

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**THE EFFECTS OF UNIAXIAL COMPRESSIVE STRESS ON
PHASE TRANSITIONS IN NaNO₂**

NEBAHAT BULUT
**A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF PHYSICS**

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THESIS SUPERVISOR
PROF. DR. MİRHASAN SEYİTŞOY

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PROF. DR. MİRHASAN SEYİTSOY

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JÜRİ

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. MirHasan SEYİTSOY

ÜYE

: Prof. Dr. Savaş BERBER

ÜYE

: Prof. Dr. Sedat ALKOY

MirHasan Seyitsoy
Savaş Berber
Sedat Alkoy

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun

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SUMMARY

In the present work, it is aimed to investigate theoretically the behaviors of dielectric constant of sodium nitrite (NaNO_2) around phase transition temperatures under uniaxial compressive stresses. Ferroelectric phase transition in NaNO_2 that is a material, which has incommensurate phase, will be studied. Temperature dependence of dielectric constant of NaNO_2 under uniaxial compressive stress will be determined by phenomenological theory that usually called Landau theory of phase transition is applied for describing the structural phase transition of sodium nitrite. Thermodynamic potential is used in the form of expansion of the series of order parameters with Lifshitsz invariant. The isobaric temperature dependence of dielectric constant (ϵ) of NaNO_2 crystal at the frequency 1 kHz under applied uniaxial pressure is studied. It is examined the response of NaNO_2 single crystal to a compressible uniaxial stress when applying uniaxial pressure in different direction. It is determined the phase diagram ($\sigma_{\perp} - T$) of NaNO_2 crystal under uniaxial compressive stresses for the first time as a theoretical study.

Key Words: Ferroelectrics, Phase Transition, Sodium Nitrite, Incommensurate Phase, Landau Theory.

ÖZET

Bu çalışmada, sodyum nitrit kristalinin faz geçiş sıcaklığı yakınlarında, dielektrik sabitinin davranışının tek eksenli basınç altında incelenmesi amaçlanmıştır. Sodyum nitrit, oransız faz geçişine sahip ferroelektrik bir malzeme ve bu ferroelektrik malzemenin faz geçişleri teorik olarak çalışılıp sunulmuştur. Sodyum nitrit kristaline uygulanan tek eksenli basıncın faz geçişlerine etkisi için daha önce yapılan deneysel veriler ile uygunluğu gösterilmiştir. Sodyum nitritin tek eksenli basınç altında sıcaklığa bağlı olarak değişim gösteren dielektrik sabiti Landau teorisi ile belirlenerek teoriye ve deneysel verilere uygunluğu gösterilmiştir. Termodinamik potansiyel düzen parametresinin serisi olarak yazılıp katsayıları hesaplanmıştır. Deneysel ölçümler 1 kHz frekans altında alınmıştır. Farklı yönlerde uygulanan tek eksenli basıncın kristale etkisi araştırılmıştır. Sodyum nitritin farklı yönlerde uygulanan basınca verdiği tepkinin faz diyagramları ilk kez bu çalışma ile sunulmuştur.

Anahtar Kelimeler: Ferroelektrik Malzemeler, Sodyum Nitrit, Landau Teorisi, Oransız Faz Geçişleri.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
T_c	: Curie temperature
ϵ	: Dielectric constant
ΔF	: Free energy
P_s	: Spontaneous polarization
Φ	: Gibbs free energy
η	: Order parameter
H	: External field
\mathcal{P}	: Polarization
$\chi_{22}^{p,T}$: Dielectric susceptibility
$C_{p,E}$: Heat capacity
$\zeta_{T,E}$: Volume comprssibility
K_E	: Thermal expansion coefficient
γ_i^p	: Pyroelectric coefficient
C_{C-W}	: Curie-Weiss constant
E_2	: Electric field along b axis
\AA	: Angstrom
C_p	: Curie-Weiss constant for paraelectric phase
C_f	: Curie-Weiss constant for ferroelectric phase
T_c	: Curie temperature
T_i	: Neel temperature
σ_{yy}	: Uniaxial compressive stress in y direction
σ_{zz}	: Uniaxial compressive stress in z direction
Eq.	: Equation
FeRAM	: Ferroelectric Random Memories
INC	: Incommensurate
kHz	: Kilohertz
NaNO ₂	: Sodium nitrite

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1. INTRODUCTION

For the last century, it has been widely investigated ferroelectricity in various materials. Ferroelectric phenomenon was firstly studied in Rochelle salt that the dielectric constant of Rochelle salt was dependent on the temperature and this material had reversible spontaneous electric polarization under the external electric field [Modani, 2012]. After this report, if a crystal has reversible spontaneous polarization, it is called ferroelectric crystal.

Ferroelectric phenomenon attracted the interest of scientists because of the advantages of these kinds of materials, especially in the electronic industry. Therefore, there have been many experimental methods to understand the nature of ferroelectrics and many new concepts have been studied about ferroelectrics. Ferroelectric materials have high dielectric susceptibility and memory effect. These properties provide ferroelectric crystals to be used in capacitors and piezoelectric devices.

My intention in this thesis is to understand the behavior of the structurally simplest ferroelectric material sodium nitrite and describe theoretically the temperature dependence of the dielectric constant of sodium nitrite in the phase transitions under uniaxial compressive stresses with the phenomenological theory of Landau, which is the useful method to combine the experimental data and theoretical treatments of materials.

The crystal shows the first order and order-disorder type transitions from the ferroelectric to paraelectric phase. It has a region called the incommensurate phase there is a sinusoidal ordering parameter of NO_2 molecules along the a-axis with a period of $8a$.

First part of this thesis is the review of the Landau theory of structural phase transitions, from ferroelectric phase to incommensurate phase and then paraelectric phase. Dielectric constant was analyzed in terms of Landau free energy for each phase.

In chapter two, literature research about the structural and dielectric properties of sodium nitrite was mentioned.

Third part is the explanation of how I solved the Landau theory when the applied uniaxial compressive stress for sodium nitrite.

All experimental details were given about the measurements of dielectric constant of the sodium nitrite under applied uniaxial pressure and the results about the phase diagrams of sodium nitrite in the effect of the uniaxial compressive stress were also discussed in the fourth part. A group of researches in Institute of Physics of Academy of Sciences of the Republic of Azerbaijan measured the experimental data.

In chapter five, the phase diagrams of sodium nitrite are discussed according to both experimental and theoretical results. The temperature dependence of dielectric constant of sodium nitrite under uniaxial compressive stress were explained near the phase transition temperature according to the Landau theory. It was mentioned about the experimental results of dielectric constant of sodium nitrite into incommensurate phase transition.

Lastly, the conclusions and the suggestions about the future were given taking into account the results of this thesis.

2. REVIEW OF FERROELECTRICITY

2.1. Ferroelectric Materials

2.1.1. Definition of Ferroelectricity

In analogy, the characteristic properties of ferroelectrics include spontaneous electric polarization, polarization reversal (switching), and disappearance of the polarization above the temperature of ferroelectric phase transition in the Curie point, T_c and hysteresis loop.

Curie temperature is one of the most important characteristic of ferroelectrics because it marks the transition for a material from the ordered to disordered phase. Dielectric constant of materials can reach the value, which is higher than in the disordered phase.

In figure 2.1, there is a graph of temperature dependence of spontaneous polarization for sodium nitrite crystal. Spontaneous polarization is constant for a while and then it rapidly goes to zero with higher temperature. The point is the Curie point that the ferroelectric phase disappears and a new structural phase occurs.

In detail, ferroelectric phase transition is a structural phase transition that appears in the unit cell of crystals with the effect of temperature on the atoms. These atoms change their positions or displacements and polarization occurs spontaneously in the domains. Furthermore, some polarization directions depend on the crystal form.

The spontaneous polarization is one of the most specific properties of ferroelectric materials. This phenomenon appears in the materials at two opposite sides and it is reversible with applied electric field. Actually, spontaneous polarization is present even there is no external electric field. More specifically, spontaneous polarization can be explained as the surface density of the bound charge on the sample surface [Strukov and Levanyuk, 1998]. Since the displacement of atoms in the phase transition exists in each unit cell and the vector of polarization is reoriented. In this point, it should be mentioned about the hysteresis loop of ferroelectric crystals.

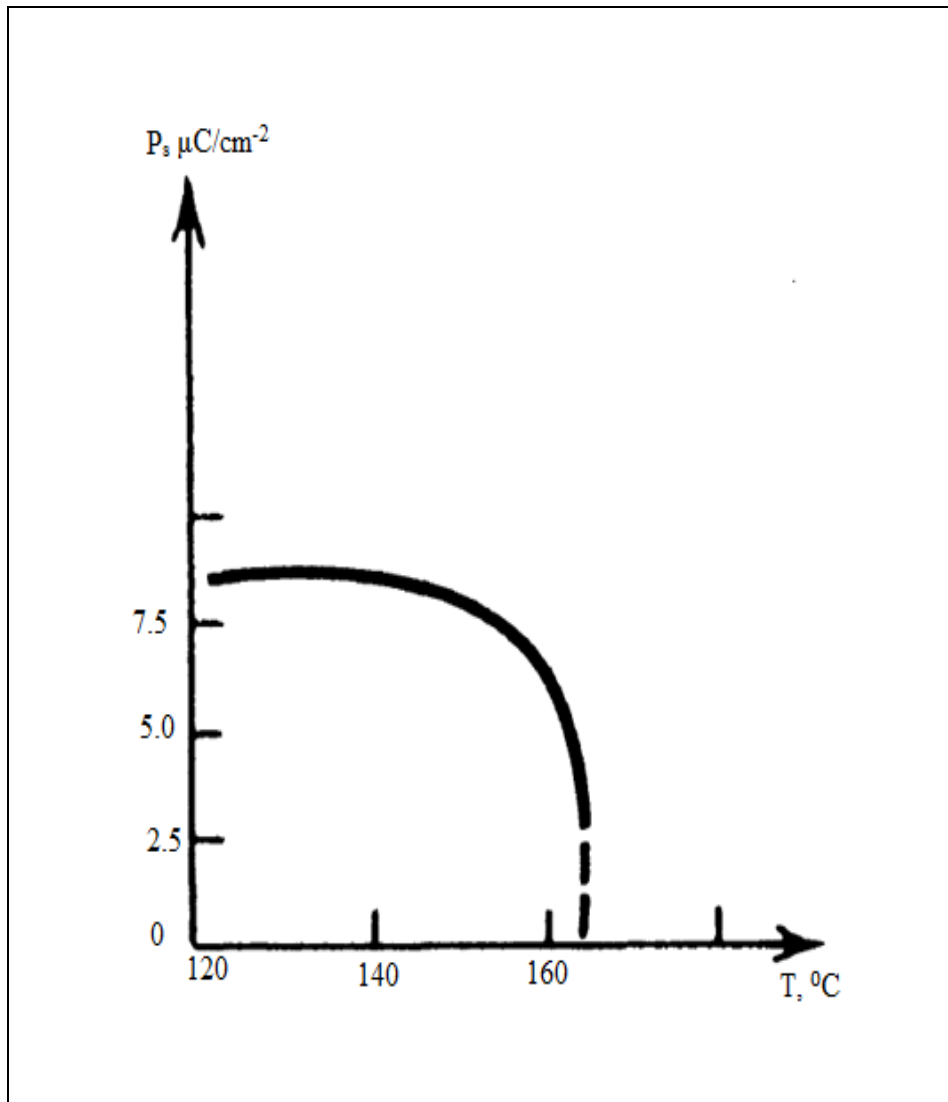


Figure 2.1: Temperature dependence of spontaneous polarization of sodium nitrite crystal.

Sawyer - Tower circuit, which is shown in figure 2.2 is generally used the observation of the ferroelectric hysteresis loop of macroscopic polarization in the effect of applied electric field. Ferroelectric sample is placed on the horizontal plates of oscilloscope and an alternating voltage is applied through the electrodes. Therefore, this voltage in C_0 is proportional to the electric field in the crystal. C_0 is linear capacitor and connected with the ferroelectric crystal in the series circuit. The hysteresis loop is screened with the oscilloscope.

Figure 2.3 shows the hysteresis loop that the behavior of polarization with the presence of applied electric field on ferroelectric sample. Polarization changes proportionally with the applied electric field. From the point A to the point B, there is small applied field so it has linear curve and ferroelectric crystal acts like a

paraelectric. Through the point C, if it is applied the field properly to change the direction of polarization, the negative atoms in the material moves along the direction of applied field. In the point C, the polarization rapidly reaches to the maximum value with respect to applied electric field. In the crystal domains, it is observed the saturation of dipole moments in the point C.

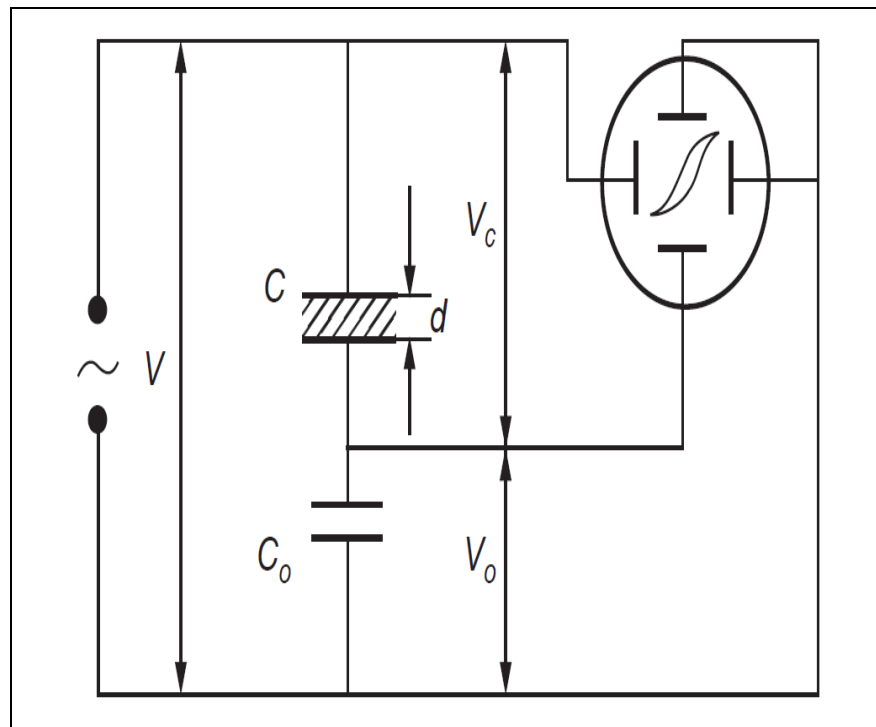


Figure 2.1: Representation of Sawyer-Tower circuit for observation of polarization and electric field description in ferroelectric materials.

The applied electric field affects the dipole moments and if it is reversed to opposite direction how the dipole moments act? For the point D, although applied electric field is zero, there is still polarization in the material. It calls spontaneous polarization P_s . Through the point E, applied field is reversed in order to obtaining zero polarization. In the point F, polarization is zero even there is applied electric field. However, the electric field, which supplies the polarization to be zero, is called coercive electric field E_c . With the increasing of the applied field in the negative direction, the polarization is aligned in new direction of dipoles and saturation in the point G. If the field strength is applied enough, the directions of dipoles in the domains change in the opposite direction. After the cycle of the applied field, there occurs hysteresis loop [Strukov and Levanyuk, 1998].

