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The Curie Temperature of LiNbO₃[1])

By

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Single crystals of $LiNbO_3$ are grown by the flux method. Measurements are made in the temperature range 20 to 1170 °C of the dielectric constant ε, dielectric loss and relative thermal expansion $\Delta l/l$ along the polar axis (the three-fold axis x_3) and perpendicular to the glide plane (x_1). A sharp maximum in ε corresponding to a decrease in volume is observed in the x_3 direction at 1140 °C. This temperature is assumed to be the Curie temperature of $LiNbO_3$ which corresponds to the transition from an electrically ordered state (ferro- or ferrielectric, rather than antiferroelectric) into a paraelectrical state. The temperature dependences of ε and $\Delta l/l$ below the Curie temperature show several similar anomalies. Some of these anomalies may be due to phase transitions.

Выращены монокристаллы $LiNbO_3$ флюсовым методом. Произведены измерения диэлектрической проницаемости ε и потерь и относительного удлинения $\Delta l/l$ в интервале температур 20 до 1170 °C вдоль полярной оси (оси третьего порядка x_3) и перпендикулярно к плоскости скольжения (x_1). При 1140 °C в направлении x_3 обнаружен резкий максимум ε, которому соответствует уменьшение объёма. Предполагается, что эта температура является температурой Кюри $LiNbO_3$, которой соответствует переход из электрически упорядоченного (скорее сегнето- или сегнетиэлектрического, чем антисегнетоэлектрического состояния) в параэлектрическое состоюяние. Ниже температуры Кюри на кривых зависимостей $\varepsilon = f(T)$ и $\Delta l/l = f(T)$ обнаружен рад аномалий, температуры которых удовлетворительно согласуются друг с другом. Некоторые из этих аномалий, по-видимому, являются фазовыми переходами.

Matthias and Remeika [1] showed for the first time that $LiNbO_3$ is a uniaxial ferroelectric. By investigating single crystals of $LiNbO_3$ and $LiTaO_3$ they observed hysteresis loops. But no more details were reported about $LiNbO_3$.

In his later works Megaw [2, 3] proposes to classify $LiNbO_3$ and $LiTaO_3$ as "frozen ferroelectrics". The Curie temperature of $LiNbO_3$ has not been reported up to the present.

In [4] an increase in the Curie temperature is observed for $LiTaO_3$–$LiNbO_3$ solid solutions if the concentration of the second component increased up to 70 mol%.[2]) Extrapolation of the Curie temperature to pure lithium niobate yields a value of about 1170 °C. This is the temperature of the melting point of polycrystalline $LiNbO_3$ [4]. On this basis the authors [4] suggest that $LiNbO_3$ may be considered as a pyroelectric or a "frozen ferroelectric".

In [6] an X-ray study of $LiNbO_3$ is made at high temperatures (20 to 700 °C). At 587 °C a phase transition is observed which was believed to be due to a transition from a ferroelectric to a paraelectric state. Originally an ilmenite structure

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[1]) The term "Curie temperature" used in this work does not mean that the phase transition to the paraelectric state is of the second type.

[2]) The Curie temperature of polycrystalline $LiTaO_3$ is about 650 °C [5].

(FeTiO$_3$) was ascribed to LiNbO$_3$ [7]. However, later investigations by Bailey [3] showed that the structure of LiNbO$_3$ is significantly different from that of ilmenite: the space group of LiNbO$_3$ is R3C (the ilmenite space group is R$\bar{3}$C). Moreover the sequence of cations along the triad axis is different in LiNbO$_3$ and FeTiO$_3$ (in LiNbO$_3$ the sequence of cations in this direction is Li–Nb–Li–Nb).

The space group R3C of LiNbO$_3$ was confirmed by neutron diffraction experiments carried out by Shiosaki and Mitsui [8]. The polarity of LiNbO$_3$ was also confirmed by the existence of a piezo- and pyroeffect at room temperature [9]. Megaw [3] derives the crystalline structure of lithium niobate from the perovskite structure by continuous ion displacements and assumes that a transition into the perovskite phase must occur at high temperatures with ion displacements of the order of 1 Å. But this assumption is doubtful since the unit cell of LiNbO$_3$ remains rhombohedral till 700 °C [6] and is quite different from the perovskite cell. Thus, the nature of the dielectric properties of lithium niobate (a compound whose structure has not been adequately investigated) still remains uncertain.

