic wave with such local deformation regions during the AFD transition in the STO-SMN system. The listed variants of interactions in STO-SMN indicate the possibility of blurring the AFD transition, but require additional experimental and theoretical studies.

4. Conclusion

Comprehensive study of acoustic and dielectric properties of solid solutions $(1-x)\mathrm{SrTiO_3}-x\mathrm{SrMg_{1/3}Nb_{2/3}O_3}$ demonstrating „giant relaxation“, showed the determining influence of the antiferrodisorsion transition on the occurrence and evolution of dielectric relaxation. The effect is manifested in the suppression of relaxation at low concentrations of $x \leq 0.03$ and in its interaction with the antiferrodisorsion subsystem in the transition region at $0.03 < x \leq 0.15$. There is also a blurring of the antiferrodisorsion transition at $x = 0.1$ and 0.15, which is assumed to be due to the influence of defects-dipoles responsible for dielectric relaxation on the antiferrodisorsion instability of the medium. Possible mechanisms of such influence are considered.

Conflict of interest

The authors declare that they have no conflict of interest.

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