

DIELECTRIC PROPERTIES OF $A_{0.33}\text{NbO}_3$ COMPOUNDS

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Dielectric properties of $A_{0.33}\text{NbO}_3$ compounds, where A stands for Nd^{3+} , La^{3+} or Sm^{3+} were investigated. Dielectric permittivity was measured in the frequency range of 1kHz to 70MHz and at temperatures from -195°C to $+300^\circ\text{C}$. It was found that ϵ as a function of temperature has a maximum; with increasing frequency this maximum shifts towards the higher temperatures and its value decreases. In the plot of thermal expansion coefficient against temperature an inflexion is observed at the temperature corresponding to this maximum. A phase transition probably occurs at this temperature. However, this is not a segnetoelectric transition, as the ϵ values are not high and no appreciable nonlinearity of ϵ is observed. Therefore, it is assumed that the ordering of vacancies in the crystallographic sites of A type, observed in the investigated compounds favours antiparallel shifts of niobium ions and this acts against the build-up of the segnetoelectric state.

The investigation of dielectric properties of various dioxides containing Nb^{5+} niobium ions is of some importance, for among these compounds many were found to exhibit segnetoelectric or antisegetoelectric behaviour [1]. Thus, all niobium dioxides with perovskite structure (chemical formula: ANbO_3) and completely filled A sites in the crystal lattice are segnetoelectric or antisegetoelectric. However, it is known that there are many compounds which crystallize in the perovskite structure and leave some lattice sites vacant.

Investigation of these compounds is interesting both from the general crystallochemical point of view, as this provides information on the influence of defects on the stability of the crystal lattice, and from a more specific point of view, when one looks for an explanation of the possible formation of segnetoelectric or antisegetoelectric states in distorted crystals. Taking this into account, we examined the dielectric properties of several compounds which have perovskite structure with defects and a general chemical formula $A_{0.33}\text{NbO}_3$, where A stands for Nd^{3+} , Sm^{3+} or La^{3+} . Preparation of the compounds, and their structure, were described earlier [2], [3], [4]. The structure exhibits rhombic symmetry, space group $P4/mmm$ (there exists a centre of symmetry), and the unit cell contains two $A_{0.33}\text{NbO}_3$

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units. There is a specific distribution of vacancies in A sites: one half of these sites is vacant, and $2/3$ of the second half is occupied by A atoms. The unit cell of $\text{La}_{0.33}\text{NbO}_3$ is shown in Fig. 1. The Nb^{5+} ions are displaced from the centers of the oxygen octahedrons (the distance between them is shortened), and the octahedrons themselves are appreciably distorted.

The investigated samples were obtained by the usual method of multiple sintering and grinding (usually the sintering was carried out four times). The last firing was carried out at $+1280^\circ\text{C}$, and the sample was kept at maximum temperature for 1 hour. To improve the quality of the sintered material, some samples were doped with 0.5–1% (weight) of Bi_2O_3 or PbO . X-ray analysis of the samples has shown well formed perovskite structure; no other phases were observed in the samples.

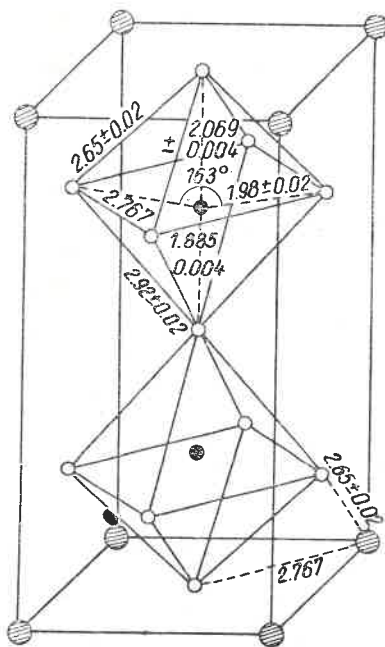


Fig. 1. Unit cell of $\text{La}_{0.33}\text{NbO}_3$, according to [4]

