Optical birefringence study of $AgNa(NO_2)_2$ crystals near the paraelectric-to-ferroelectric phase transition

Kityk A.V.

Faculty of Electrical Engineering, Czestochowa University of Technology,
Al. Armii Krajowej 17, 42-200 Czestochowa, Poland

Received: 06.09.2010

Abstract

The paper reports nearly tricritical behaviour of $AgNa(NO_2)_2$ crystal in the region of its paraelectric-to-ferroelectric phase transition studied by a high-resolution optical birefringence technique. The results obtained are analysed within the phenomenological approach based on the Landau theory for second-order phase transitions. Anomalous changes in the optical birefringence below the Curie point are found to be driven by the spontaneous polarisation via a spontaneous quadratic electrooptic effect. In the region of the Curie point $AgNa(NO_2)_2$ exhibits slightly discontinuous behaviour at cooling and practically continuous behaviour at heating, with the critical exponent for the order parameter equal to 0.25, as expected for the tricritical point.

Keywords: $AgNa(NO_2)_2$ crystals, ferroelectrics, optical birefringence, phase transitions

PACS: 78.20.Ek, 78.20.Fm, 78.20.Hp, 78.20.Jq
UDC: 535.5

1. Introduction

Structural phase transformations in solids are characterised by appearance of an order parameter η related to a certain static distortion of the parent crystal structure. In the case of ferroelectric crystals, a structural distortion below the Curie point is accompanied by arising of a macroscopic spontaneous polarisation P_s which may be related linearly or in some different way to the order parameter, depending on the type of ferroelectric crystal structure being considered. In particular, bilinear coupling (ηP_s) is a characteristic feature of proper or pseudoproper ferroelectrics, whereas higher-order one ($\eta^n P_s$, $n = 2, 3, ...$) results in an improper ferroelectricity. Irrespective of the type of coupling between η and P_s, which is defined directly by a symmetry change at the phase transition, the temperature behaviour of η, likewise that of P_s, results mainly from fundamental thermodynamic properties of a system itself, giving rise basically either to their discontinuous (a first-order transition) or continuous (a second-order transition) changes at the Curie point. These first- and second-order transitions may be presented on the pressure-temperature ($P - T$) phase diagrams by the lines which merge together in a tricritical point (P_k, T_k). The latter represents a special point which, to some extend,

combines the features characteristic for the second-order transitions like, e.g., a continuous behaviour of the order parameter at T_k, with the features of the first-order transitions like, e.g., divergence of the heat capacity in its vicinity. The tricritical behaviour has been a subject of many experimental and theoretical studies embracing different types of ferroic materials, including the ferroelectric ones (see, e.g., the work [1] and references therein). Nevertheless, the origin of the corresponding phenomena still remains far from being well-understood in many aspects. This explains a general interest in their further investigations.

In the present paper we report a nearly tricritical behaviour of ferroelectric silver sodium nitride crystals ($AgNa(NO_2)_2$, abbreviated hereafter as SSN) studied using an optical birefringence technique. In contrast to the former publications on these crystals [2–4] where the spontaneous polarisation has been studied in order to ascertain the order parameter behaviour, the optical birefringence represents a highly precise and, at the same time, 'noninvasive' method which is especially suitable when determining critical exponents of the phase transitions.

The SSN crystals exhibit a phase transition at $T_c \approx 311$ K [3, 4] from a paraelectric phase (space group D_{2h}^{24}) to a proper ferroelectric phase (space group C_{2v}^{19}). The structure of the SSN keeps the same number of formula units on the both sides of the transition point so that the ferroelectric phase can be characterised as a proper one. The dielectric [3–5], specific-heat [6] and elastic measurements [7] have indicated that the phase transition is of the first order, though very close to the second-order one. For this reason the anomalies of dielectric and thermal properties can be well explained by a Landau theory taking into account the near-tricritical character of this transition. As a consequence, the leading term in the free-energy expansion is of sixth order in the polarisation P. Ferroelectricity in the SSN is known to appear due to ordering of NO^{2-} dipoles [8], which induce quite a large spontaneous polarisation at the room temperature (about 8 μC/cm^2) and are oriented along the [010] crystallographic direction [3–5].