On the other hand, much attention is paid to lithium niobate due to its large importance as a material for non-linear optics. It was possible to use LiNbO$_3$ for modulating light of a laser source due to a strong electrooptic effect. LiNbO$_3$ [10, 11] is reported to have great advantages in comparison with other nonlinear materials for coherent second harmonic generation. This is connected with a large negative birefringence of this material in the visible and near infrared and a large nonlinear coefficient which is an order of magnitude higher for LiNbO$_3$ than for other known crystals. Moreover, lithium niobate can be used for optical parametric devices, for electromechanical transducers, and microwave applications.

The above-mentioned results indicate that careful investigations of LiNbO$_3$ in a wide temperature range up to the melting point are of great interest. It is also desirable to carry out measurements on oriented single crystals.

In the present work single crystals of LiNbO$_3$ have been grown and the temperature dependence of dielectric permeability, losses, and thermal expansion have been investigated in the temperature range 20 to 1170 °C.

In [9, 12, 13] it has been reported that LiNbO$_3$ single crystals were grown by the Czochralski technique. In this work single crystals have been grown by the flux method. Li$_2$CO$_3$ and LiCl "pro analysi" and Nb$_2$O$_5$ of 99,5% purity were used and a mixture consisting of 5 mol% Li$_2$CO$_3$, 5 mol% Nb$_2$O$_5$, and 90 mol% LiCl was put in a platinum crucible and heated in furnace to a temperature of 1250 to 1300 °C. Then the furnace was cooled slowly to 800 °C at the rate of 5 to 7°/h. In this way crystals with an area up to 1 cm^2 have been obtained. The colour of the crystal varied from pale pink to brown. After annealing in air at a temperature of 1120 to 1150 °C the crystals became colourless. When the measurements were repeated at high temperatures the crystals in some cases had at first a light green and then a pink colour. It may be supposed that crystal coloration is caused by the character of oxygen defects.

The melting points of different samples varied in the temperature range from 1185 to 1210 °C which may be also connected with the number and character of oxygen defects.

Two single crystals without any twins and visible defects were chosen for optical and X-ray experiments. The crystals were oriented by using X-ray technique. We chose the usual orientation of a crystal of space group R3C [14], i.e. x_3 is the three-fold polar axis and x_1 is the direction perpendicular to the

glide plane and therefore perpendicular to the three-fold axis. The crystals were cut to an accuracy of $\pm$ 2°. Measurements of ε and tg δ were carried out in the interval between room temperature and 1160 °C with a Q-meter ,,TESLA" BM 220 in a coaxial dielectrometer. The frequency of 75 MHz was used to diminish the influence of conductivity at high temperatures. Coaxial sample holders were made of stainless steel, each of them was used for no more than two high-temperature measurements. Water cooling was used to prevent heating of the Q-meter.

Heating was performed in a muffle furnace with a heating rate of 1.5 to 2° per minute. The temperature was measured by a Pt/Pt–Rh thermocouple, the junction of which was placed in a hole of one of the electrodes 0.5 mm apart from the sample. The temperature gradient across the sample did not exceed 1 to 2 °C. The values of ε and tg δ were measured with an error of $\pm$ 10% and $\pm$ 20%, respectively, and changes of ε and tg δ of about $\pm$ 2% and $\pm$ 10%, respectively, could be measured.

A dilatometer equipped with an "ИКВ" optimeter and a vacuum dilatometer, type "УВД", were used to investigate the temperature dependences of thermal expansion.

During dilatometric measurements the heating rates were different for different temperature ranges: From room temperature to 700 °C the heating rate was 100 °C/h and each measuring temperature was kept constant during 30 min. From 700 to 1180 °C the heating rate increased up to 300 °C/h and each measuring temperature was kept constant during 10 min.

All investigated samples were previously annealed in air at 1150 °C.

For dielectric measurements the samples were provided with palladium electrodes which were obtained by firing palladium paste.

The values of ε, tg δ, and the relative thermal expansion during cooling were in good agreement with those measured during heating.

The data obtained from different samples for both crystallographic directions are in good agreement with each other.

The temperature dependences of ε and tg δ of LiNbO₃ along the polar axis (x_3) and perpendicular to the glide plane (x_1) are presented in Fig. 1 (a, b). The values of ε in the high temperature range may be somewhat higher due to the increase in conductivity.