Dielectric permittivity was measured using bridge and Q -meter techniques. Thermal expansion was determined by a mechanico-optical quartz dilatometer. The temperature dependence of the dielectric permittivity at various frequencies and the temperature dependence of the thermal expansion coefficient for the investigated compounds are shown in Figs 2, 3 and 4. The plot of ϵ as a function of temperature shows a weak maximum, which shifts with increasing frequency. The results of dielectric measurements for samples with and without Bi^{3+} and Pb^{2+} admixtures are similar.

No appreciable nonlinearity of dielectric polarization was observed within measuring accuracy, which for the Q -meter was $\pm 3\%$ and for the bridge methods $\pm 1\%$, in electric fields up to 20kV/cm . In the graph of thermal expansion of $\text{Nd}_{0.33}\text{NbO}_3$ vs. temperature we found an inflexion point at a temperature near -140°C . There are also certain changes in the slope

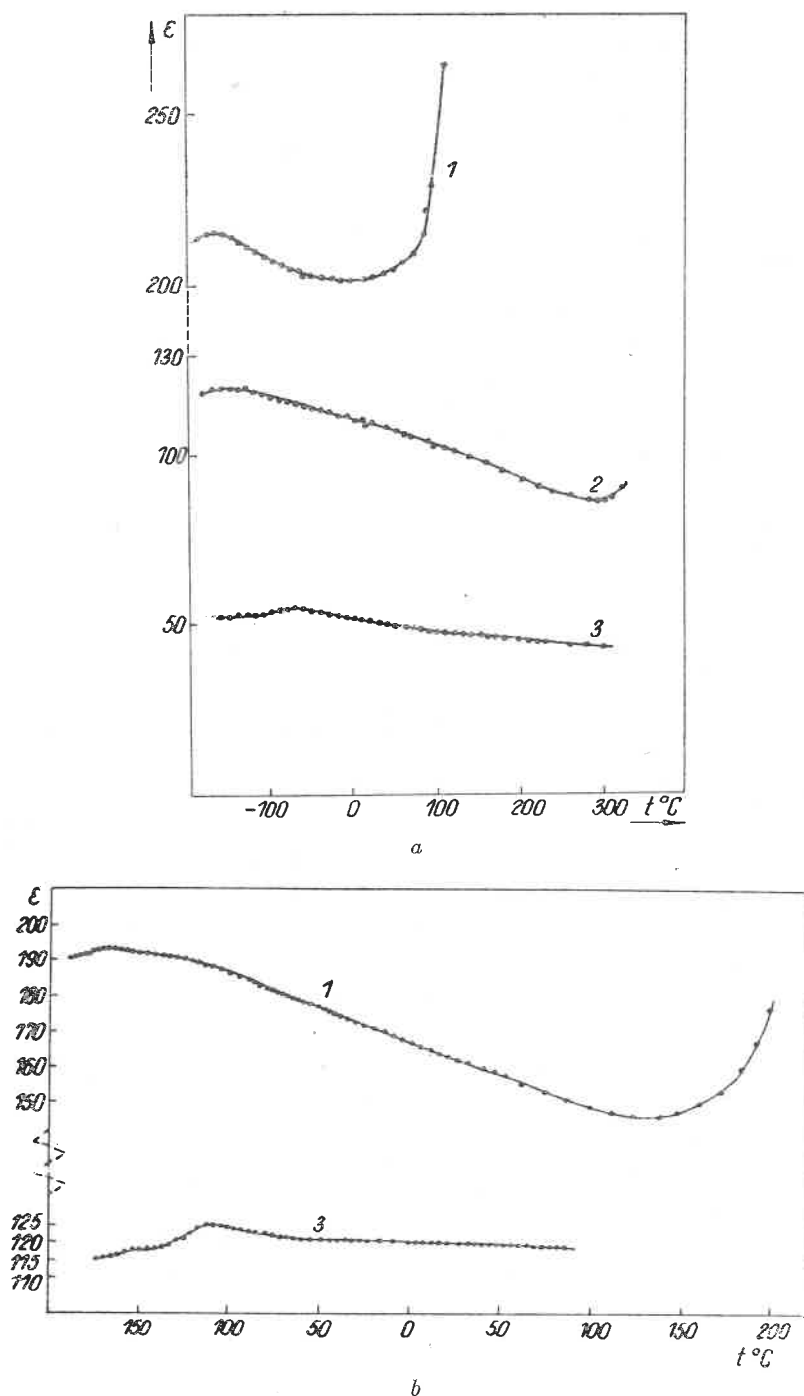


Fig. 2. Dielectric permittivity ϵ as a function of temperature. a) $\text{Nd}_{0.99}\text{Bi}_{0.01}\text{NbO}_3$ with 1% admixture of Bi_2O_3 , b) $\text{Nd}_{0.99}\text{NbO}_3$ without doping. 1 — at 1 kHz, 2 — at 500 kHz, 3 — at 70 MHz

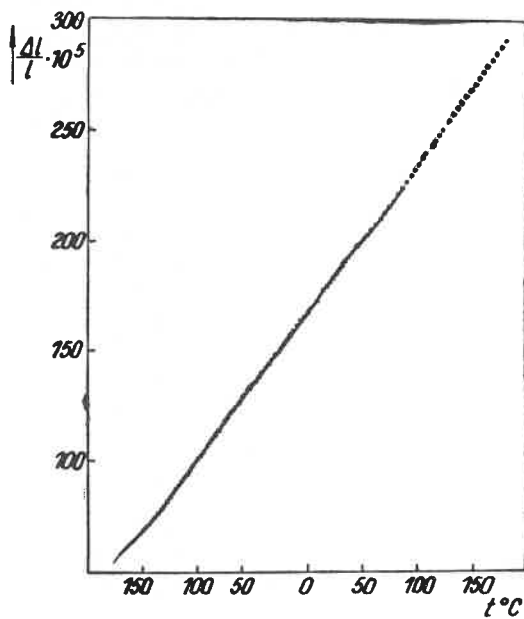


Fig. 3. Thermal expansion coefficient $\Delta l/l$ as a function of temperature for $\text{Nd}_{0.33}\text{NbO}_3$

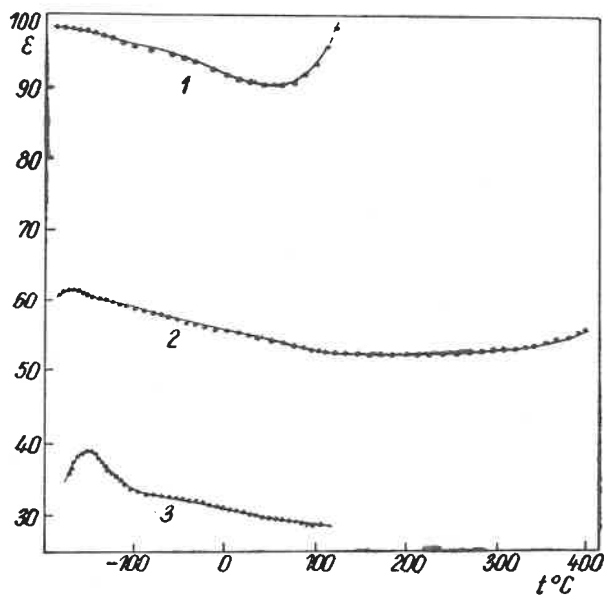
of the expansion coefficient curve near -50°C and $+100^\circ\text{C}$, but these are much smaller and less sharply defined than the change at -140°C . In the same temperature range there is a relaxational maximum of ϵ . Therefore, one can suppose that both these effects are associated with a phase transition in this temperature range.