Polarisation dynamics of the SSN crystals demonstrates quite unique behaviour. Unlike most of ferroelectric materials, it slows down in the kilohertz region [5, 9, 10] in the vicinity of the Curie point. The SSN is also characterised by very attractive nonlinear optical properties. The second harmonic generation in the ferroelectric phase has been found to be driven by the spontaneous polarisations [11, 12]. Relatively high magnitudes of the effective second-order nonlinear optical susceptibilities are combined with availability of a number of phase-matching geometries, allowing to consider these crystals as a high-performance material for potential nonlinear optical applications.

2. Experimental

Single SSN crystals were grown from an aqueous solution containing 9.8 wt % of $AgNO_2$ and 37.2 wt % of $NaNO_2$, using a slow evaporation method at a constant temperature (~ 25 °C). We used a standard set of crystallographic axes for the paraelectric phase:

a = 8.05 Å, b = 10.77 Å, and c = 10.76 Å [13]. The SSN crystals are yellowish, with perfect cleavage planes perpendicular to [101] or [$10\bar{1}$] directions. A strong ability of the SSN to cleaving reduces considerably a number of sample geometries suitable for optical polarisation measurements. As a consequence, the geometry of samples had to be adjusted to these planes. Namely, we used thin plates (the thicknesses d < 0.5 mm) having perfectly cleaved faces [101] or [$10\bar{1}$], with no further polishing [11, 12]. One should stress that the both directions are equivalent in the meaning of their physical properties.

The phase retardation (*PR*) appearing between two orthogonally polarised wave components of the light transmitted through the samples was measured by a modulation optical polarisation technique. High resolution in our experiments was achieved by applying a photoelastic modulator (PEM-90, with the modulation frequency of f = 50 kHz) in a dual lock-in detection scheme, for minimising the influence of uncontrolled light intensity fluctuations [14]. The outgoing laser light intensity (the wavelength of λ = 632.8 nm) was detected by a photodiode supplied with two lock-in amplifiers and then consequently passed to a computer, in order to determine simultaneously the amplitudes of the first (U_Ω) and second ($U_{2\Omega}$) harmonics, respectively. The phase retardation introduced by a sample is given by the formula $PR = \text{atan}[U_\Omega J_2(A_0)]/[U_{2\Omega} J_1(A_0)]$, where $J_1(A_0)$ and $J_2(A_0)$ are the Bessel functions corresponding to the chosen retardation amplitude of PEM-90 ($A_0 = 0.383\lambda$). The samples were set into a thermostabilised optical cell operated by a temperature controller (the accuracy of temperature stabilisation being about 0.01 K). The measurements were performed in a temperature ramp regime, with a cooling/heating rate of about 0.05 K/min.

3. Results and discussion

Fig. 1a shows change in the optical birefringence δ(Δn) versus the temperature T being measured at cooling and heating for the sample oriented normally with respect to the incident laser light. The paraelectric-to-ferroelectric phase transition is accompanied by a prominent kink of the δ(Δn(T)) dependence, which is typical rather for the continuous transitions. Nonetheless, the cooling and heating runs reveal a small temperature hysteresis in the both temperature dependences, as well as a specific property of the first-order transitions, a hysteresis of the transition point ($\Delta T_c = T_c^h - T_c^c$ ~ 0.2 K). Basically, the behaviour of the optical birefringence observed in the vicinity of T_c well fits into the concept of the first-order phase transition very close to the tricritical point.

A lack of a clear jump at the Curie point has also been realised in the recent nonlinear optical studies [11, 12]. This has been assumed to be associated with coexisting metastable polar and nonpolar regions in the vicinity of the phase transition. A smeared character of the paraelectric-to-ferroelectric transition is thus an evidence for such coexistence, indicating a rather spatially inhomogeneous structure that occurs in the region of the Curie point.