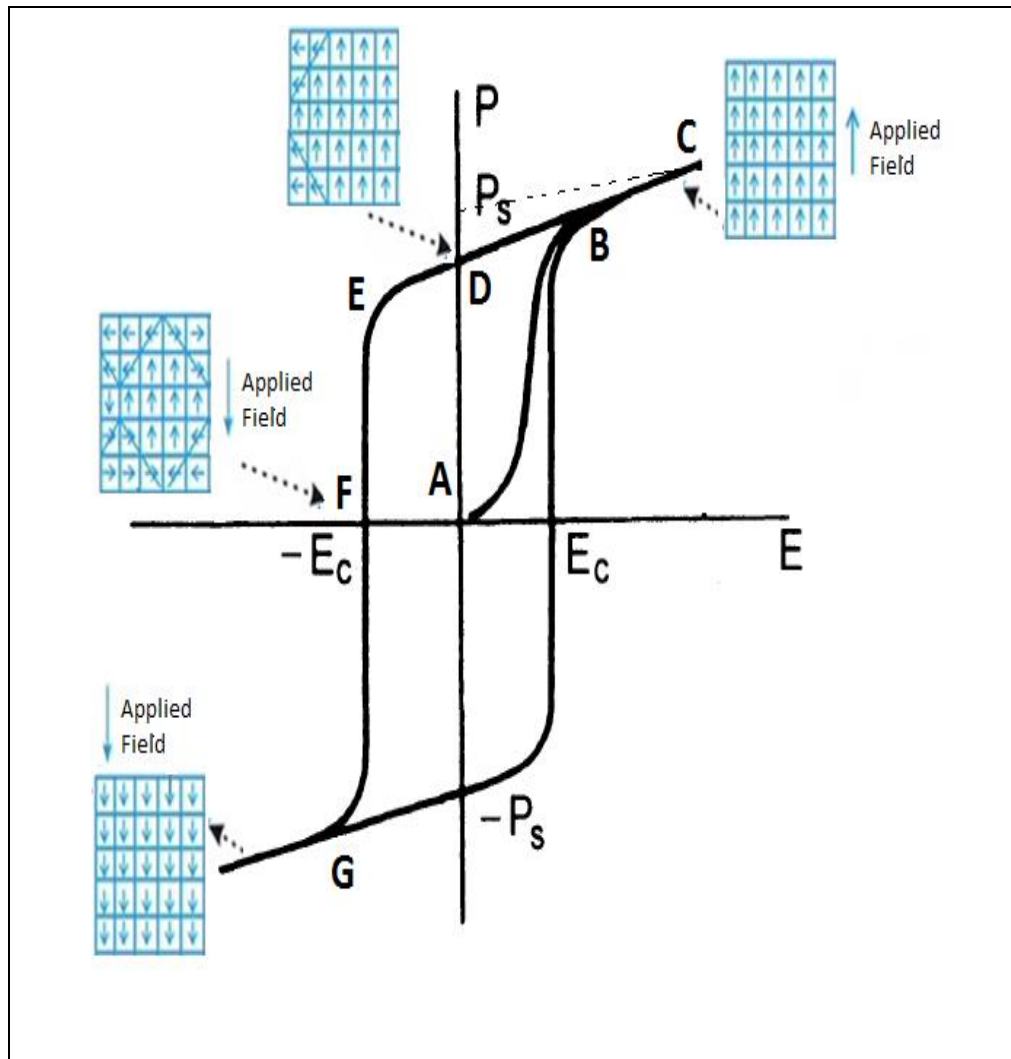


Figure 2.2: Hysteresis loop of the polarization and electric field dependence for a ferroelectric material.

From the result of the hysteresis loop, the reversible polarization by applied electric field is exactly linked to the alignment of the domain walls in the crystal. This hysteresis loop can be observed in the ferroelectric phase.

2.1.2. Applications of Ferroelectric Materials

As in the scientific fields, the phenomena ferroelectricity has attracted the attention of industrial committees. Ferroelectric materials are used in many technological applications with the different areas such as sensors, cell phones, ultrasound machines, optical, microelectronic and non-volatile computer memory devices because of the remarkable properties of them. In 20th century, these materials were firstly used for naval operations as a sensor in sonar devices that is

affected by the underwater sound vibrations and this causes the electric field, which gives the information about the depth [Grinberg et al., 2004]. There have been many systems, which are developing fast and easily adapted to in our daily life.

With the development of technology, the needs of the huge memory devices and more safe ones are also growing day by day. In general, it is important that the cycle times of the read and write the data for the memory storage devices or the capacity of the memory. Ever since ferroelectric materials have been started to use for random access memory these types of problems have been overwhelmed. Ferroelectric random access memories (FeRAM) are preferred due to gaining non-volatile access random memory with using the ferroelectric layer to store data. FeRAM eliminates the battery backup to store the data. There is no battery folder and mechanisms of erasing memory cells. Thus, it has high-speed rewrite. The read cycle time is equal to the write cycle time and this is approximately 150 ns range and small power requirements. Figure 2.4 shows the comparing FeRAM with the other two non-volatile memories [Web 3, 2015].



Figure 2.3: There are no mechanisms of erasing and writing operations. Byte writing speed is fast even power down in FeRAM.

FeRAM is used also in industrial equipments (printers, gas meter etc.), communication devices (POS, video conference system etc.) [Web 2, 2015].

Sensor technologies are growing with the class of ferroelectric materials. The sensors have the mechanism, which change mechanical signals into electrical signals. They act as accelerometers and are used for measurement of pressure, force, temperature, and vibrations [Damjanovic and Muralt, 2001].

In 1982, Ruppel and his colleagues presented the invention of ferroelectric sensors using sodium nitrite layer, which has simple crystal structure so economically manufacturing is easy. This sensor includes equipments that detect the energy difference while applying electrical energy to the sensing elements. It is used for radiation detector to measure the radiation changes. Figure 2.5 represents a sensor invention, which is a radiation detector includes a sodium nitrite layer is numbered with 6, that is between the electrodes. This sensor detects an optical representation of an object and translates this image to electrical signals. In here electrodes measure the radiation of images [Web 1, 2015].

Fig. 6

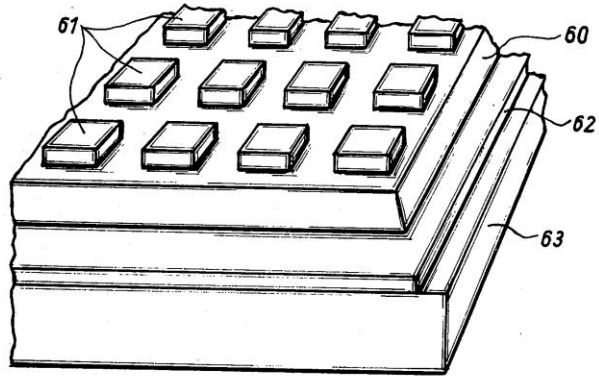


Fig. 7

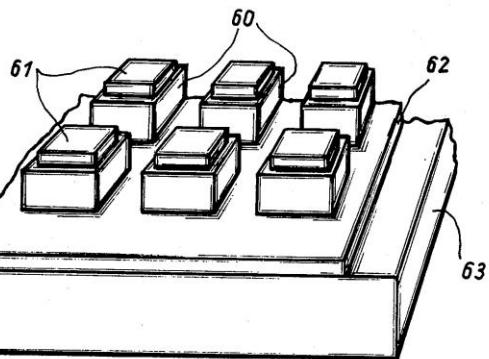


Figure 2.4: Radiation detector invention with sodium nitrite layer.

2.2. Phenomenological Theory of Structural Phase Transition

Structural phase transitions can be introduced, as the change of the symmetry of the system. The symmetry change should be occurred via the parameters like temperature, pressure, external electric field and magnetic field. It is expected that the structure of crystal is turned to the new crystal structure while the temperature or pressure of the crystal is changing. A crystal structure is more distorted if the parameter is temperature or pressure while they are changed rapidly. It is expected that a crystal structure turns into one another crystal structure. Thus, occurrence of this change should be at the temperature that is called transition temperature, Curie point (T_c). At Curie point, T_c the system is more stable and has the minimum internal energy.

While the non-symmetric crystal structure, which losses some of the symmetry elements comes out the symmetric structure during the phase transitions. Small distortions are occurred in the crystal such as displacement of atoms or distances in the atoms. These remarkable distortions are named as order parameters (η) and important for realizing them. As it should be introduced the order parameters mathematically, it can be written as $c_1m_1 + c_2m_2 + \dots + c_nm_n$.

It can be described some lattice modes where n is the number of the invariant subspaces and the order parameters is known as defining the mode with these invariant subspaces. The order parameter (η) is an array of real parameters $\eta = [c_1 c_2 \dots c_n]$. When these modes are in different side $\eta \neq -\eta$ nonsymmetrical phase occurred and $\eta = 0$ determines the high symmetric phase.

As I introduced all these terms for phase transitions will be helpful for understanding the ferroelectric phase transition which can be described as structural phase transition. In the phase transition of ferroelectric crystal, to understand how the external electric field affects the crystal it will be easier using the theoretical approach that the phenomenological Landau theory. The detail of Landau theory was developed by Lev Davidovich Landau (1908 – 1968) to study behavior of ferroelectric and ferromagnetic materials.

Theory of phase transition is called as Landau theory because of the contribution of Lev Davidovich Landau for the remarkable development in the theory of phase transition. In the structural phase transition, Landau theory is just

interested in the change of the structural symmetry in a crystal and applied to the phase transition, which causes the symmetry change in a crystal.

Landau theory is in the origin of the several condensed matter physics to be interested in. For almost all condensed matter physics researches, Landau theory is one of the most important tool and in the center of this studying, such as structural phase transitions, magnetism, and superconductivity. While the structural phase transition Landau theory is interested in the symmetry of the crystal and is used for the phase transition that causes only the changing of the symmetry of the crystal rather than interaction of atoms, ionic and covalent bond interactions, Coulomb, and Van der Waals interactions.

The main part of Landau theory is that it should create a quantity that must introduce the energy of the system in the vicinity of the phase transition. At this point, this energy is named as Landau free energy and depends on the parameters that are temperature, pressure electric and magnetic field same as Helmholtz and Gibbs free energies that are thermodynamic potential. Thus, the ideal modes of the system appear with this quantity, which is called order parameter.

By analyzing the dependence of the Landau free energy on the order parameters, some questions are lightening in minds that how the order parameters are included to the thermodynamic potentials. And one other question is that is it possible that showing the thermodynamic potential as a series of order parameter at the temperature of phase transition (T_c)?

It is known that the energy of the system can be changed the external parameters, which are temperature, pressure, electric and magnetic fields and if the energy of the system depends on these variables, it can be easily said that there is a variable called as order parameter which is included in the energy of a system.

Landau free energy \mathcal{F} , can be stated as,

$$\mathcal{F} = \mathcal{F}_0 + \Delta\mathcal{F}(\eta^i) \quad (2.1)$$

\mathcal{F}_0 is the part of the thermodynamic potential function which is independent of the variables that are order parameters, η^i . Meanwhile, \mathcal{F}_0 indicates that the energy of the system is symmetric. In eq. 2.2, $\Delta\mathcal{F}(\eta^i)$ describes the small energy vicinity of

the phase transition. The free energy of a ferroelectric material, without external electric field,

$$\Delta\mathcal{F}(\eta^i) = -\eta H + \frac{a}{2}\eta^2 + \frac{b}{3}\eta^3 + \frac{c}{4}\eta^4 + \dots \quad (2.2)$$

The changes of symmetry, for example, the case of $\eta \rightarrow -\eta$ these values are not include the Taylor expansions of free energy \mathcal{F} , in order not to influence the power of odd-numbered in the expansion. In the term $-\eta H$, H is the external field thus it is multiplied with -1 . The term of $-\eta H$ can exist for free energy only if there is external applied field H . Order parameter, η should be changed by rotation thus $-\eta H$ is written for the system. This kind of transition is called ferroic phase transitions. There are some common examples such as ferroelectric, ferromagnetic and ferroelastic transitions. In ferroelectric phase transition, \mathcal{P} polarization is written with the minimizing of \mathcal{F} free energy with respect to H external electric field. Generally the order parameter η is polarization for ferroelectric transition, same as other ferroic (magnetization and strain etc.).

$$\mathcal{P} = -\frac{\partial\mathcal{F}}{\partial H}\eta \quad (2.3)$$

In other words, the order parameter η is proportional with the electrical polarization \mathcal{P} in ferroelectric phase transition. Near the phase transition temperature T_c , as observed in many experimental investigations, ferroelectric phase transitions occurs when one of the coefficients of the quadratic term of order parameter in the expansion of free energy changes sign for example from positive to negative.

The order parameters are also known as the displacement of an ion in the unit cell of a crystal for structural phase transitions. Applying the external electrical field, the electrical dipole moments are aligned along the electrical field and thus the order parameter equals the electrical polarization.

For a dielectric crystal, when an electrical field is applied there appears work on the crystal. When the electric field applied, thermodynamic equation for mechanical work dW of dielectric crystal can be analyzed as,

$$dW = \frac{1}{4\pi} E_i dD_i = E_i dP_i + d\left(\frac{E_i^2}{8\pi}\right) \quad (2.4)$$

E_i refers the components of the vector of electrical field strength and D_i and P_i are displacement vectors and polarization vectors respectively. According to 1st law of thermodynamic, if dU is the differential of the internal energy of a dielectric crystal, it has the form,

$$dU(S, v, P_i) = T dS - p dv + E_i dP_i \quad (2.5)$$

Gibbs free energy is in the form,

$$\Phi = U - TS + pv \quad (2.6)$$

the differential of Gibbs potential can be written by,

$$d\Phi(T, p, E) = -S dT + v dp - P_i dE_i \quad (2.7)$$

this form verifies the properties of dielectric crystals. In eq. 2.7, $\Phi = \Phi(T, p, E)$ defines that the potential difference of the dielectric crystal is constant. T , v , S , and p are the parameters in the thermodynamic potential which refers temperature, volume, entropy and pressure.

The first derivatives of Gibbs potential Φ give the information about the dielectric crystal. For instance, to obtain polarization P_2 , dielectric susceptibility $\chi_{22}^{p,T}$ and dielectric constant $\varepsilon_2^{p,T}$ can be derived from the thermodynamic potential.

$$P_2 = -\left(\frac{\partial\Phi}{\partial E_i}\right), \quad \chi_{22}^{p,T} = \left(\frac{\partial P_2}{\partial E_2}\right), \quad \varepsilon_2^{p,T} \approx 4\pi\chi(T) \quad (2.8)$$

Additionally, the second derivatives of Gibbs potential determine the properties of materials that are the heat capacity $C_{p,E}$ at constant pressure and electric field, the volume compressibility $\zeta_{T,E}$ at constant temperature and electric field, the thermal

expansion coefficient K_E at constant electric field, and the pyroelectric coefficient γ_i^p .

$$C_{p,E} = -T \left(\frac{\partial^2 \Phi}{\partial T^2} \right), \quad \zeta_{T,E} = \left(\frac{\partial^2 \Phi}{\partial p^2} \right) \quad (2.9)$$

$$K_E = - \left(\frac{\partial^2 \Phi}{\partial p \partial T} \right), \quad \gamma_i^p = - \left(\frac{\partial^2 \Phi}{\partial E_i \partial T} \right)$$

As mentioned in previous about Landau free energy, Gibbs free energy, which is defined for dielectric crystal, can be written as a function of the order parameter, temperature and pressure. The thermodynamic potential can be given the expansion of order parameter.

$$\Phi = \Phi(T, p, \eta) = \Phi_0(p, T) + \Phi_1(p, T, \eta_1, \dots, \eta_n) \quad (2.10)$$

In this form, there is a term that is independent from the order parameter $\Phi_0(p, T)$. This term defines the symmetric phase of the material.

Landau theory is the useful method to determine the structurally phase transition. Therefore, it can be easily understood the behavior of first and second order ferroelectric phase transition with the studying of landau theory of thermodynamic potential.

2.2.1. First and Second Order Transitions

Transformation of structure of a crystal can be described as continuous and discontinuous. Thus, first order phase transition is characterized by a discontinuity in different state variables. Melting of ice, vaporization of water are the example of first order phase transition. In low and high temperature, two phases can be exist at the same time. For melting ice, there are water and ice in a system, solid-liquid, liquid-gas transitions at critical transition temperature. The change of the entropy in the system corresponds to latent heat. For first order phase transition, thermodynamic quantities that are internal energy, entropy, enthalpy and volume have discontinuity.

In the system, if there is total thermodynamic equality, it can occur structural phase transition in any phase transition temperature, however this is impossible for experimental observations. Clausius – Clapeyron equation in 2.11 has the basic information about the discontinuous phase transitions.

$$\frac{dT}{dp} = \frac{\Delta\vartheta}{\Delta S} \quad (2.11)$$

Second order phase transition is described with continuous change in the system. It involves a continuous change in entropy. Therefore, there is no latent heat. In other words, if the phase transition reaches the transition parameter but it is still constant and there is no change for transition parameters, these structural phase transitions are continuous. Moreover, this kind of phase transition is related to the structure of crystal and deformation of the lattice. There occurs symmetry transformation in the crystal. Continuous deformations cause the second order phase transitions.

Although in the first phase transition, positions of the atoms change in a jump wise manner, near the second phase transition the distortion of the structure in unit cell may be as small as desired. With decreasing of the temperature and in the vicinity of the transition temperature due to the small deformations there is symmetry breaking in the crystal. Thus, the symmetry group of the crystal changes to the other subgroup.

Second order phase transitions have some anomalies of the various physical properties. These anomalies are different characteristics of the crystal, such as heat capacity, elastic moduli, dielectric constant, thermal expansion coefficient etc.

The majority of ferroelectric phase transitions occur with the transformations of the order parameters near the transition point. The structure and symmetry of a phase can be in the class of first order phase transition and has a tendency to second order phase transition.