The decrease of ϵ values with an increase in frequency can be apparently attributed to various electron effects caused by the oxygen defects in the lattice which remains electrically neutral. Oxygen defects are typical for compounds containing niobium and having the perovskite structure. The above-mentioned electron defects enhance conductivity and possibly the dielectric permittivity, too. In particular, the increase of the slope of curves 1 and 2 in Fig. 2 can be explained by the increase of conductivity with temperature. The influence of conductivity on the ϵ value decreases at higher frequencies, and as a result the dielectric permittivity decreases and the slope increases at the higher temperatures.

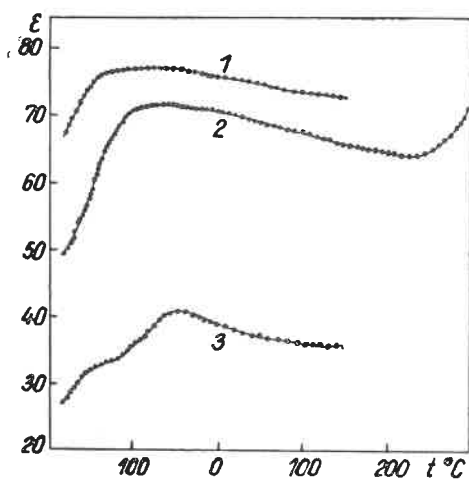
Our results (low value of ϵ , and lack of electric nonlinearity) indicate that the examined compounds have no segnetoelectric properties. Antisegnetoelectric properties cannot, however, be excluded.

The formation of segnetoelectric or antisegnetoelectric states in compounds with perovskite structure is primarily caused by the presence of oxygen octahedrons containing ions of the transition elements; the presence or absence of the A -type ions is of much lesser significance. For example, tungsten trioxide WO_3 is antisegnetoelectric and its structure is identical with the perovskite structure with completely vacant A sites. Therefore, it appears that a deficiency in the A ions should not hinder the rise of spontaneous polarization. However, it should be noted that the aniparallel configuration of dipole moments, caused by the displacement of Nb^{5+} ions towards each other [(head to head) *cf.* Fig. 1], is rather

inconvenient as far as the electrostatic energy of dipole-dipole interaction is concerned. More probably, this configuration should be linked with the absence of ions in half of the A -type sites and the formation of an empty A layer, towards which the A ions are "pushed". This sort of ion displacement apparently acts against the formation of a segnetoelectric state which is characterized by parallel displacement of ions. This may prove to be a plausible cause of the lack of segnetoelectricity in the examined compounds.



a



b

Fig. 4. Dielectric permittivity ϵ as a function of temperature. a) $\text{La}_{0.33}\text{NbO}_3$, b) $\text{Sm}_{0.33}\text{NbO}_3$. 1 — at 1 kHz, 2 — at 500 kHz, 3 — at 70 MHz

Recapitulating, when investigating dielectric properties of the $A_{0.33}\text{NbO}_3$ compounds, where $A = \text{Nd}^{3+}$, La^{3+} or Sm^{3+} , we found that the dielectric permittivity of these compounds exhibits relaxational behaviour. The absence of segnetoelectric states is caused by the ordering of vacancies in the A -type sites, which ordering apparently favours antiparallel shifts of niobium ions.

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REFERENCES

- [1] F. Iona, D. Shirane, *Segnetoelectric Crystals* (in Russian), Mir, Moscow 1965.
- [2] A. J. Dyer, A. A. D. White, *Trans. Brit. Ceram. Soc.*, **63**, 301 (1964).
- [3] H. B. Rooksby, A. A. D. White, Z. A. Zargston, *J. Amer. Cer. Soc.*, **48**, 447 (1965).
- [4] P. N. Iyer, A. J. Smith, *Acta Cryst.*, **23**, 740 (1967).