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Dielectric relaxation in $NaNbO_3$ single crystal

K.Konieczny

Institute of Physics and Computer Science, Pedagogical University,
2 Podchorążych Str., 30-084 Kraków, Poland

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Dielectric permittivity studies of reduced samples of $NaNbO_3$ single crystal in the range of temperatures 30–500 °C and frequency 20 Hz-1 MHz are reported. In this temperature range a relaxation process is observed in the frequency range of about 100 kHz. This is an additional process to the earlier reported one [7]. The obtained data were fitted to Cole-Cole formula. The dispersion step $\Delta\epsilon$ (the maximum value of $\Delta\epsilon$ =1000) is temperature dependent. The mean relaxation time τ does not obey the Arrhenius law above T_C. The occurrence of this relaxation process may be connected with oxygen vacancies.

Key words: *$NaNbO_3$, single crystal, reduced sample, dielectric relaxation, oxygen vacancies*

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1. Introduction

The sodium niobate is a typical antiferroelectric with the perovskite structure. In the temperature range from –200 °C to 650 °C its structural, dielectric and optic properties are being changed in the six phase transitions. All these transitions are connected with the oxygen octahedrons tilts and, in addition, the off-centre displacement of the Nb ion takes place in the first three cases (–200 °C, 360 °C and 480 °C). The phase transition, at the temperature 360 °C, from antiferroelectric phase with orthorhombic structure (Pbma) to the antiferroelectric orthorhombic structure (Pnmm) is accompanied by the maximum change of dielectric permittivity [1-6]. The results of the investigations carried out for $NaNbO_3$ single crystal in the temperature range 30–500 °C and for frequencies 20 Hz-1 MHz have revealed the low-frequency relaxation processes [7]. The mean relaxation times in these processes obeyed the Arrhenius law in the vicinity of T_C and the dispersion step $\Delta\epsilon$ was dependent on temperature. Both relaxation parameters $\Delta\epsilon$ and τ revealed the distinct discontinuity at the temperature T_C. The arising of low-frequency relaxation has