Structural inhomogeneities occurring in the vicinity of phase transitions are usually associated with the order parameter fluctuations. However, this explanation is not quite

applicable to the proper ferroelectrics for which the fluctuation effects are considerably reduced due to long-range dipole-dipole interactions. For this reason the smeared behaviour of the physical properties observed by us and, in particular, a continuous temperature change of the optical birefringence near T_c should be attributed to defects or uncontrolled impurities rather than the polarisation fluctuations. The defects and/or impurities stabilise the inhomogenities of the order parameter and so their manifestation is nearly identical to the order parameter fluctuations; usually it is impossible to distinguish in practice between these mechanisms. In case of the SSN crystals, the origin of the uncontrolled impurities may be attributed preferably to free silver atoms available in the parent crystal structure due to photodecomposition processes.

More detailed inspection of the optical birefringence reveals another interesting

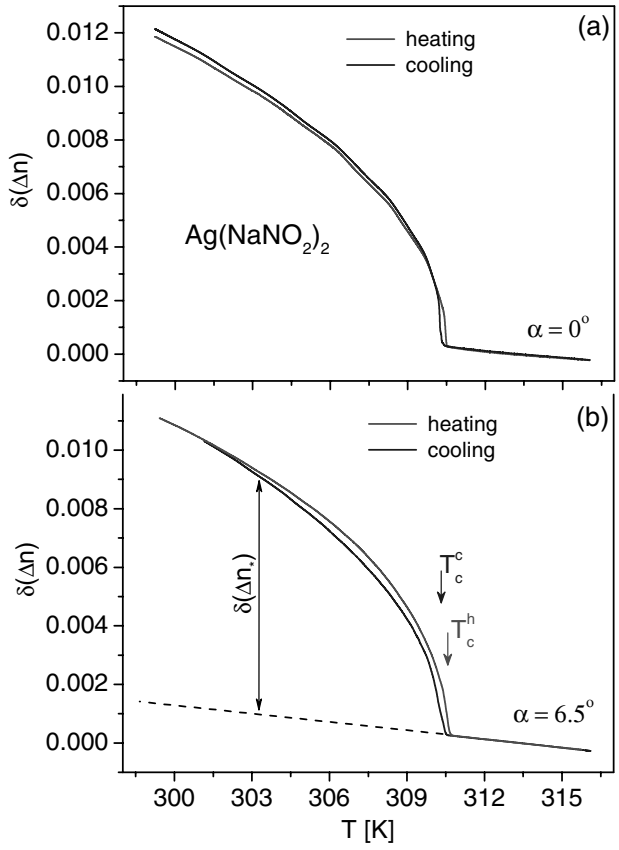

Fig. 1. Temperature behaviours of optical birefringence δ(Δ*n*) measured for the SSN crystals at cooling and heating using (a) geometry of normal light incidence (the incident angle α = 0°), and (b) slightly tilted incidence geometry (α = 6.5°). The sample is a thin plate (*d* = 0.36 mm) with perfectly cleaved faces perpendicular to [101] direction (no further polishing has been performed). Arrows mark phase transition points (Curie temperatures) at heating (T_c^h) and cooling (T_c^c).

feature. The temperature dependence of the birefringence in the ferroelectric phase is evidently characterised by a series of consequent kinks providing its slightly "wavy" shape (see Fig. 2a). Such behaviour appears to be reproducible in the heating and cooling runs and vanishes in the paraelectric phase only. The origin of this phenomenon is a challenging question. To some extent it is similar to that observed earlier in incommensurate dielectrics where the corresponding anomalies are usually attributed to either so-called lock-in effects, providing appearance of a sequence of commensurate and incommensurate phases (a devil's staircase [15]), or locking of the wave vector of the modulated structure on the defect density wave (a so-called thermal memory effect – see [16]).

Although the SSN crystals do not exhibits an incommensurately modulated structure, at least in its classical meaning, one could think about a quasi-periodic structure like, e.g., an array of ferroelectric domains with some walls which, in an analogous way, can interact with defects and/or impurities. This, however, is not the case since the temperature dependence of the optical birefringence looses its wavy character if one rotates a sample out of the normal-incidence geometry. As an example, Fig. 1b and a more detailed plot in Fig. 2b show the temperature changes in the optical birefringence for the sample rotated as said above by the angle of about 6.5 deg.