To define the kind of the phase transition of a crystal, it is used the properties of Landau theory. As introduced before, Landau theory uses the expansion of the thermodynamic potential, which depends on the order parameter.

$$\Phi(\eta) = \Phi_0(0) + \Phi'\eta + \frac{1}{2}\Phi''\eta^2 + \dots \quad (2.12)$$

Thermodynamic potential can be written in the form of the series expansion in powers of order parameter and the coefficients depend on the temperature.

$$\Phi(T, \eta) = \Phi_0(T) + A(T)\eta^2 + B(T)\eta^4 + C(T)\eta^6 + \dots \quad (2.13)$$

The coefficients that depend on the temperature in the thermodynamic potential is used their series expansion in powers of phase transition temperature $(T - T_c)$ because it is difficult to find exact form of the coefficients.

$$\begin{aligned} A(T) &= A(T_c) + A'(T - T_c) + \frac{1}{2}A''(T - T_c)^2 + \dots \\ B(T) &= B(T_c) + B'(T - T_c) + \frac{1}{2}B''(T - T_c)^2 + \dots \end{aligned} \quad (2.14)$$

With the first expansion terms, the thermodynamic potential has the form in the series expansion of both temperature and order parameter.

$$\Phi(T, \eta) = \Phi_0(T) + \frac{1}{2}\alpha(T - T_c)\eta^2 + \frac{1}{4}\beta\eta^4 + \frac{1}{6}\gamma\eta^6 - aE_2\eta \quad (2.15)$$

where $\alpha = 2A'$, $\beta = 4B(T_c)$ and $\gamma = 6C$ can be written for abbreviation. To determine what kind of phase transition there occurs in the system, the coefficient β defines the first or second order phase transition according to if β is bigger or lower than zero. For first order phase transitions, the condition is $\alpha, \gamma > 0, \beta < 0$ and for the second order phase transition β is bigger than zero ($\beta > 0$).

First order phase transition can be analyzed with the minimizing of the thermodynamic potential. At equilibrium condition, $\Phi(T) = \Phi(T, \eta_0(T))$;

$$\frac{\partial \Phi}{\partial \eta} = 0, \quad \frac{\partial^2 \Phi}{\partial \eta^2} > 0 \quad (2.16)$$

In this condition, the solving of the thermodynamic potential,

$$\frac{\partial \Phi}{\partial \eta} = \eta_0 [\alpha(T - T_c) + \beta \eta_0^2 + \gamma \eta_0^4] = 0 \quad (2.17)$$

$$\eta_0^4 = x^2 \quad (2.18)$$

$$\gamma x^2 + \beta x + \alpha(T - T_c) = 0 \quad (2.19)$$

$$x = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha} \quad (2.20)$$

$$\eta_0^2 = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha(T - T_c)\gamma}}{2\gamma} \quad (2.21)$$

In the specific temperature range, when β is smaller than zero ($\beta < 0$), there are five roots of the order parameter. This range of specific temperature can be introduced with the eq. 2.24.

$$\eta_0^2 = -\frac{\beta}{2\gamma} \left\{ 1 \pm \left[\sqrt{1 - \frac{4\alpha(T - T_c)\gamma}{\beta^2}} \right] \right\} \quad (2.22)$$

$$\frac{4\gamma\alpha(T_c^* - T_c)}{\beta^2} = 1 \quad (2.23)$$

$$T_c^* = T_c + \frac{\beta^2}{4\gamma\alpha} \quad (2.24)$$

However, for higher temperature when $T > T_c$, this means crystal is in symmetric phase,

$$\eta_0 = 0 \quad (2.25)$$

when temperature is lower than the transition point $T < T_c$, the order parameter has three roots.

$$\eta_0^2 = -\frac{\beta}{2\gamma} \quad (2.26)$$

The crystal transforms the structure in a new one with the change of temperature and pressure or any external parameter. However, it must have the minimum internal energy to keep its stable crystal structure. The equilibrium condition of thermodynamic potential has been written in eq. 2.16. The main purpose of Landau theory is to find the polarization value for minimizing the free energy. In addition to this is to define the dependence of the external parameter for the properties of ferroelectric crystal. In the second order phase transition, in equilibrium condition the thermodynamic potential is same in the first order phase transition.

$$\eta_0 = 0, \quad T > T_c \quad (2.27)$$

$$\eta_0^2 = -\frac{\alpha(T - T_c)}{\beta}, \quad T < T_c \quad (2.28)$$

$$\Phi(T) = \begin{cases} \Phi_0(T), & T > T_c \\ \Phi_0(T) - \frac{[\alpha(T - T_c)]^2}{4\beta}, & T < T_c \end{cases} \quad (2.29)$$

2.3. Incommensurate Phase Transition

Over five decades, there have been remarkable interests to investigate in many materials, which have incommensurate (INC) phase transition. In 1936, Tunel and his colleague was studying the material which was calavarite X-ray diffraction pattern they realized that there were some extra points, these causes did not explain with crystal lattice structure [Cummins, 1993].

Normally, superstructure that can be described as the changing in the translational symmetry of crystal during the phase transition. However, in some ferroelectric materials such as, NaN02, NH4hBeF4, TlInS2 and TlGaSe2, while there occur phase transitions into polar phase recognized a new specific phase, which is called incommensurate phase. Subsequently, this phenomena appears in many materials, such magnetic materials, metallic alloys, some compounds of graphite, liquid crystals and recently very popular superconductor materials.

Incommensurate phase can be described as the irrational ratio between the wavelength of the modulation wave vector (λ) and the unit cell lattice parameter (a) in paraelectric phase. In other words, incommensurate phase can be defined as a phase that the lattice period is modulated with a spatial modulation wavelength. There is no periodicity in any directions. Usually the INC phase is stable in a limited temperature range, and the lattice modulation wavelength becomes longer with decreasing temperature.

Truly incommensurate phase shows many new phenomena so it is attractive for theoretical and experimental studying because in periodic crystals these phenomena are not found. In this section, it is introduced how the incommensurate phase occurs in a crystal while changing a phase.

The stages of the phase transition start from the paraelectric (normal) symmetric phase to the ferroelectric (commensurate) phase and between these two

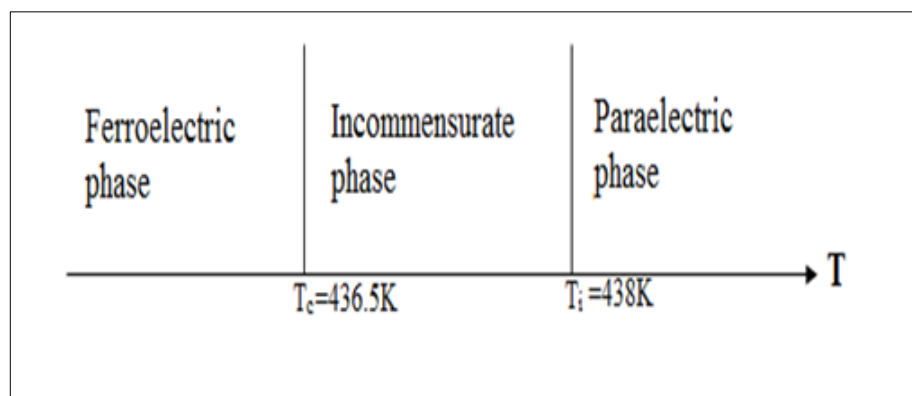


Figure 2.6: The phases of the temperature dependency for the ferroelectric sodium nitrite crystal.

phases, an incommensurate phase appears for a limited range with the external parameters, such as decreasing of temperature or increasing of pressure. In figure 2.6, the incommensurate phase exists for about 1.5 K.

When the incommensurate phase was found in NaNO_2 , researchers realized a sinusoidal modulation wave, which had a period approximately $8a$ along a -axis. It is represented in figure 2.7, NO_2^- ions has two orientations, up and down. Na^+ ions are oriented with the position of NO_2^- ions.

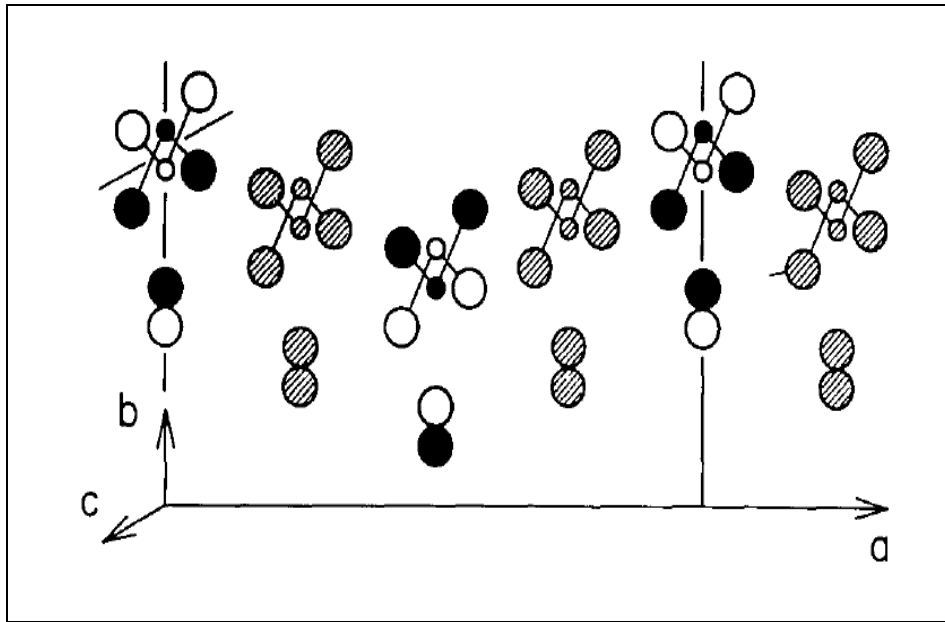


Figure 2.7: Schematic structure of the incommensurate phase of NaNO_2 . Upper row: The two positions of the NO_2 ions. Lower row: Corresponding positions of Na ions. The repeat distance is shown $\sim 8a$.

3. LITERATURE SURVEY OF SODIUM NITRITE (NaNO₂)

Sodium nitrite is an inorganic non-polar compound, and a member of ABO₂ group of crystal, which is transparent with yellowish color. In general, ABO₂ group of crystals is predicted with the angle of 120° between the cation and oxygen, thus between the angle of the nitrogen and the oxygen atoms is same 120° for one of the member of this group of crystal NaNO₂.

Sodium nitrite (NaNO₂) is one of the ferroelectric materials that ferroelectricity in NaNO₂ was discovered along the b axis with an experiment about dielectric constant in 1958[Sawada, 1958]. In this experiment, ferroelectricity appeared during the phase transition point. Since the discovery of ferroelectric property of sodium nitrite, there have been various investigations both experimentally and theoretically. One another important thing about sodium nitrite is that it was the first dielectric material with the existence of incommensurate phase was found [Qui, 1985]. All attention is on that material for which the crystal structure of sodium nitrite is simple, and a real model to be studied experimentally. For this reason, a large number of investigations about sodium nitrite both experimentally and theoretically are gradually developing day by day.

Characterizations of phase transition of sodium nitrite have been discussed with the number of reports via different techniques [Cummuns, 1993]. X-ray and neutron diffraction studies, Raman and infrared spectroscopy, hydrostatic pressure are some of the measurement methods of the dielectric constants and thermal conductivity, specific heat and thermal expansion, crystal structure and optical properties.

Many reporters have also carried out theoretical studies in detail. Mean field theory, Ising model and phenomenological theory are basic studies about the phase transition of sodium nitrite crystal. It will be introduced theoretical reports about the sodium nitrite crystal in following chapter. In present section, there are information about the crystal structure and properties of sodium nitrite material with experimental studies.

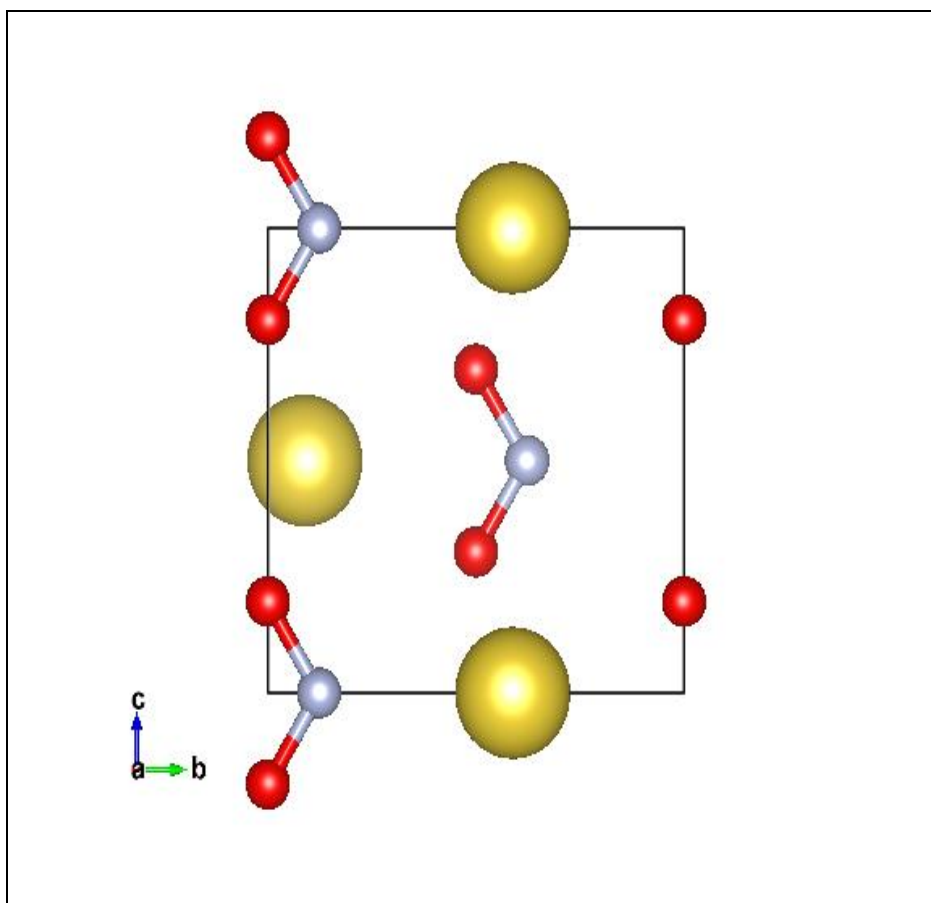


Figure 3.1 Unit cell of the sodium nitrite at room temperature ferroelectric phase. Nitrogen is grey, oxygen is red and sodium is yellow.

3.1. The Crystal Structure of Sodium Nitrite

The investigation of the crystal structure of NaNO_2 was first published with the experiment of evaporation of a water solution of NaNO_2 [Zeigler, 1931]. At room temperature, NaNO_2 is known as a ferroelectric crystal and polar along the b-axis. It has body-centered orthorhombic crystal structure with space symmetry group of $C_{2v}^{20} - Im2m$. The lattice parameters for unit cell size are $a = 3.57\text{\AA}$, $b = 5.578\text{\AA}$, $c = 5.39\text{\AA}$ and there are two molecules in the unit cell [Naberezhnov and Fukin, 2003]. In paraelectric phase, above the phase transition temperature 438 K, the crystal has an orthorhombic crystal structure, which is non-polar, and space group is $D_{2h}^{15} - Immm$. The lattice constants are $a = 3.652\text{\AA}$, $b = 5.652\text{\AA}$, $c = 5.362\text{\AA}$ with the body-centered lattice.

Table 3.1: Crystal structures of sodium nitrite for ferroelectric, incommensurate and paraelectric phases.

Phases of NaNO ₂	Phase Transition Temp. Points	Crystal Structures	Space Groups
Paraelectric	438K<	Orthorhombic	$D_{2h}^{15} - Immm$
Incommensurate	436.5K < T _i <438K	Orthorhombic	$D_{2h}^{15} - Immm$
Ferroelectric	< 436.5K	Orthorhombic	$C_{2v}^{20} - Im2m$

Ferroelectricity in NaNO₂ is seen when the NO₂ molecules turns in the same direction. In figure 3.1, there is a unit cell of sodium nitrite at room temperature, the red atoms is indicating the oxygen, the grey is nitrogen, and the yellow shows sodium. Because of the V shape of NO₂ molecules, there occurs dipole moments that causes the spontaneous polarization. To the Curie temperature, it is in order type and ferroelectric phase.

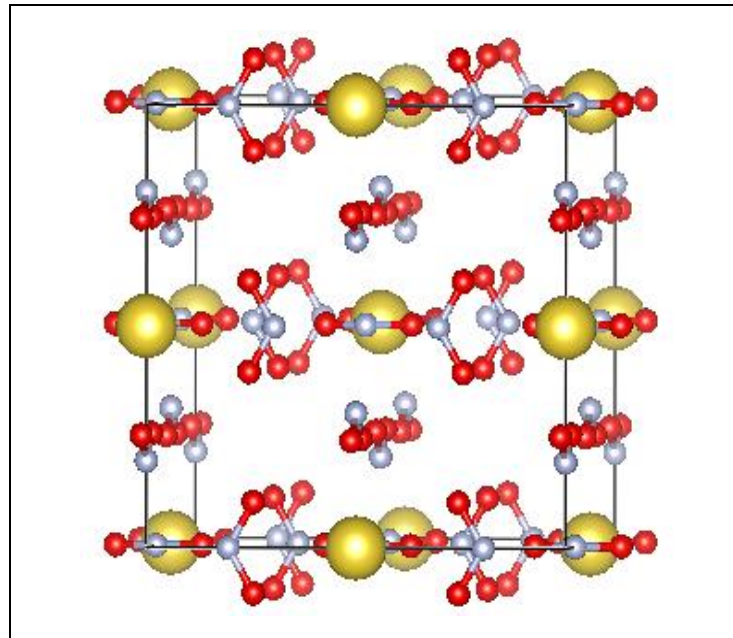


Figure 3.2: Incommensurate phase of NaNO₂. Disordered structure and more symmetric than ordered type in ferroelectric phase.