The temperature dependences of the relative thermal expansion in the same directions are shown in Fig. 2. The curves of the dielectric constant and relative expansion in Fig. 1 and 2 show several anomalies and the temperatures at which they occur agree fairly well with each other. A sharp peak of the dielectric constant ε which corresponds to the decrease in volume along the polar axis occurs at a temperature of 1140 °C.

It can be concluded that a phase transition to the paraelectric phase occurs in this temperature range. It should be reminded that the Curie temperatures in the series of LiTaO₃–LiNbO₃ solid solutions are extrapolated to approximately the same temperature region [4]. It can be also supposed that in whole temperature range (20 to 1170 °C) no phase transitions to the perovskite phase occur since such transition apparently requires a large increase in volume, which has not been observed (Fig. 2).

By comparing the curves $\varepsilon = f(T)$, it is seen from Fig. 1 (a, b) that the value of ε at high temperatures is substantially smaller in the direction perpendicular to the polar axis than in the polar direction. In the transition range the values
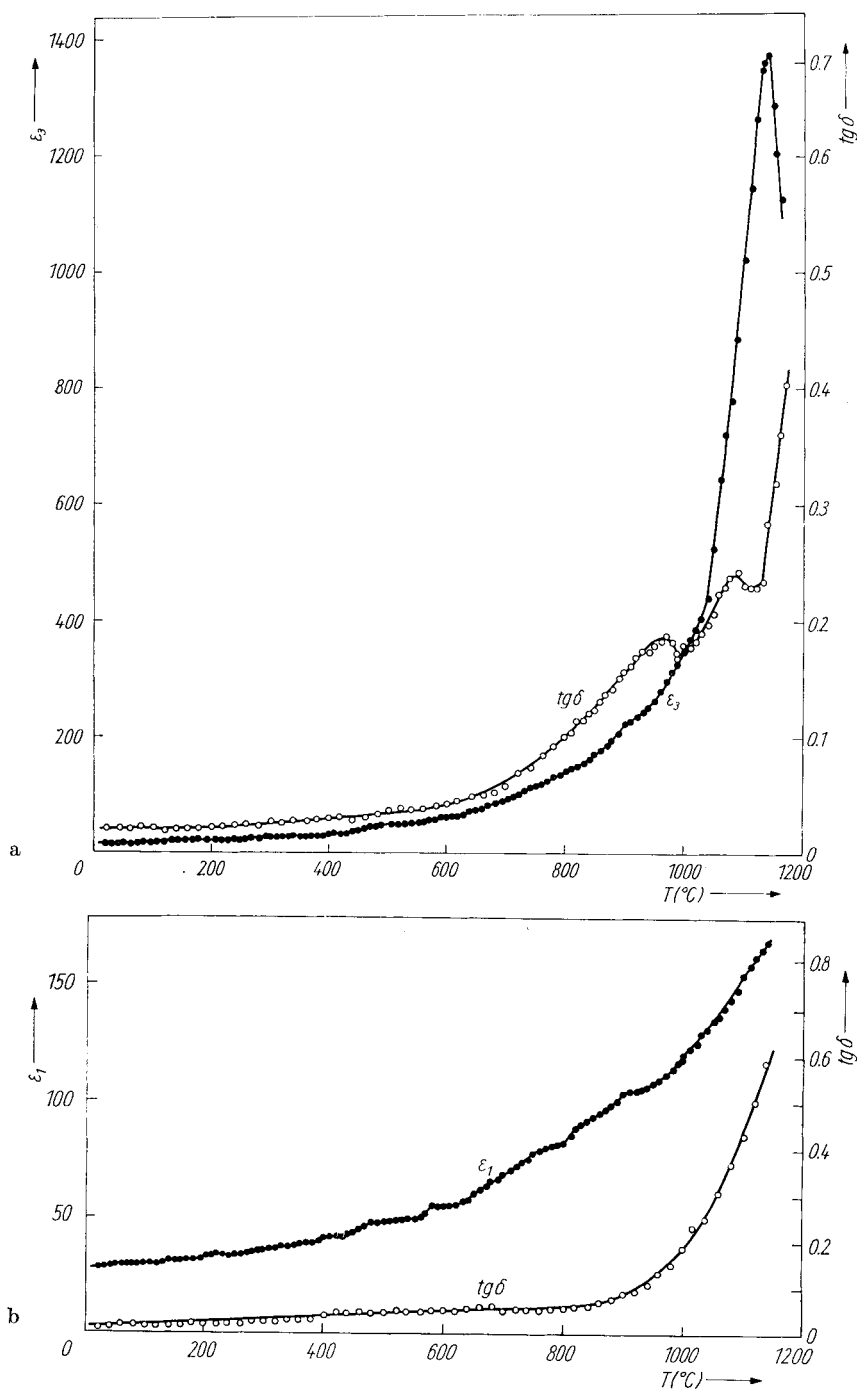
Fig. 1. Temperature dependence of the dielectric constant ε and losses tg δ of LiNbO$_3$ single crystals
a) refers to the direction of the polar axis (threefold axis x_3), b) refers to the direction perpendicular to the polar axis and glide plane x_1
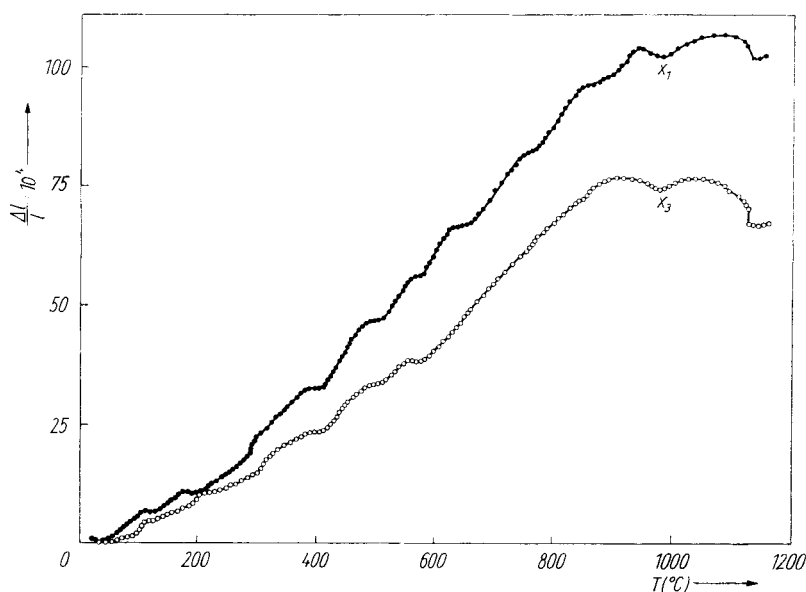
Fig. 2. Temperature dependence of relative expansion $\Delta l/l$ in the direction x_3 and x_1 (● refers to x_1, ○ refers to x_3)