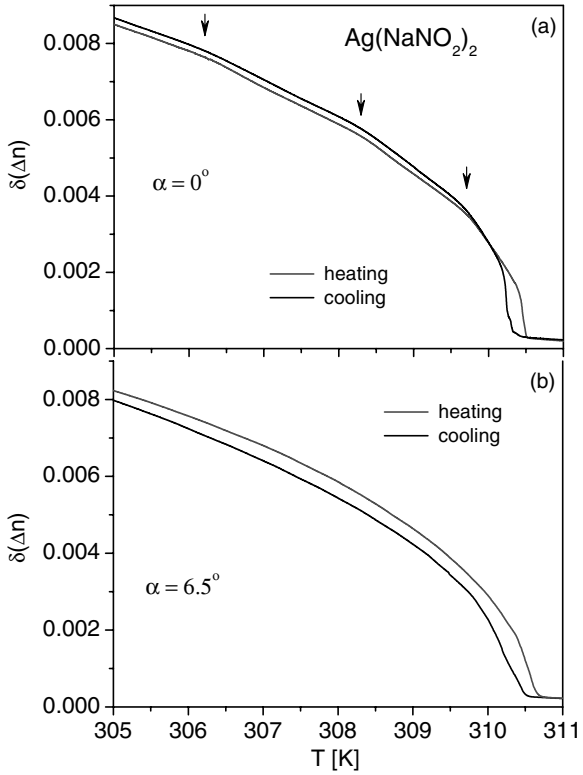

Fig. 2. Detailed plots of temperature dependences shown in Fig. 1: (a) geometry of normal light incidence (the incident angle $\alpha = 0^{o}$), and (b) slightly tilted incidence geometry ($\alpha = 6.5^{o}$). Arrows in panel (a) mark the kinks observed only for the normal incidence geometry (see the text).

We do not know an exact reason for the observed behaviour. One can only assume that it may be either a result of a weak interference contribution due to multiply reflections from the sample faces or it appears due to a superposition of the linear and circular birefringences. In regard to the latter one should notice that the circular birefringence (i.e., the optical activity) in the SSN crystals is indeed allowed by the symmetry only in the ferroelectric phase. In addition, the gyration tensor is characterised by only two nonzero components, $g_{13} = g_{31}$, if we adjust the principal axes of crystal as chosen above. For this reason the maximum of the circular birefringence is expected in the *XZ* plane along the diagonal directions between the principal axes *X* and *Z*. A sufficiently large effect is also expected along the crystallographic direction [101], or the direction $[10\bar{1}]$ which is symmetrically equivalent. The latter directions appear to be very close to the optic (isotropic) axes of the crystal.

Hence, the linear and circular birefringence for the geometry of normal incidence may be of the same order of magnitude, providing a slightly wavy dependence for the optical retardation. Rotation of the sample resulting in deviation of the wave normal from the optic axis increases the linear birefringence fast. This should considerably reduce the influence of circular birefringence on the optical retardation, thus explaining the fact why the kinks evidently disappear in the temperature dependence of the optical birefringence measured in the tilted-sample geometry. However, the gyrotropy of the SSN crystals does not appear in a scope of the present study, being a subject of a separate work and so our further consideration is limited to the results obtained for the tilted geometry only. In other words, the data presented in Fig. 1b (Fig. 2b) are considered as appropriate for that analysis.

We start from a general description of the paraelectric-to-ferroelectric transition in the SSN crystals using a phenomenological Landau theory. Following from the actual symmetry transformation ($D_{2h} \rightarrow C_{2v}$), we may write out the free energy as [11, 12]

$$F_P = \frac{1}{2}A(T - T_0)P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6, \tag{1}$$

where *P* is the order parameter associated with the *Y*-component of the polarisation, *A*, *B* and *C* the free energy expansion coefficients, and T_0 the Curie–Weiss temperature. The SSN exhibits a weakly first-order transition very close to the tricritical point. This means that the coefficient *B* can be considered as small and negative, whereas the two other coefficients, *A* and *C*, are essentially positive. The equilibrium value of the order parameter, i.e. the spontaneous polarisation P_s, may be obtained in a usual way by solving a set of the two equations, $F_P = 0$ and $\partial F_P/\partial P = 0$, which yields