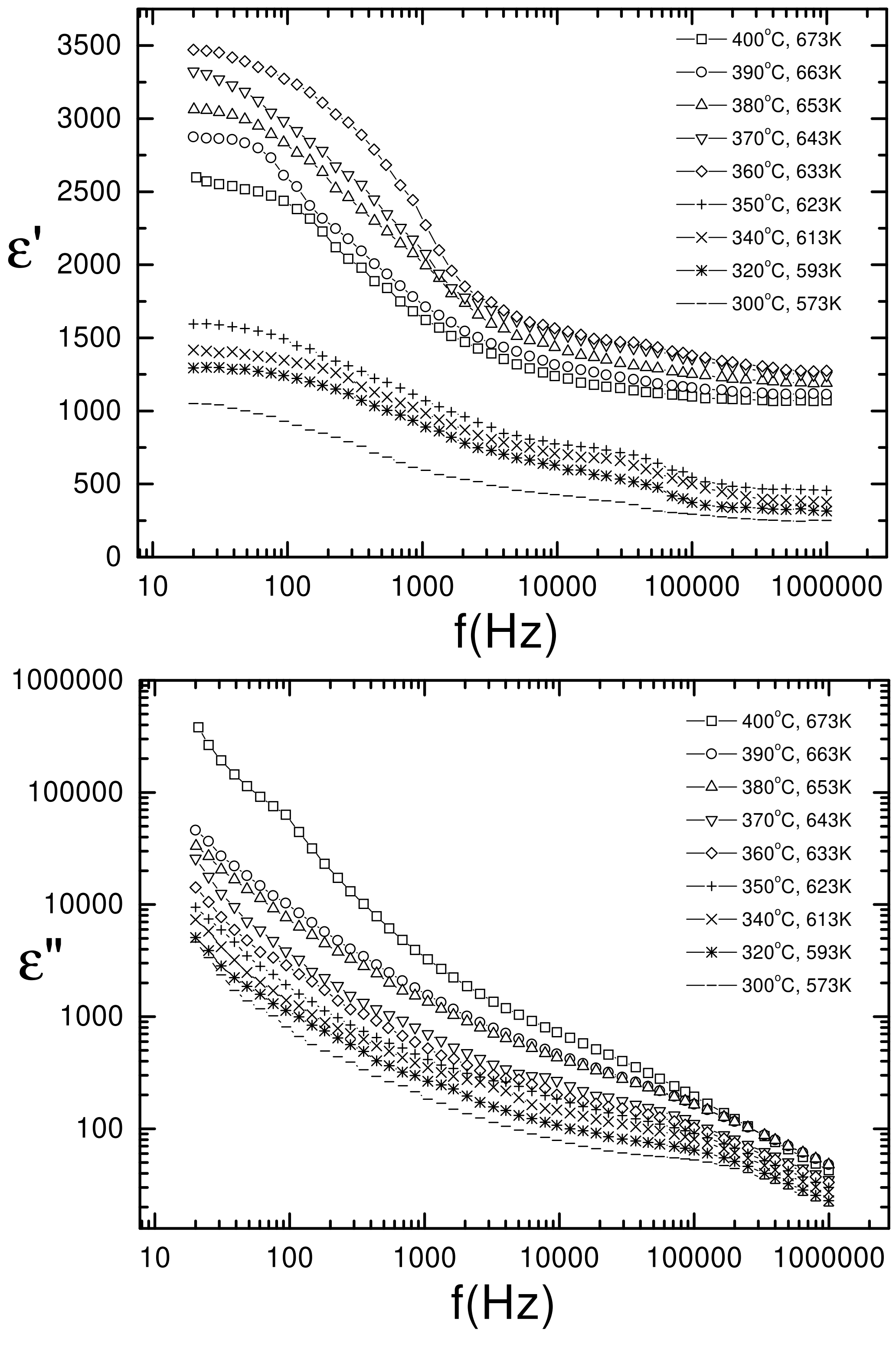

Figure 1. The frequency dependence of real ϵ' and imaginary ϵ'' part of electric permittivity.

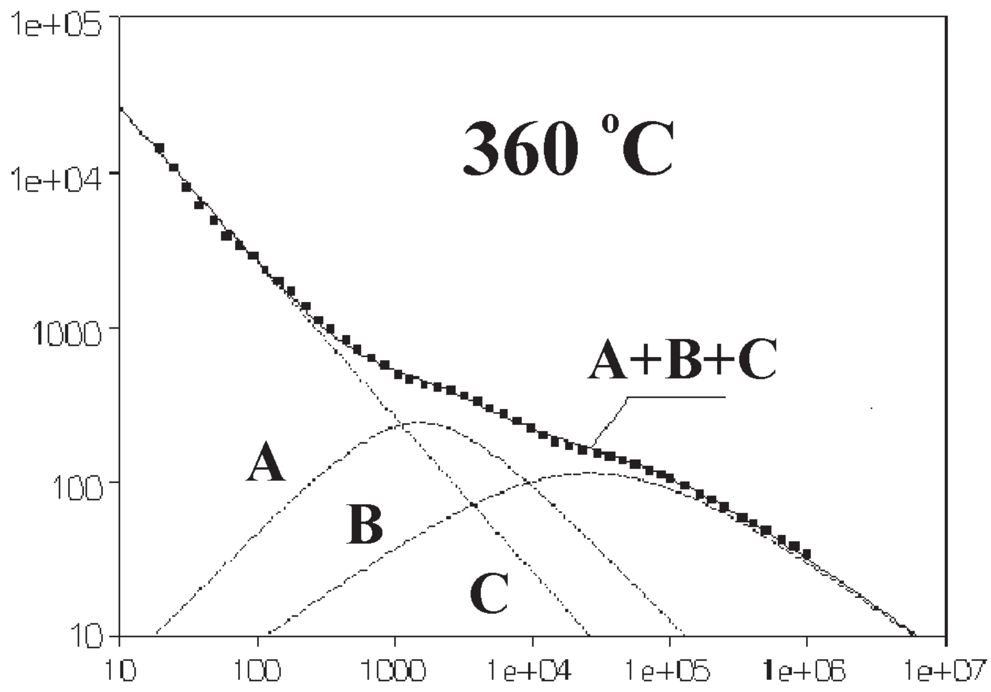

Figure 2. The example of fitting for 360 °C.

been connected with the disorder occurring in the crystalline structure already at high temperatures, which can lead to the arising of local dipoles (polar regions). These dipoles can be responsible for relaxation processes. In order to verify this hypothesis, additional dielectric investigations of single crystals have been carried out for reduced samples.

2. Experimental

The measurements were performed for a single crystal obtained by means of the "flux" method (the crystal used in the investigations described in the paper [8] was obtained using the same method). The crystal used in the measurements was annealed at the temperature of about 550 °C during three hours in the vacuum chamber (0.01 hPa) and then cooled (in vacuum) to the room temperature [8]. After depositing the silver electrodes they were placed in the thermostat. The temperature measurements were performed by means of a chromel-alumel thermocouple with the accuracy equal to 0.1 °C. The capacity and dielectric loss measurements were carried out using the HP 4284A LCR meter. The frequency of the measuring field was 20 Hz up to 1 MHz. Measurements were performed in regular steps of temperature (each 10 °C) at a constant rate of temperature changes and at a constant time of stabilisation.

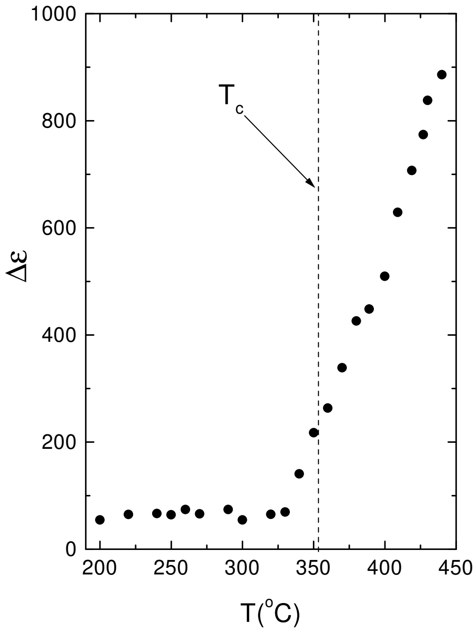

Figure 3. The temperature dependence of dispersion step $\Delta\epsilon$ for B relaxation.