With the change of the phase from ferroelectric to one another, there occurs disorder structure that is shown in figure 3.2. NO₂ molecules turn the opposite sites. In addition, the structure is more symmetric than in figure 3.1.

3.2. Dielectric Properties of Sodium Nitrite

Ferroelectricity was found in sodium nitrite crystal by the dielectric measurement [Sawada et al., 1958]. One experiment for determine dielectric properties of sodium nitrite was studied by gamma-ray and radiation-induced change [Gesi and Takagi, 1963]. The disappearance of Curie point, the increasing of coercive field and the decrease of dielectric constant of the crystal were detected with the change of irradiation. Narita reported a paper that defined the nonlinear dielectric constant of sodium nitrite in paraelectric phase in 1977 [Narita, 1977].

Temperature dependence of the dielectric constant of ferroelectric crystal sodium nitrite was studied under the temperature change near the Curie point [Takagi and Gesi, 1966].

There is one another research about dielectric properties, which was reported by Nomura in 1961. It was described the behavior of dielectric constant of sodium nitrite as a function of frequency and temperature. It was measured the dielectric constant at temperature range from room temperature to 200°C and there were two peaks in heating it was showed 164.2°C and in cooling 162.6°C.

Table 3.2: Lattice parameters of sodium nitrite in the different phases ferroelectric, incommensurate and paraelectric.

Lattice Parameters (Å)	RmT	150°C	162°C	180°C
a	3.570	3.642	3.652	3.671
b	5.578	5.653	5.652	5.670
c	5.390	5.375	5.362	5.341

The spontaneous polarization was observed with the value of 8.6 $\mu\text{C}/\text{cm}^2$ at room temperature via the measurement of the pyroelectric current. In same paper,

phenomenological theory of free energy same as in eq. 2.13 was discussed and the coefficients of the function were calculated as $A=1.22 \times 10^{-3} \text{K}^{-1}$, $B=-0.3 \times 10^{-10} \text{esu}$ and $C=1.0 \times 10^{-19} \text{esu}$ [Nomura et al., 1961]. Figure 2.4 shows that the temperature dependency of dielectric constant to the change of temperature corresponding to different frequency range along the b axis.

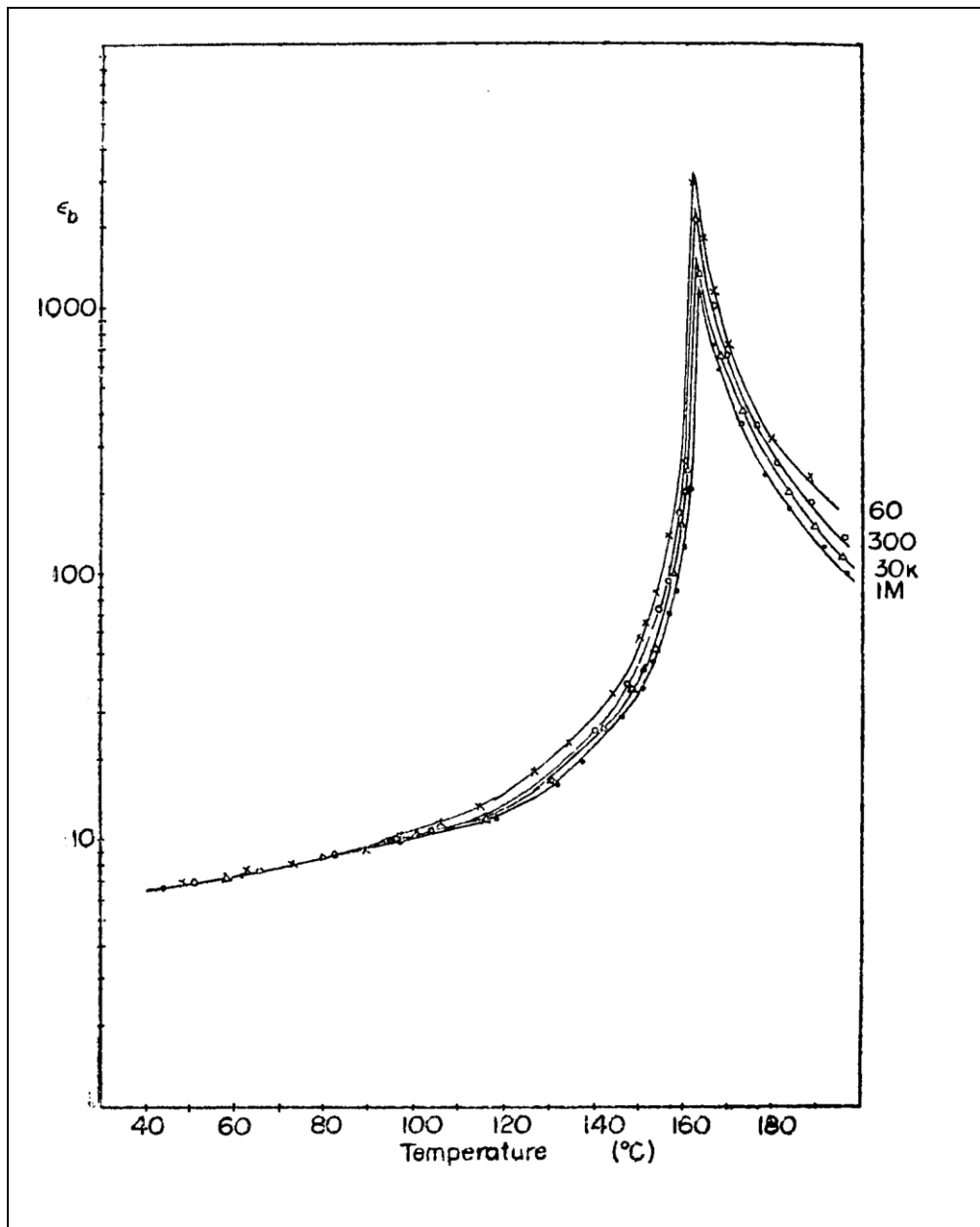


Figure 3.3: Representation of temperature dependence of the dielectric constants for sodium nitrite with different frequencies in b-axis.

2.3. X-Ray Diffraction

Sodium nitrite is the first insulating material, which has an intermediate modulated structure. The existence of modulated phase of sodium nitrite was discovered with the X-rays diffraction measurements [Durand et al., 1986]. Incommensurate phase of sodium nitrite appears in a narrow temperature range (1.5 K) between the ferroelectric and paraelectric phases. X-ray diffraction is one of the most important methods to investigate incommensurate phase.

In 1983, Durand and his colleagues performed one another experimental study. In that experiment, neutron diffraction pattern was measured for NaNO_2 with applied electric field along b axis [Durand et al., 1983]. The data are shown in figure 3.3 concluded that this crystal has three phases and there is a point called triple point and later it is called Lifshitsz point.

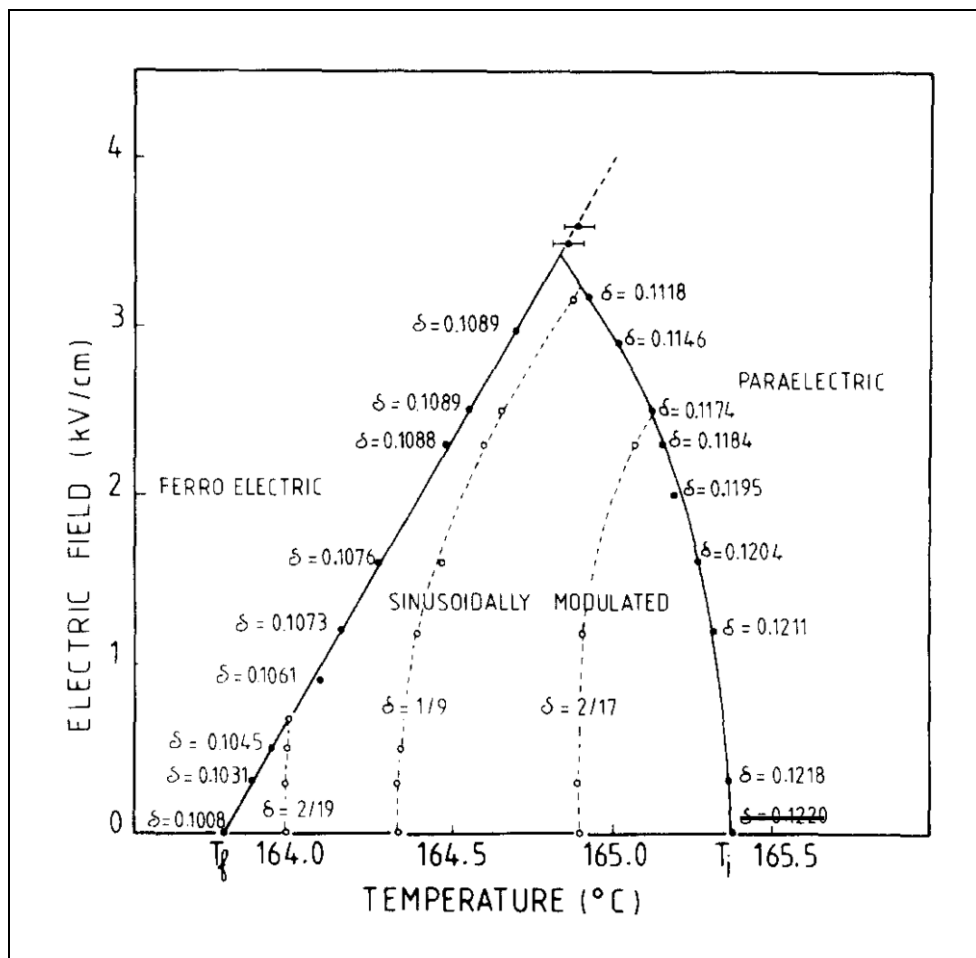


Figure 3.4: (E_b, T) phase diagram of NaNO_2 in a longitudinal electric field determined from neutron diffraction experiments.

Ferroelectric, incommensurate and paraelectric phases meet in very small temperature range $\sim 1.5^\circ\text{C}$.

One other X-ray study was performed for determining the structure of incommensurate phase of sodium nitrite [Böhm, 1978]. The author defined the orientation of Na^+ and NO_2^- ions during the phase transitions.

3.4. Raman Study for Sodium Nitrite

The hydrostatic pressure and non-hydrostatic pressure was applied and with Raman spectroscopy experiments [Adams, 1980]. The phase transition of sodium nitrite from paraelectric to ferroelectric phase studied with Raman spectroscopy [Dalterio and Owens, 1989]. Moreover, the effect of pressure on lattice vibrations of NaNO_2 was measured with Raman spectroscopy in figure 3.5. Low and high-pressure ranges were used and observed the frequencies were shifted close to each other by changing the pressure. There are five lines about polarization studies. At line 121 cm^{-1} indicates the orientational vibration of the NO_2 molecules around b-axis.

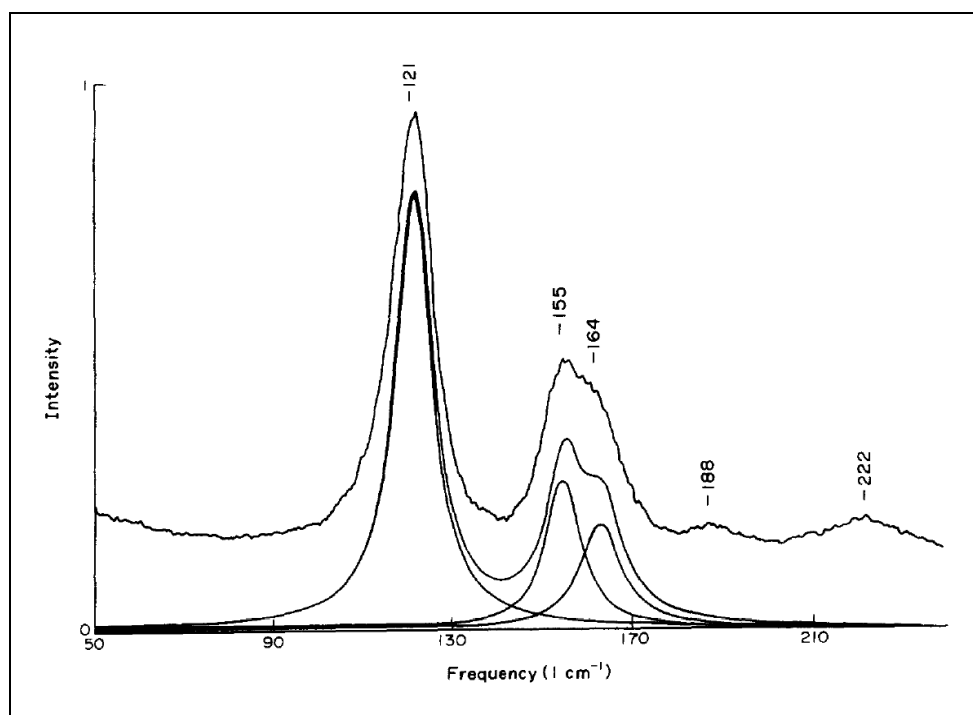


Figure 3.5: Upper curve indicates Raman spectrum in the lattice mode of NaNO_2 . The Lorentzian part of some of modes is shown with lower curve.

4. THEORY OF PHASE TRANSITION IN SODIUM NITRITE

Sodium nitrite is the material that has been studied detailed microscopic properties with theoretical approaches. Determination of free energy coefficients with experimental studies is more difficult than the theoretical ones.

4.1. Phenomenological Theory

4.1.1. Temperature Dependence of Dielectric Constant

In previous section, it is discussed the Landau theory with the first and second order phase transitions. One of the most valuable consequences for second order phase transition for ferroelectric crystals is electrical anomaly. For example, in the vicinity of the Curie point, ferroelectric crystal shows the phenomenon called dielectric anomaly that the dielectric constant for ferroelectric crystals is very abnormal value up to 10^5 .

Recently, Prof. Ishibashi has proposed a different way to investigate dielectric susceptibility behaviour of the ferroelectric material. However, according to Landau theory the temperature dependence of dielectric constant of a ferroelectric crystal can be expressed as the expansion of the thermodynamic potential into a series in η and T_c . From the first order phase transition thermodynamic potential equation, η the order parameter can be called as the displacement of an ion in the unit cell, and a is the density of the effective ionic charge.