$$T_c = T_0 + 3B^2/(16AC), \tag{2}$$

$$P_s = 0, \ T \geq T_c, \tag{3}$$

$$P_s = \frac{-B + \sqrt{B^2 - 4AC(T - T_0)}}{2C}, \ T < T_c. \tag{4}$$

As long as the expansion coefficient B remains negative, the temperature dependence of P_s exhibits a jump-like behaviour at $T = T_c$. The jump of P_s obviously vanishes in the tricritical point where $B \to 0$. In order to describe the optical birefringence changes, one must introduce additional terms into the free energy, which describe interaction between the order parameter P and the optical (electromagnetic) wave represented by the electric displacement $\mathbf{D}(\omega, k)$. Following the symmetry principle, the corresponding part of the free energy may be written as

$$F_{P,D} = \frac{b_{ii22}}{2} D_i^2 P^2 + \frac{a_{ii}^o}{2} D_i^2 , \tag{5}$$

where D_i are the components of the displacement vector, a_{ij}^o the bare optical impermeability coefficients and b_{ijkl} the coupling constants. The impermeability coefficients a_{ij} are determined as $\partial^2 F/\partial D_i \partial D_j$, which leads to

$$a_{ii} = a_{ii}^o + b_{ii22} P_s^2 . \tag{6}$$

Here the thermooptic contribution is defined by temperature dependence of the coefficients $a_{ii}^o(T)$. The second term in the r.h.s. of Eq. (6) describes the anomalous change in the optical birefringence driven by the spontaneous polarisation P_s, i.e. it represents a so-called quadratic electrooptic effect induced by the spontaneous polarisation [17]. All of off-diagonal ($i \neq j$) components of the a_{ij} tensor are equal to zero so that one can expect only deformation of the optical indicatrix, without its rotation in both the paraelectric and ferroelectric phases. Accordingly, the anomalous changes of the linear birefringence for any principal direction are expected to be proportional to P_s^2. More precisely, we have $\delta(\Delta n_*) = R_* P_s^2$, where R_* is the effective quadratic electrooptic coefficient expressed in terms of the directional angles θ and φ, the principal refractive indices n_i, and the tensor of coupling constants b_{ijkl}.

It is important that, in contrast to some ferroelectric materials like, e.g., lawsonite (see Refs. [18, 19]), the SSN does not exhibit any indications on pretransitional effects in its paraelectric phase (above T_c) where the thermooptic birefringence behaves quite linearly with temperature. This fact also suggests that the fluctuation effects are considerably suppressed as it usually takes place in most of the proper ferroelectrics. Thus, one can simply extract the thermooptic contribution from the total birefringence changes while extrapolating the linear temperature dependence of the optical birefringence from the paraelectric phase (see the dashed line in Fig. 1b). The remaining part marked as $\delta(\Delta n_*)$ represents an anomalous birefringence. It is shown in Fig. 3a for both the heating and cooling runs. The insert in Fig. 3a shows the plot $\delta(\Delta n_*)^{1/2}$ versus P_s at heating, where the $P_s(T)$ dependence has been taken from the work [4]. As expected, $\delta(\Delta n_*)^{1/2}$ indeed changes linearly with P_s ($\delta(\Delta n_*)^{1/2} = R_*^{1/2} P_s$), in good agreement with Eq. (6).

From the slope of this dependence one readily determines the effective quadratic electrooptic coefficient, $R_* = 1.88$ m^{4}C^{-2}. Fig. 3b displays a log-log plot of $\delta(\Delta n_*)^{1/2}$ versus

($T_c - T$) for both the cooling and heating runs. Notice that the plots of this kind make formal sense basically for the second-order phase transitions. Then the slopes of these dependences would enable one to evaluate the critical exponent describing behaviour of the order parameter near the transition point. Nevertheless, similar analysis may also be applied to weakly first-order transitions, at least in order to have a rough idea about the nearly tricritical behaviour.