of ε differ by one order of magnitude which is characteristic of uniaxial ferro-electrics.

The fact that lithium niobate has a higher Curie temperature than lithium tantalate is typical of octahedral oxygen compounds and this is assumed to be associated with the greater polarizability of the oxygen octahedron with Nb than of the oxygen octahedron with Ta.

Several anomalies of the dielectric constant and relative expansion observed at lower temperatures seem to correspond to phase transitions. Some evidence for the existence of phase transitions in LiNbO₃ slightly above room temperature was obtained in [9]. The existence of phase transition in the range 120 to 130 °C does not contradict the results obtained in [11]. The phase transition in the range 580 to 590 °C was first discovered by X-ray studies [6].

Measurements of the dielectric polarization as a function of alternate field strength in the temperature range 20 to 220 °C have shown that dielectric hysteresis loops do not exist up to a field strength of 30 kV/cm. Similar results were obtained by Matthias et al. [1].

Phases existing below the Curie temperature may be rather ferro- or ferrielectric than antiferroelectric. According to available data a phase existing at room temperature seems to be a hard ferroelectric one. Some phase transitions in LiNbO₃ may not be associated with a substantial change of the polarized state. These phase transitions may be similar to that caused by the steric effect in compounds having the perovskite structure [15 to 17].

Final conclusions about the nature of low temperature phases can be drawn only after dielectric investigations in strong electric fields and precise X-ray and neutron studies over the whole temperature range up to the melting point.

Thus, by investigating the temperature dependences of dielectric permeability, losses, and relative expansion of LiNbO₃ single crystals it was possible to deter-

mine the Curie temperature of this compound to be about 1140 °C. It should be noted that among the ferro- and antiferroelectric substances known to date, LiNbO$_3$ has the highest Curie temperature.

In the whole temperature range (20 to 1170 °C), the curves $\varepsilon = f(T)$ and $\Delta l/l = f(T)$ (l is the length of the sample) reveal a large number of anomalies, some of which seem to correspond to phase transitions.

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