By minimizing thermodynamic potential in eq. 2.16 function with respect to η , the equilibrium value of the order parameter can be determined.

$$\alpha(T - T_c)\eta_0 + \beta\eta_0^3 - aE_2 = 0 \quad (4.1)$$

$$\eta_0 = \eta_0(T - T_c, E_2) \quad (4.2)$$

When $E_2 = 0$, this mean is if there is no external electric field, η_0 order parameter will be zero above the Curie temperature T_c , and below the phase

transition temperature order parameter has a value which depends on the coefficients α and β .

$$\eta_0 = \begin{cases} 0, & T > T_c \\ \pm \left(\frac{\alpha(T - T_c)}{\beta} \right)^{1/2}, & T < T_c \end{cases} \quad (4.3)$$

In order to find electrical equation of state, when there is external electric potential, it is substituted the order parameter with the function of polarization, $P(E)$ in the thermodynamic potential. P_2 is the polarization which is induced by external electric field with the direction of b axis E_2 for ferroelectric crystals.

$$P_2 = -\frac{\partial \Phi}{\partial E_2} = a\eta_0 \quad (4.4)$$

$$P_s = \begin{cases} 0, & T > T_i \\ \pm \alpha \left(-\frac{(T - T_c)}{\beta} \right)^{1/2}, & T < T_c \end{cases} \quad (4.5)$$

Dielectric susceptibility $\chi_{22}^{p,T} = \frac{\partial P_2}{\partial E_2}$ is determined with the second derivative of the thermodynamic potential function. The temperature dependence of dielectric constant of a ferroelectric crystal can be calculated according to the formula.

$$\varepsilon_{22}^{p,T}(T) = 1 + 4\pi\chi(T) \quad (4.6)$$

The dielectric susceptibility of a material describes the variation of polarization which response to the changes in the applied electric field:

$$P = \chi\varepsilon_0 E = (\varepsilon_r - 1)\varepsilon_0 E \quad (4.7)$$

The dielectric susceptibility can be introduced:

$$\chi_{22}^{p,T} = \left(\frac{\partial P_2}{\partial E_2} \right) = - \left(\frac{\partial^2 \Phi}{\partial E_2^2} \right) \quad (4.8)$$

$$\left(\frac{\partial P_2}{\partial E_2}\right) = \frac{\partial(a\eta_0)}{\partial E_2} = a \frac{\partial \eta_0}{\partial E_2} \quad (4.9)$$

from the derivative of thermodynamic potential with the absence of the E_2 :

$$\frac{\partial^2 \Phi}{\partial E_2^2} = [\alpha(T - T_c) + 3\beta\eta_0^2] \quad (4.10)$$

in the commensurate ferroelectric phase:

$$\chi_{22}^{p,T} = -\frac{1}{\alpha(T_c - T) + 3\beta\eta_0^2}, \quad T < T_c \quad (4.11)$$

and in the paraelectric phase:

$$\chi_p = \frac{1}{\alpha(T - T_i)}, \quad T > T_i \quad (4.12)$$

according to the solutions of dielectric susceptibility:

$$\chi_{22}^{p,T} = \begin{cases} a/[\alpha(T - T_c)], & T > T_i \\ -a/[2\alpha(T - T_c)], & T < T_c \end{cases} \quad (4.13)$$

temperature dependence of dielectric constant $\varepsilon(T)$ can be expressed in eq. 4.14. For each temperature range, $\varepsilon_2^{p,T}$ has the below formula:

$$\varepsilon_2^{p,T} \approx 4\pi\chi(T) = \begin{cases} 4\pi a^2/[\alpha(T - T_c)], & T > T_i \\ -2\pi a^2/[2\alpha(T - T_c)], & T < T_c \end{cases} \quad (4.14)$$

In ferroelectric crystals, the temperature dependence of dielectric constant can be reasonably showed by the Curie-Weiss law. Above the transition temperature, the dielectric constant of a ferroelectric crystal trough the polar axis depends on temperature according to the expression:

$$\varepsilon_2^{p,T} = \frac{C_{C-W}}{T - T_c} \quad (4.15)$$

in which $C_{C-W} = 4\pi a^2/\alpha$ is Curie-Weiss constant.

In incommensurate phase, dielectric constant also depends on temperature or pressure. It can be calculated same as in section 2.2., according to Landau theory. Between ferroelectric and paraelectric phases, temperature dependence of dielectric constant can be easily found with the thermodynamic potential coefficients.

$$\chi_i \approx \frac{1}{\alpha - 2 \left(\alpha - \alpha_0(T_i - T_c) \frac{1 - \frac{\mu\delta}{6\beta\lambda}}{1 - \frac{\mu\delta}{3\beta\lambda}} \right)}, \quad T_c < T < T_i \quad (4.16)$$

the coefficients μ and β are very small comparing with α , so the division of $|\mu|/|\beta|$ is ignored.

$$\chi_i \approx \frac{1}{2\alpha_0(T_i - T_c) - \alpha} = \frac{1}{\alpha_0((T_i - T_c) - (T_i - T))}, \quad T_c < T < T_i \quad (4.17)$$

For incommensurate phase, temperature dependence of dielectric constant can be substituted with the equation 4.6.

$$\varepsilon_2^{p,T} \approx 4\pi\chi(T) = 4\pi a^2/2\alpha_0(T_i - T_c) - \alpha, \quad T_c < T < T_i \quad (4.18)$$

4.1.2. Incommensurate Phase of Sodium Nitrite

To clarify the phase transition mechanism, Landau theory has been developed by many theoreticians. The phenomenological theory of incommensurate phase of sodium nitrite can be described by the Landau thermodynamic potential and equilibrium value can be derived by using variation method. Euler-Lagrange equations are available for this method.

$$\phi(x) = \phi_1(x) + \phi_2(x) + \phi_3(x) \quad (4.19)$$

To analyze the phase diagram of sodium nitrite, it is written a total thermodynamic potential $\phi(x)$ as in eq. 4.19 using Landau theory.

$$\begin{aligned} \phi_1(T, \eta, E_2) = & \frac{1}{2}\alpha(T - T_x)\eta^2 + \frac{1}{4}\beta\eta^4 \\ & + \left(\frac{\delta}{2}\right)\left(\frac{d\eta}{dx}\right)^2 + \left(\frac{\lambda}{2}\right)\left(\frac{d^2\eta}{dx^2}\right)^2 + \left(\frac{\mu}{2}\right)\eta^2\left(\frac{d\eta}{dx}\right)^2 \end{aligned} \quad (4.20)$$

$\phi_1(T, \eta, E_2)$ indicates the thermodynamic potential density depends on the invariants, which are composed of the one order parameter. When considering incommensurate phase, it is clearly seen that the order parameter η depends on x . If the coefficients δ , λ , and μ are zero there is no incommensurate phase, in section 2.2 it is explained. For the condition $\delta < 0$, the incommensurate modulated structure is present. The coefficient δ can be increase with the external parameters.

In the equilibrium, when minimizing the thermodynamic potential density with respect to order parameter and the derivatives of the potential are written as,

$$\frac{\partial \phi_1}{\partial \eta} - \frac{d}{dx} \frac{\phi_1}{\left(\frac{\partial \eta}{\partial x}\right)} + \frac{d}{dx^2} \frac{\partial \phi_1}{\left(\frac{\partial^2 \eta}{\partial x^2}\right)} = 0 \quad (4.21)$$

these derivatives are guiding to the non-linear Euler-Lagrange differential equation, which has the degree of four in the following form,

$$\alpha(T - T_x)\eta + \beta\eta^3 + \frac{d^4\eta}{dx^4} - \frac{\delta}{\lambda} \frac{d^2\eta}{dx^2} - \frac{\mu}{\lambda} \left[\eta^2 \left(\frac{d^2\eta}{dx^2}\right) + \eta \left(\frac{d\eta}{dx}\right)^2 \right] = 0 \quad (4.22)$$

The solution of the Euler-Lagrange equation has generally a spatial periodic Fourier series form,

$$\eta_i(x) = \sum_{n=0}^{\infty} \rho_{2n+1} \cos[(2n + 1)qx] \quad (4.23)$$

The n-th harmonic number is found from the periodic solution and ρ_n is amplitude. The existence of this solution, which is presented in eq. 4.20, appears only if incommensurate phase is stable.

The incommensurate phase range is small. Thus, it can be just written the first harmonic solution as a plane wave approximation.

$$\eta_q(x) = \rho_1 \cos qx \quad (4.24)$$

Static polarization wave is described by eq. 4.24 in the incommensurate phase of sodium nitrite. Plane wave solution is described with eq. 4.24 where ρ_1 is amplitude and q is wave number. The modulation wave can be calculated at the equilibrium condition,

$$\frac{\partial \phi_1}{\partial \rho_1} = \frac{\partial \phi_1}{\partial q} = 0 \quad (4.25)$$

Writing the plane wave solution into potential in eq. 4.22, the thermodynamic potential is integrated with respect to $\eta_i(x)$ after the substitution;

$$\frac{1}{L} \int_0^1 \cos^n(qx) dx = \begin{cases} 0, & \text{for any odd } n \\ 1/2, & \text{for } n = 2 \\ 3/8, & \text{for } n = 4 \end{cases}, \quad (4.26)$$

The thermodynamic potential ϕ_1 has the form in eq. 4.20 in the incommensurate phase; the transition temperature is equal for ferroelectric and incommensurate phases. At equilibrium conditions, derivatives of both thermodynamic potentials are equal. Thus, there is no spontaneous polarization, and $\mu = 0$,

$$\phi_1(T, \eta, E_2) = \frac{1}{4} \alpha (T - T_x) \rho_1^2 + \frac{1}{4} \delta \rho_1^2 q^2 + \frac{1}{4} \lambda \rho_1^2 q^4 + \frac{3}{32} \beta \rho_1^4 \quad (4.27)$$

at equilibrium conditions;

$$\frac{\partial \phi_1}{\partial \rho_1} = \frac{1}{2} \alpha (T - T_x) \rho_1 + \frac{1}{2} \delta \rho_1 q^2 + \frac{1}{2} \lambda \rho_1 q^4 + \frac{3}{8} \beta \rho_1^3 \quad (4.28)$$

$$\rho_1^2 = -\frac{4}{3\beta} (\alpha (T - T_x) + \delta q^2 + \frac{1}{2} \lambda q^4) \quad (4.29)$$

$$\frac{\partial \phi_1}{\partial q} = \frac{1}{2} \delta \rho_1^2 q + \lambda \rho_1^2 q^3 \quad (4.30)$$

$$q \left(\frac{1}{2} \delta \rho_1^2 + \lambda \rho_1^2 q^2 \right) = 0 \quad (4.31)$$

$$q^2 = -\frac{\delta}{2\lambda} \quad (4.32)$$

With the solution of wave vector q , the amplitude of the polarization wave can be written as;

$$\rho_1^2 = \frac{4}{3\beta} \left(\frac{\delta^2}{4\lambda} - \alpha (T - T_x) \right) \quad (4.33)$$

These coefficients give the information for defining the transition temperatures. If the transition occur from paraelectric phase to incommensurate phase the temperature T_i equals,

$$\alpha (T_i - T) = \frac{\delta^2}{4\lambda}, \quad T_i = T + \frac{\delta^2}{4\lambda\alpha} \quad (4.34)$$

The incommensurate phase transition to the ferroelectric phase transition is realized in transition temperature T_c . The minimum of the thermodynamic potentials are also equal. Same as in eq. 4.34,

$$\alpha (T - T_c) = \frac{\delta^2}{4\lambda}, \quad T_c = T - \frac{\delta^2}{4\lambda\alpha} \quad (4.35)$$

4.1.3. The Effects of Uniaxial Compressive Stresses

It has to be very broadly studied the effect of uniaxial stress or hydrostatic pressure on the properties of ferroelectrics in order to provide a detailed analysis of the phase transformations and to propose a phase diagram that is helpful for understanding the thermo - mechanical characteristics. It is also useful for developing constitutive phenomenological model of phase transitions in investigated materials.

When it is applied uniaxial stress to NaNO_2 the Landau thermodynamic potential in eq. 4.19, it has to be added by strain dependent terms (ϕ_2). The NaNO_2 crystal, which has orthorhombic crystalline structure in paraelectric phase, the expression of ϕ_2 by which is provided a coupling between primary and the secondary order parameters, that is the linear elastic strain tensor components and the polarization contain the following form.

$$\phi_2 = \frac{1}{2}(b_1 u_{xx} + b_2 u_{yy} + b_3 u_{zz})\eta^2 + \frac{1}{2}(s_1 u_{xx} + s_2 u_{yy} + s_3 u_{zz})\left(\frac{\partial \eta}{\partial x}\right)^2 \quad (4.36)$$

In eq. 4.19, $\phi_3(x)$ refers the elastic energy stored in the NaNO_2 crystal, which is given by:

$$\phi_3(x) = \frac{1}{2} \sum_{k,j=1}^3 C_{kj} u_{kk} u_{jj} - \sum_{j=1}^3 \sigma_{jj} u_{jj} \quad (4.37)$$

First part of the eq. 4.37 shows Hook's law [Strukov and Levanyuk, 1998]. C_{kj} refers one of the elastic constant of the crystal. Other part of this equation, σ_{jj} is mechanical stress tensors and u_{jj} is elastic strain. There is an operation that it is a subtraction of the work, which is reason of uniaxial compressive stress from the mechanic energy. k and j are symbolized the Cartesian coordinate components.

All the three diagonal components of the elastic strain u_{ii} are independent invariants in materials with orthorhombic crystalline structure. From the eq. 4.36, it is very obviously seen that in the compressed NaNO_2 crystal coupling between primary order parameter and it spatial derivatives with the appropriate independent

elastic strain component arising upon uniaxial compressive loading has the same form. For this very reason, it can be expected for the effects of uniaxial compressive stress on phase transitions and dielectric properties of NaNO₂ applied to a crystal in the different directions to should contain similar character.

It is now easily to determine the equilibrium properties of compressed NaNO₂ by minimizing Φ with respect to corresponding u_{jj} , that is $\partial\Phi/\partial u_{jj} = 0$. In eq. (4.24), by using the expression for complete thermodynamic potential, which now consists of the terms in eq. (4.24) and (3.25) utilized for relevant external mechanical stress applied to crystal, the Poisson expansion of the NaNO₂ crystal lattice along the other two perpendicular dimensions due to the applied uniaxial compressive stress is neglected.

From the renormalization of the coefficients α and δ at the quadratic invariants of order parameter and the spatial derivative in the Landau thermodynamic potential expansion it can be deduced the changes in phase transition temperatures T_i and T_c in NaNO₂ under the influence of corresponding uniaxial compressible mechanical stress σ_{ii} :

$$\alpha(\sigma_{jj}) = \alpha + b_j C_{jj} \sigma_{jj} \text{ and } \delta(\sigma_{jj}) = \delta + s_j C_{jj} \sigma_{jj} \quad (4.38)$$

The phase transition temperature is shifted because of the uniaxial compressive stress. It is acting along the x, y, and z direction. These shifts can be obtained from the condition into incommensurate phase:

$$\alpha(\sigma_{jj}) = \frac{\delta^2(\sigma_{jj})}{4\lambda} = \frac{(\delta + s_j C_{jj} \sigma_{jj})^2}{4\lambda} = \frac{\delta^2}{4\lambda} + \frac{\delta}{2\lambda} (s_j C_{jj}) \sigma_{jj} + \frac{(s_j C_{jj})^2}{4\lambda} \sigma_{jj}^2 \quad (4.39)$$

With the solution of the coefficients, in the ferroelectric phase and the incommensurate phase transition temperature should be equal. An expression for the incommensurate phase temperature with the influence of uniaxial stress $T_i(\sigma_{jj})$:

$$T_i(\sigma_{jj}) = T_i(\sigma_{jj} = 0) - A_j \sigma_{jj} + B_j \sigma_{jj}^2 \quad (4.40)$$

$$A = \frac{(b_j - q_0^2 s_j) C_{jj}}{\alpha_0} \text{ and } B = \frac{(s_j C_{jj})^2}{4\lambda\alpha_0} \quad (4.41)$$

A and B are the constants which contain the coefficients of Landau thermodynamic potential. They give an information about elastic properties of sodium nitrite crystal. For example, the constant B in eq. 4.40 is a bulk modulus of the crystal. The uniaxial stress is compressive so the value of σ_{jj} is smaller than zero ($\sigma_{jj} < 0$). It is noticeable that the coupling constant b_j and s_j are always positive, in order for the sign of the A coefficient to depend on the ratio of their magnitude.

After this, it is considered the effect of uniaxial mechanical stress on T_c . Taking into account the condition $|\mu|/|\beta| \ll 1$:

$$T_c(\sigma_{jj}) - T_0 = \frac{1}{\sqrt{\frac{3}{2} - 1}} \frac{\delta^2(\sigma_{jj})}{4\alpha_0\lambda} \quad (4.42)$$

$$\approx \frac{4.45}{\alpha_0} \left(\frac{\delta^2}{4\lambda} + \frac{\delta}{2\lambda} (s_j C_{jj}) \sigma_{jj} + \frac{(s_j C_{jj})^2}{4\lambda} \sigma_{jj}^2 \right)$$

It is noted that;

$$\frac{\delta^2}{4\lambda} = \alpha_0 [T_c(\sigma_{jj} = 0) - T_0] - b_j C_{jj} \sigma_{jj} \quad (4.43)$$

and the Curie temperature T_c reaches to T_0 . Finally, the compressive stress is negative ($\sigma_{jj} < 0$):

$$T_c(\sigma_{jj}) = T_i(\sigma_{jj} = 0) + b_j C_{jj} \sigma_{jj} + \frac{5.45}{\alpha_0} \left(\frac{\delta}{2\lambda} (s_j C_{jj}) \sigma_{jj} - \frac{(s_j C_{jj})^2}{4\lambda} \sigma_{jj}^2 \right) \quad (4.44)$$

or

$$T_c(\sigma_{jj}) = T_i(\sigma_{jj} = 0) + \Gamma_j \sigma_{jj} - \Upsilon_j \sigma_{jj}^2 \quad (4.45)$$

Where Γ and Y are algebraic expression composed from the Landau thermodynamic potential coefficients. Γ and Y are the elastic constants of the NaNO_2 crystal. It should be noted that the temperature interval of the INC – phase existence in NaNO_2 should vary with respect to the magnitude compressive uniaxial stress as:

$$T_i(\sigma_{jj}) - T_c(\sigma_{jj}) = -(\Gamma_j + A_j)\sigma_{jj} + (B_j + Y_j)\sigma_{jj}^2 \quad (4.46)$$

The interval of the incommensurate phase of sodium nitrite crystal is defined in eq. 4.46 with the effects of uniaxial compressive stress applied on the crystal.