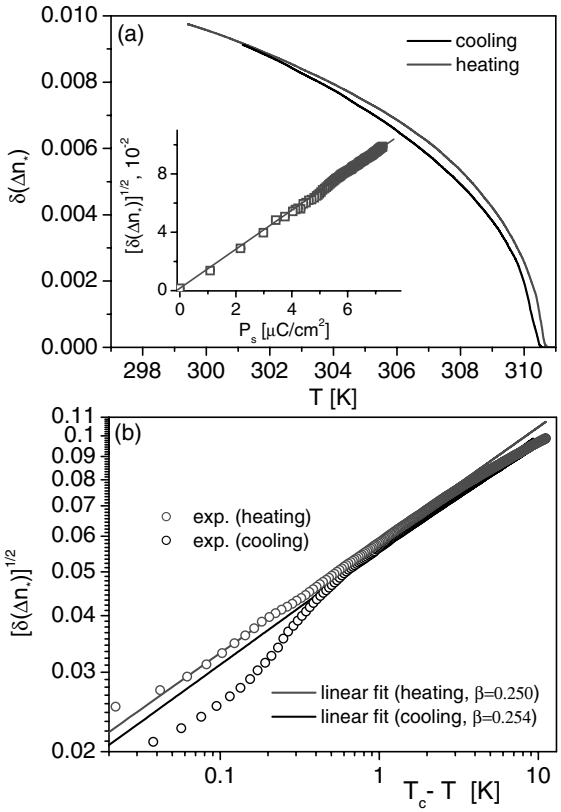

Fig. 3. Analysis of the data shown in Fig. 1b. Panel (a): anomalous birefringence $\delta(\Delta n_*)$ versus temperature T obtained after subtracting thermooptic contribution as shown in Fig. 1b. Insert shows dependence of $[\delta(\Delta n_*)]^{1/2}$ versus P_s at heating (the $P_s(T)$ dependence is taken from [4]). Panel (b): log-log plots of $[\delta(\Delta n_*)]^{1/2}$ versus $(T_c - T)$ at cooling and heating. Open points correspond to experiment and solid lines to linear fits. Assuming that the square root of the anomalous birefringence $\delta(\Delta n_*)$ obeys the law $[\delta(\Delta n_*)]^{1/2} \sim P_s \sim (T_c - T)^{\beta}$, one can determine the critical exponent β from the slopes (see the text).

In particular, the analysis gives a quite interesting result in case of the SSN crystals. A certain difference might be observed in the plots obtained for the cooling and heating runs. One can see that the SSN exhibits essentially continuous behaviour in the vicinity of the Curie point T_c at heating, with the critical exponent equal to 0.25±0.01 as should be expected for the tricritical point. This seems to be not the case for the cooling run where deviation from the linear dependence, due to slightly first-order character of the transition, is well seen already below $T_c - 0.3$ K. One must remember that this deviation

is continuous due to a smeared character of the first-order transition as discussed above. Furthermore, the difference found between the heating and cooling runs points out somewhat unusual features related to metastability of the SSN structure near T_c. Quite probably, this will require a more detailed further investigation.

4. Conclusions

Summing up, we have reported here the nearly tricritical behaviour of the SSN crystals in the region of the paraelectric-to-ferroelectric phase transition studied by a high-resolution optical birefringence technique. The results obtained are analysed within the phenomenological approach based on the Landau theory for the second-order phase transitions. The anomalous changes of the optical birefringence below the Curie point are found to be driven by the spontaneous polarisation via a spontaneous quadratic electrooptic effect. In the region of the Curie point, the SSN exhibits a slightly discontinuous behaviour at cooling and practically continuous behaviour at heating, with the critical exponent for the order parameter equal to 0.25, as expected for the tricritical point.

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Анотація. *В статті повідомляється про близьку до трикритичної поведінку кристалів $AgNa(NO_2)_2$ в області параектричного-сегнетоелектричного фазового переходу, яка досліджувалась високо-роздільним методом вимірювання двозаломлення. Отримані результати проаналізовані в рамках феноменологічного підходу на основі теорії Ландау для фазових переходів другого роду. Виявлено, що аномальні зміни двозаломлення при температурах нижчих від температури Кюрі викликані спонтанним квадратичним електрооптичним ефектом, індукованим спонтанною поляризацією. В області температури Кюрі кристали $AgNa(NO_2)_2$ проявляють деяке незначне відхилення від неперервної температурної залежності двозаломлення при охолодженні і практично неперервну залежність - при нагріванні з критичним індексом для параметра порядку рівним 0,25, як це є передбачено за умови існування трикритичної точки.*