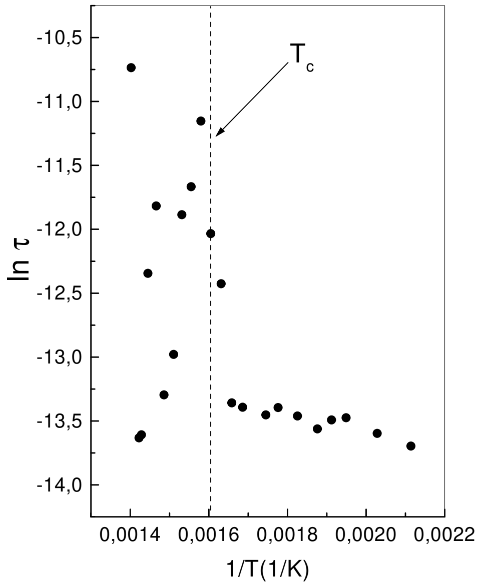

Figure 4. Arrhenius plot of the mean relaxation time τ for B relaxation.

3. Results

Two relaxation processes were obtained. Except the weak relaxation process below 10 kHz (the same as in the paper [7]) we can see the strong additional relaxation arising below 100 kHz (figure 1). This relaxation shifts itself to lower frequencies, when the temperature decreases. The results were fitted to the Cole-Cole model:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\mathrm{i}\omega\tau)^{1-\alpha}},$$

where ϵ_s is the static permittivity at low frequency, ϵ_∞ is the permittivity measured above the dispersion region, τ is the mean relaxation time, ω is the angular frequency and α determines the distribution of relaxation times and has got values between 0 and 1. The increase of ϵ'' towards low frequencies is associated with d.c. conductivity represented by σ_C and giving a contribution to ϵ^* in the form:

$$\epsilon^* = \epsilon' + \mathrm{i}\left(\epsilon''_p + \frac{\sigma_C}{\omega\epsilon_0}\right)$$

$$\sigma_C = \exp\left(-\frac{W}{kT}\right).$$

The example of such a fitting for the temperature 360 °C is shown in figure 2. From this figure we can distinguish two broad $\epsilon''(f)$ contributions – A (the same as in the paper [7]) and the additional one – B. The parameters of this relaxation are: A –

$\Delta\epsilon$=389, $\tau = 6.049 \cdot 10^{-6}$, and B – $\Delta\epsilon = 550$, $\tau = 1.042 \cdot 10^{-5}$ for temperature 360 °C (above T_C). The temperature dependence of dispersion step $\Delta\epsilon$ for B-relaxation is presented in figure 3. In the temperature range up to T_C $\Delta\epsilon \approx$ const, however above the temperature T_C dispersion step $\Delta\epsilon$ increases. The relaxation time in this process does not obey the Arrhenius law above the temperature T_C (figure 4).

4. Conclusions

It is well known, that the oxygen vacancies can be produced during the crystal growth. Moreover these vacancies can be also produced by annealing the sample in several oxygen atmospheres [8]. In the present paper the increase of the oxygen vacancy concentration was produced by annealing the sample in a lower air pressure atmosphere. The arising of the oxygen vacancies can be equivalent to the creation of the local dipoles. The behaviour of these local dipoles in a.c. electric field leads to the arising of an additional relaxation process in the $NaNbO_3$ in the frequency range of about 100 kHz (curve B in figure 2). This relaxation clearly evolves with temperature (with decreasing of temperature it moves towards lower frequencies). The studies of forming the vacancies and their effect on the behaviour of $NaNbO_3$ requires additional investigations which are now in progress.

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Діелектрична релаксація в монокристалі $NaNbO_3$

К.Конєчни

Інститут фізики та обчислювальної техніки,
Педагогічний університет,
Польща, 30-084 Краків, вул. Подхоронжих, 1

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Досліджено діелектричну сприйнятливість зразків монокристалу $NaNbO_3$ в діапазонах температур 30–500 °C і частот 20 Гц–1 МГц. У цьому температурному проміжку в частотній області поблизу 100 кГц спостерігається релаксаційний процес, що є доповнювальним до виявленого раніше процесу [7]. Отримані дані апроксимуються за формулою Коул-Коула. Значення дисперсії $\Delta\varepsilon$ (максимальне значення $\Delta\varepsilon$ = 1000) залежить від температури. Закон Арреніуса не виконується для середнього часу релаксації τ вище T_{C}. Поява цього релаксаційного процесу може пов'язуватися з кисневими вакансіями.

Ключові слова: *$NaNbO_3$, монокристал, діелектрична релаксація, кисневі вакансії*

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