4.2. Order-Disorder Phase Transition

There are many different studies for understanding the phase transition mechanism of sodium nitrite. There is another phase transition, which contains the displacement of atoms in the ferroelectric crystals that is called the order-disorder phase transition. The volume and the shape of crystal body will change with the transition. Yamada [1963] and his co-worker examined the X-ray diffraction patterns of sodium nitrite in the vicinity of transition temperature to specify the mechanism of phase transition of ferroelectricity [Yamada and Shibuya, 1963].

In the experiment of Yamada [1963], incommensurate phase of magnitude of electric moments between ferroelectric and paraelectric phase was reported. Figure 4.1, order-disorder arrangement for the orientation of NO_2 ions shows the transition mechanism of the crystal. NO_2 ions in the unit cell are aligned in the opposite direction while the changing of phase from paraelectric to ferroelectric.

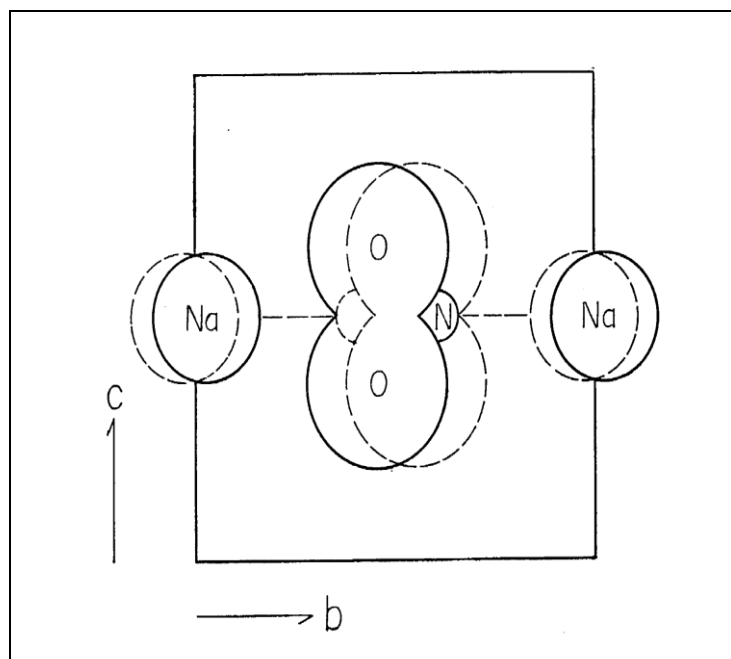


Figure 4.1: The arrangement of order-disorder for unit cell of sodium nitrite.

The temperature dependence of the diffraction patterns near the transition temperature were taken using the photographic method with the control of temperature by electric furnace. Figure 4.2 represents the intensity of the layer reflection in the vicinity of Curie point decreases near the 163°C.

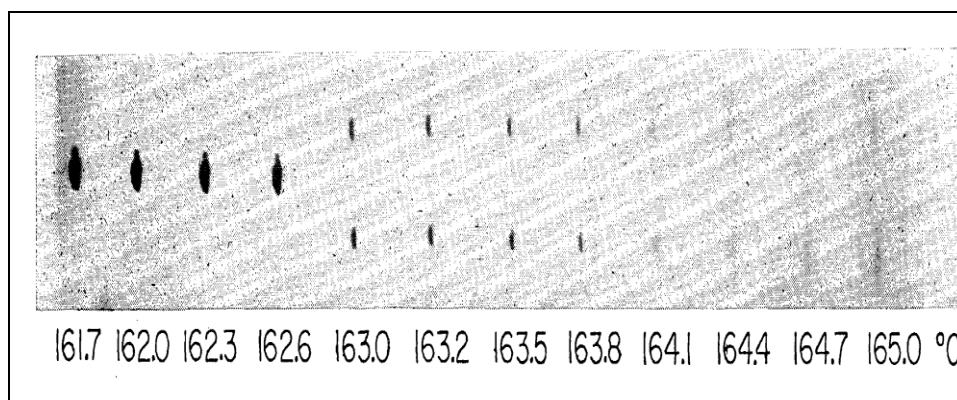


Figure 4.2: The diffraction pattern of sodium nitrite near the transition temperature.

5. EXPERIMENTAL

The sodium nitrite crystal belongs to the class of inorganic compound with the chemical formula ABO_2 , where A is a cation of Na^+ and BO_2 is NO_2^- anion. The sodium nitrite is transparent yellow crystalline powder and very soluble in water. The melting point temperature of sodium nitrite is $271^\circ C$ and decomposes $320^\circ C$.

A group of scientists did the experimental studies in Institute of Physics of Academy of Sciences of the Republic of Azerbaijan. The crystal growth of sodium nitrite and applying the uniaxial compressive stress were done in the same laboratory. The data for the dielectric constant of sodium nitrite were calculated and then I just analyzed the taken data on the computer.

The samples of crystals for the experiment were obtained with a crystal growth of sodium nitrite from melt powder of 98% purity by Kyropoulos method in air. This method is suitable for the growth of single crystals, which have low thermal conductivity and bigger thermal expansion coefficient [Feigelson, 2004]. Therefore, they chose this growth of crystal method, sodium nitrite has low thermal conductivity. This technique is based on the melting of the materials. A schematic diagram of the original Kyropoulos furnace is shown in figure 5.1.

The crystal growth system contains heating system, cooling system and insulating system. The heating system was melting powder of sodium nitrite, cooling system was the rod with cold water and the insulating system was the thermocouple to stabilize the temperature of the crystal seed. The water-cooling rod was used to cool the melting powder of sodium nitrite to create the single crystal seed on the bottom of the rod.

For preparing the sample to measure the dielectric characterization, the rectangular prism was produced from the growth of $NaNO_2$ single crystal seed with the length of 2.5 mm x 5 mm x 2 mm. To gain flat and parallel surfaces, the sample was polished with mixture of distilled water and ethanol. Obtaining samples in the crystal coordinate system was realized by the X - ray diffraction analysis and the data of the lattice parameters of sample was recorded $a = 3.57 \text{ \AA}$, $b = 5.58 \text{ \AA}$ and $c = 5.40 \text{ \AA}$ with two molecules per unit cell. The crystal structure was observed body-centered orthorhombic. The data of the sample are same as in the literature [Sawada, 1985].

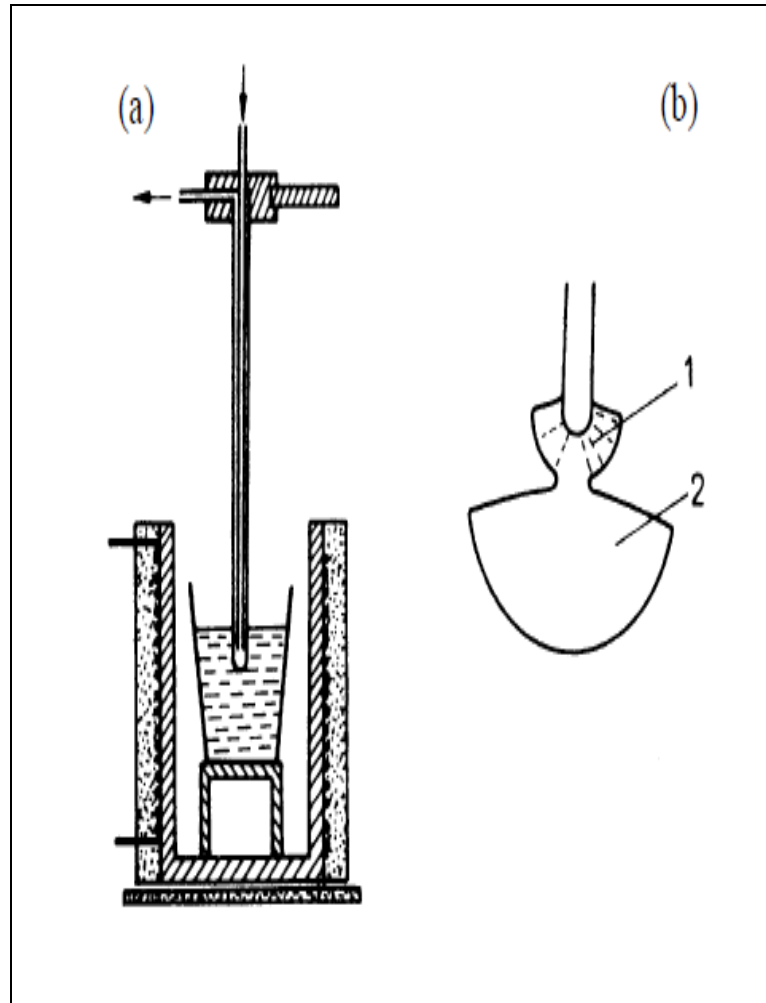


Figure 5.1: Schematic diagram for Kyropoulos method. a) the systems of Kyropoulos method; melting, cooling and insulating. b) The sample of crystal seed.

The chamber shown schematically in figure 5.2 was used for experimental study of dielectric characterization of NaNO_2 . Uniaxial compressometer was specially designed to transmit the compressive force to the sample in the holder with moveable rod of mechanical lever system. The ratio for the load transfer of weights to the sample was 1:5. This rod was made of stainless steel. There was a syphon under the rod to transfer the force directly onto the sample in chamber. The crystal sample was fixed with the special holder in order to be perpendicular the compressive force on the copper layer plane or another sample surface. The compressive force occurred via the weights on the top of the steel rod. The temperature of the samples was measured by using copper-constantan thermocouple with crystal holder near the sample.

While the forepump emptying the air from the chamber, there occurred pressure difference between the cryostat and the chamber. Cryostat is an insulating container. There is a gap between these two parts that the air is evacuated and which protects the temperature of material against to heat transfer with outside. Cryostat was containing liquid nitrogen to create positive pressure with the flowing of the cooler nitrogen to the chamber. The experimental chamber gap was connected to liquid nitrogen vessels while measuring the temperature changes, heating or cooling. Since the fluctuation of nitrogen vapor pressure must be stabilized to realize with camera.

The studying crystal sample was placed into the holder which to be used inside of the liquid - nitrogen cryostat. This cryostat allowed measuring the dielectric properties of samples. The main aim of the cryostat was that the temperature gradients of sample and thermometer location were reduced. In the cryostat, silicone oil is heated to fix the temperature. The liquid-nitrogen cryostat was enabling to calibrate sample temperature within the range 77 to 450 K. Two polished opposite edges of the sample that the surfaces were perpendicular to polar axis were coated with silver paint for producing the electrodes. The sample was attached by the silver electrodes with the thin copper wire to the measurement of the input circuit connection.

The dielectric characteristics of sodium nitrite were determined with the LCZ-meter. This instrument was used to measure circuit components of the experimental system, especially the capacitance of the sample as a parallel plate using frequency.

Firstly, at low temperature uniaxial compressive stress was applied and while the temperature was increasing the temperature change rate of 0.1 K min^{-1} , the data of capacitance were recorded at frequency of 1kHz. With the equation of parallel plate capacitor;

$$\varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot S} \quad (5.1)$$

the dielectric constant of sodium nitrite was calculated. In this equation, C is the capacitance of the sample, which was measured via LCZ-meter. S and d are the thickness and the area of sample respectively and change with the direction of the

electrode sample according to y and z axis. The dielectric permittivity of vacuum is ϵ_0 and the value is $8.854 \cdot 10^{-12}$ F/m.

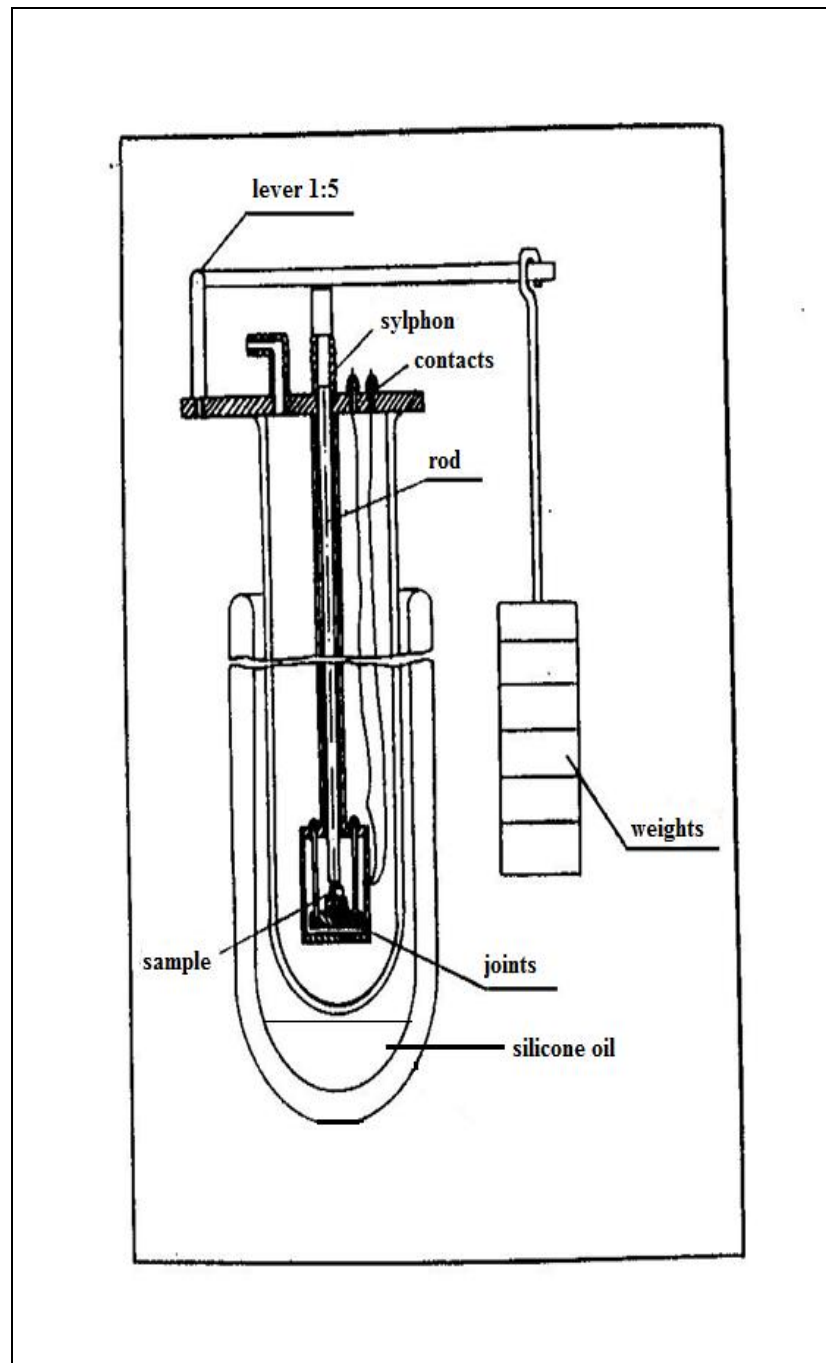


Figure 5.2: The chamber used for measuring the temperature dependence of dielectric constants of sodium nitrite with the effect of uniaxial compressive pressure.

6. RESULTS AND DISCUSSION

The temperature dependence of the dielectric constant of sodium nitrite in b-axis were calculated from the collected data of the experimental measurements of capacitance of sodium nitrite crystal both free-stress and under the effects of uniaxial compressive stress in y and z directions. The scientist measured the data. I have analyzed the temperature dependence of dielectric constant with plotting the graphs for each sample.

Under the condition of free-stress, the temperature dependence of the dielectric constant of sodium nitrite is shown in figure 6.1. The crystal is in b axis while heating process at frequency of 1 kHz. There is information about the crystal that the

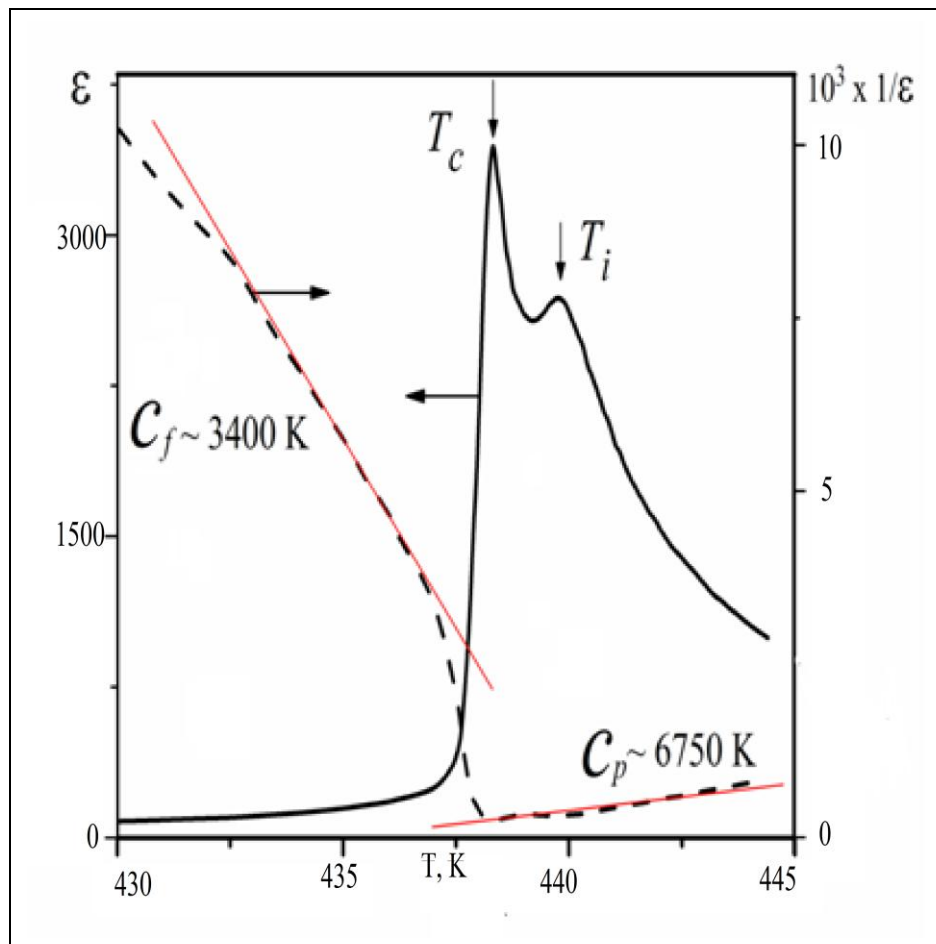


Figure 6.1: Temperature dependence of the b - axis dielectric constant of NaNO_2 under free-stress. Thermal evolution of inverse dielectric constant is shown in dashed line.

inverse of the dielectric constant is presented in the same inserted figure with the black dashed line.

The fitting of the data of the inverse of the dielectric constant results the red line in figure 6.1. Curie-Weiss constant for sodium nitrite was calculated for both phases para and ferroelectric phases. It is clearly seen with the values for paraelectric phase $C_p = 6750 K$ and ferroelectric phase $C_f = 3400 K$. The paraelectric phase temperature is located at about $T_i = 440 K$. In the ferroelectric phase, temperature T_c is $438.4 K$. The ratio of the Curie constant is calculated $C_p/C_f = 1.98$.

According to solution of the thermodynamic potential with Landau theory in eq. 4.14, it gives the results that the temperature dependence of dielectric constant in ferroelectric phase should be lower than in paraelectric phase with the ratio of $1/2$.

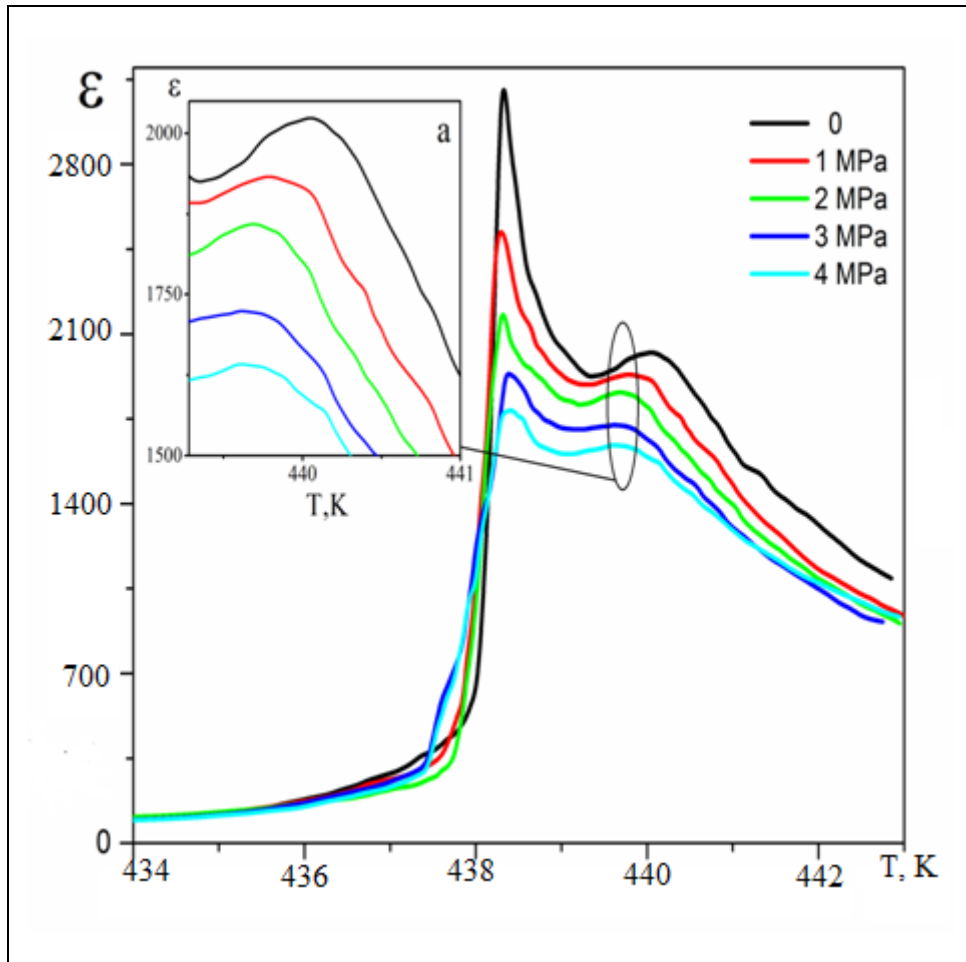


Figure 6.2: Temperature dependence of dielectric constant of NaNO_2 along b axis under different uniaxial stress σ_{zz} .

The experimental and theoretical results for the temperature dependence of the dielectric constant are in good agreements.

The main purpose of the present work is to find out the anomalies in the temperature dependence of the dielectric properties of sodium nitrite crystal on study of influence of external uniaxial compressive stress near the transition temperature. There are two type anomalies for dielectric constant with applied uniaxial pressure.

In the first type, the uniaxial compressive stress is applied in z direction. The temperature dependence of the dielectric constant decreases with the increasing of applied uniaxial compressive stress in the range of 0 to 4 MPa. Temperature dependence of dielectric constant of NaNO_2 has the value of $\sim 3 \times 10^3 \text{ F/m}$ without any stress, however, under the magnitude of applied stress is 4 MPa, dielectric constant goes down to the value of $\sim 1.5 \times 10^3 \text{ F/m}$.

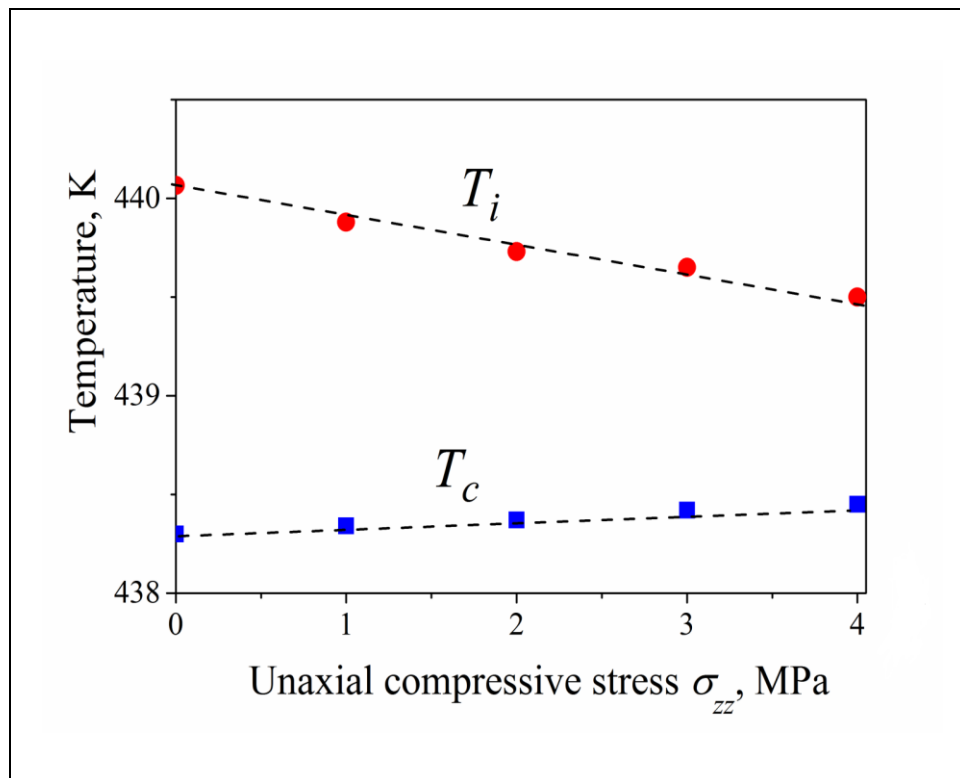


Figure 6.3: Between the transition temperatures, $(\sigma_{zz} - T)$ phase diagram of NaNO_2 .

In figure 6.2, it is shown in the incommensurate phase between two peaks the curves are significantly changed. There were not found any considerable changes in the positions of the dielectric constant maximums at temperatures T_i and T_c when the NaNO_2 applied compressive stress was increased from 0 to 4 MPa, as it is clearly

shown from phase diagram represented in figure 6.3. While the stress σ_{zz} increases from 0 to 4 MPa T_i linearly decreases varying by pressure coefficient $dT_i/d\sigma_{zz} = -A_j = -0.125$ K/MPa.. This experimental result agrees with the eq. 4.40 as it is supposed.

The T_c linearly increase with the increasing of compressive stress σ_{zz} with positive slope $dT_c/d\sigma_{zz} = \Gamma_j = 0.025$ K/MPa which is in a fair agreement with eq. 4.45. The fact that the fitting coefficients B_j and Y_j in eq. 4.40 and eq. 4.45 must be equal to zero is indicated by a good linear relationship with the uniaxial compressive stress σ_{zz} for both temperatures ($T_i(\sigma_{zz})$ and $T_c(\sigma_{zz})$) predicted on basis of eq. 4.40 and eq. 4.45.

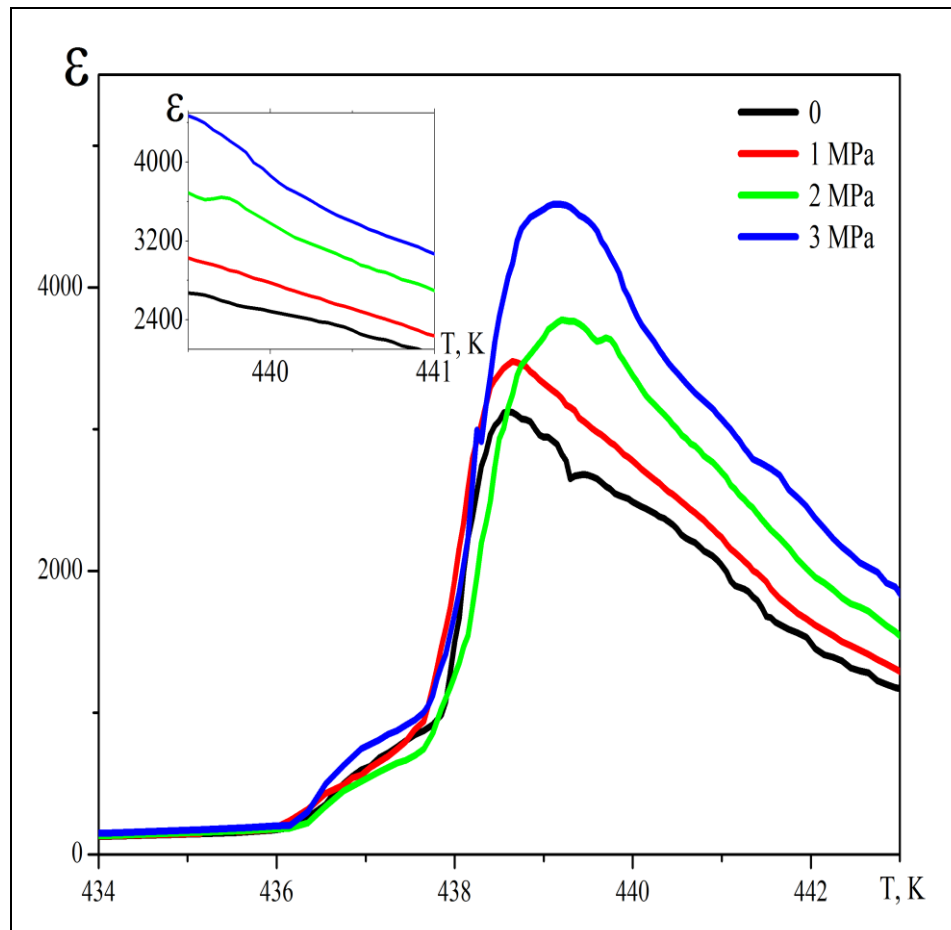


Figure 6.4: First crystal sample data were taken from experimental measurement of temperature dependence of dielectric constant in y direction.

The behavior of dielectric constant of sodium nitrite is shown with the curves in figures 6.4-6.6 in b axis on study of the effects of uniaxial compressive stress

along y direction σ_{yy} . There are four measurements for different samples of temperature dependence of dielectric constant in y direction at a frequency of 1 kHz.

In figure 6.4, the temperature dependence of dielectric constant ($\epsilon(T)$) behavior of sodium nitrite at 1.0, 2.0 and 3.0 MPa is given. The value of the $\epsilon(T)$ is increasing to approximately 4.5×10^3 F/m with the applied increasing pressures.

The measurement of second experiment with same procedure in y direction is shown as second graph in figure 6.5. For second sample, the uniaxial pressure has a range 0 to 6 MPa with two differences. The value for the dielectric constant is about 9×10^3 . The dielectric constant of the crystal is still increasing with the pressure.

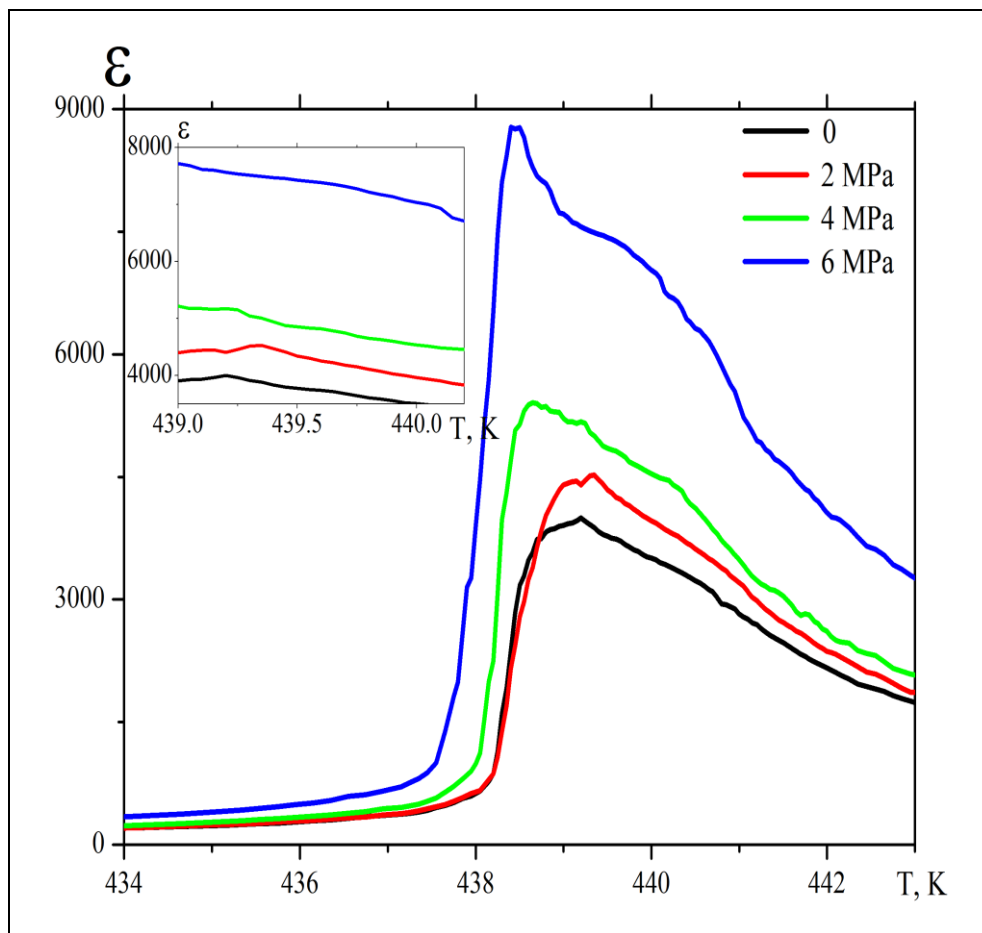


Figure 6.5: Temperature dependence of dielectric constant of NaNO_2 in y direction for second crystal sample.

For one another measurement, the plotted graph is shown in figure 6.6. the applied uniaxial pressure has the values that are changes 0 to 6MPa. The temperature dependence of dielectric constant is close to the value of 7.2×10^3 . Although the magnitude of applied uniaxial compressive stress is same for both figure 6.5 and 6.6

at 6 MPa, the temperature dependence of dielectric constant has the different value. Since the thickness of the samples are different. The last graph shows in figure 6.7

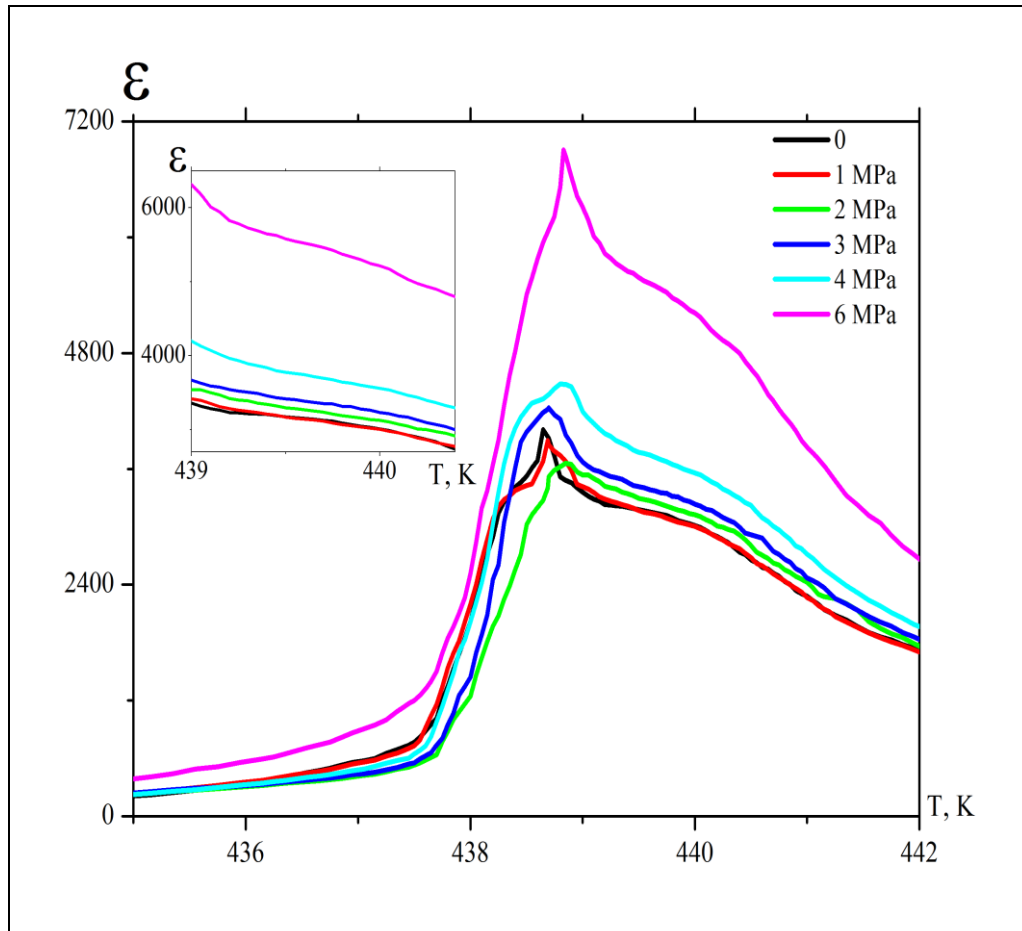


Figure 6.6: Third crystal sample measurements in y direction.

there are more details about the temperature dependence of dielectric constant under higher applied pressure. It is changed from zero to 10 MPa. It is easily seen from the curves that the dielectric constant is raising to the value about $15 \times 10^3 F/m$ under applied pressure at 10 MPa. When comparing the dielectric constant with the free-stress, it is greater than five times. The dielectric constant depends on the applied pressure, it is enhancing by increasing the applied uniaxial pressure.

Each figure involves the dielectric constant at three phases of the material that are ferroelectric, incommensurate and paraelectric. Increasing of the temperature in ferroelectric phase to the transition point, the dielectric constant of the material is reaching to the top value of $\sim 10^5$ in figure 6.7.

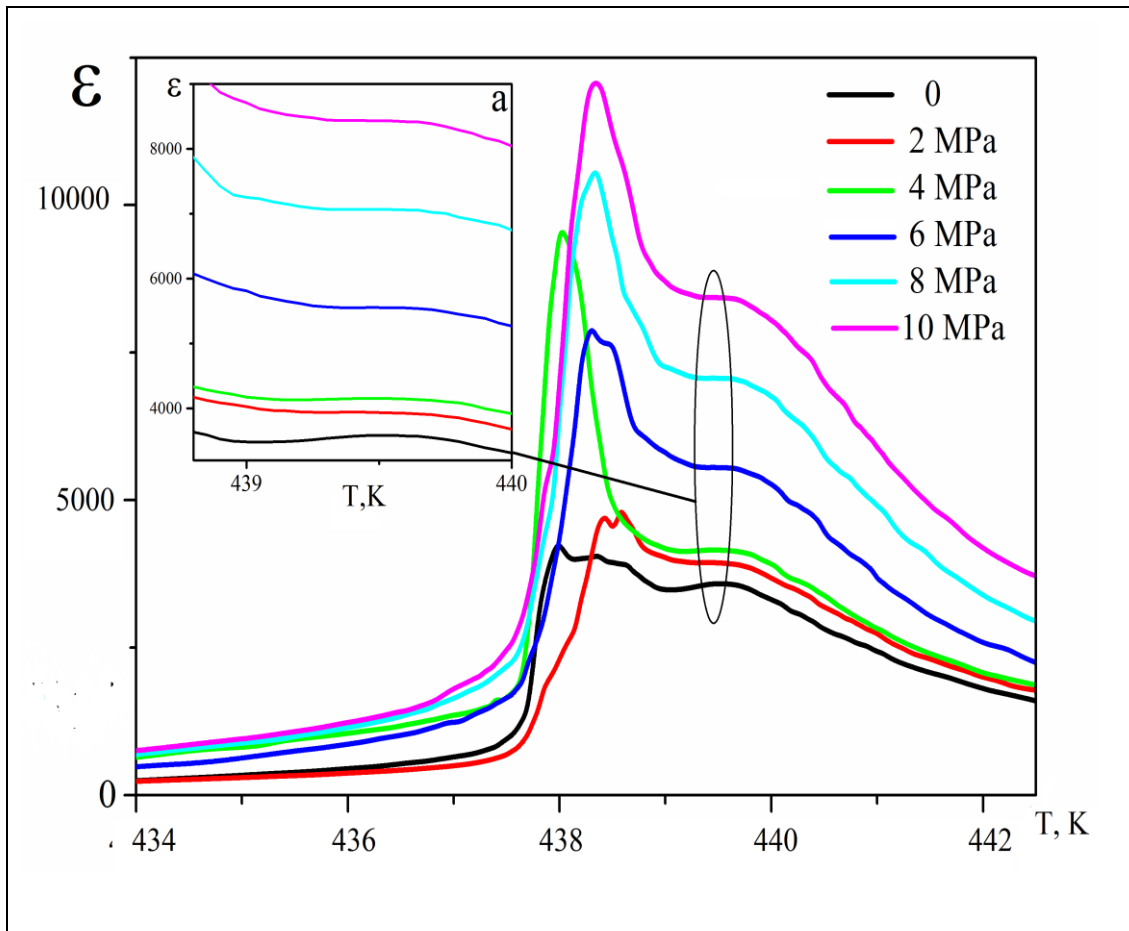


Figure 6.7: Temperature dependence of dielectric constant with the effect of uniaxial pressure along y direction.

After the peak of the curves, the incommensurate phase starts and dielectric constant is decreasing though increasing of temperature. Coming through the T_i , there is no sharp changing of phase transition from incommensurate to paraelectric phase. The applied uniaxial compressive stress is gradually increasing and it causes the higher dielectric constant in each step for the material.

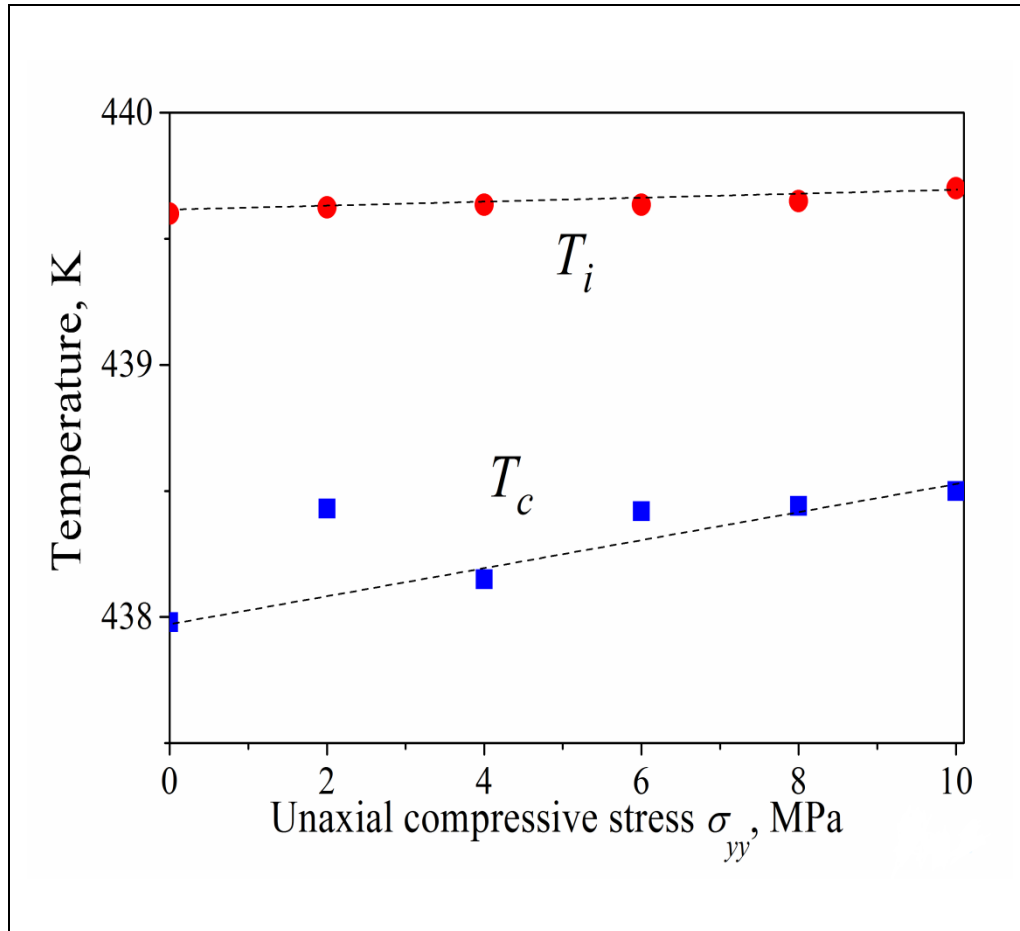


Figure 6.8: (σ_{yy} - T) phase diagram of NaNO₂ under effect of uniaxial compressive stress along y direction.

Figure 6.2 and figure 6.7 contain a fascinating point of the uniaxial pressure effect on the dielectric properties of NaNO₂ inside the INC – phase.

The insert of figure 6.2 consists of the temperature dependence of the dielectric constant within the INC – phase measured along the b - axis direction under stress - free and compressive stress σ_{zz} condition at the frequency of 1 kHz. It can be easily noticed that with increasing compressive stress from 0 to 4 MPa the dielectric constant decrease. It is important to note that an anomaly in the form of a shoulder with increasing pressure was transformed from an anomaly in the form of maximum corresponding to the paraelectric – INC phase transition.

The explanation of this result can be given by either pressure variations of the Curie - Weiss (C_w) constant inside the INC – phase or by suppression higher harmonics of the INC – modulation wave. The substitution should take into account the uniaxial stress dependence of Curie constants:

$$\alpha = \frac{1}{\varepsilon_0 C_w} = \left[\varepsilon_0 \left(C_{w0} + \frac{dC_w}{d\sigma_{zz}} \cdot \sigma_{zz} \right) \right]^{-1} \quad (6.1)$$

At the same time, the influence of the higher harmonics of the INC – modulation wave may be taken into account by (the non - linear term $\beta\eta^3$ in eq. 3.22 may generate an odd harmonics only).

$$\eta_i(x) = \rho_1 \cos qx + \rho_3 \cos 3qx + \rho_5 \cos 5qx + \dots \quad (6.2)$$

However, this consideration goes way beyond the scope of this particular article. It can be found out with order-disorder transition theory.

Figure 6.7 contains the appearance of the temperature dependence of the dielectric constant inside the INC – phase measured along the b - direction under stress - free and compressive stress σ_{yy} condition at the frequency of 1 kHz. Increasing with compressive stress from 0 to 10 MPa, the dielectric constant also increases. There is found that the dielectric constant anomaly form near INC – phase returns the same when increasing σ_{yy} stress from 0 to 10 MPa. When the stress is removed, the value returns to slightly higher than its original value. Generally, the changing of the dielectric constant with increasing mechanical stress does follow the same path.

The Landau's thermodynamic theory of phase transition in NaNO_2 ferroelectrics cannot, in terms of the order parameter, illuminate the observed major increase for the temperature dependence of dielectric constant of NaNO_2 under uniaxial compressive stress σ_{yy} . A microscopic atomic interactions model has the ability to give an explanation for the observed phenomenon in figure 6.7. For this very reason, in order to understand the dielectric properties of NaNO_2 under uniaxial stress σ_{yy} , it is necessary to examine in a more careful way the structure of order - disorder.

The system is in a disordered state because randomly the dipole vector of the V - shaped nitrite anions (NO_2^-) aligned at higher temperatures. In paraelectric phase, the ordering orientation is in the NO_2 ions and these ions cause the dipole moments in the direction of $+b$ and $-b$ with the equal magnitude. The dipole vector of nitrite ions are aligned parallel to the crystallographic b – direction when the phase

transition occurs. The system comes to an ordered form and a net spontaneous polarization is also parallel to the b - axis.

As it is clear from the above discussion, it is obvious that the extraordinary increase of the dielectric anomalies in NaNO_2 under uniaxial stress σ_{yy} are attributed with destruction of the long – range dipolar ordering along the ferroelectric b – axis by uniaxial stress. We believe that the magnitude of the dipolar ordering distortions in an order - disorder NaNO_2 crystal has the ability to change because of uniaxial press influence in the same direction of spontaneous polarization.

7. CONCLUSION

The main point of this thesis is to investigate the phase diagram of ferroelectric crystal sodium nitrite. This work is theoretical study of the temperature dependence of dielectric constant of sodium nitrite in b - axis under uniaxial compressive stresses σ_{yy} and σ_{zz} of NaNO_2 order – disorder ferroelectric. It was firstly measured, in the vicinity of the structural phase transition, the temperature dependence of dielectric constant of sodium nitrite under uniaxial compressive stresses both σ_{yy} and σ_{zz} by a group of researchers in Institute of Physics of Academy of Sciences of the Republic of Azerbaijan. With the analyzing of the experimental data, the graphs of temperature dependence of dielectric constant and phase diagrams are plotted for each sample.

It has been appropriately explained, in terms of a phenomenological Landau theory, the effect of uniaxial pressure σ_{yy} and σ_{zz} on the phase transition temperatures T_i and T_c . We, also, granted and showed the good agreements of the studied Landau theory and experimental results for phase diagrams of NaNO_2 in the stress – temperature plane.

The temperature dependence of dielectric constant under the effects of uniaxial compressive stress along z direction acts as expected in the theoretical solutions. Increasing with uniaxial stress σ_{zz} , the temperature dependence of dielectric constant of sodium nitrite crystal is decreasing. However, under applied uniaxial compressive stress σ_{yy} is increasing, the temperature dependence of dielectric constant of sodium nitrite crystal is also increasing. The studied theory has no ability to define this behaviour of dielectric constant. It is supposed that this issue can be figured out by a different theoretical study.

Dielectric anomalies of NaNO_2 are in a noticeable way affected by uniaxial compression along the $[010]$ axes. A pressure – induced additional disorder in the arrangement the V - shaped nitrite anions (NO_2^-) is the interpretation of the substantial increase of the dielectric anomaly, which produced by $[010]$ stress.

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BIOGRAPHY

Nebahat Bulut was born in 1987. She went to school primary till high school in Bursa. After graduation, she decided to be a physicist, for this reason she went to and completed her bachelor studies in Izmir Institute of Technology in 2012. To continue her studies in physics she graduated in master degree in Graduate School of Natural and Applied Sciences in Gebze Technical University. Now she is a theoretician physicist. For the moment, she participates in a project as a project assistant.