Temperature dependent conductivity and broadband dielectric response of precursor-derived Nb$_2$O$_5$

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ABSTRACT

Different polymorphs of niobium pentoxide (Nb$_2$O$_5$) were synthesized using niobium ethoxide as a precursor by varying the pyrolyzing temperature. The room temperature X-ray diffractograms revealed the irreversible phase evolution from amorphous to pseudohexagonal (823 K) to orthorhombic (1023 K) and to monoclinic crystal structure (1223 K). While phase evolution was also confirmed by thermogravimetry and dilatometry, Raman spectroscopy clearly suggested complete elimination of free carbon in the pyrolysed ceramics. The sintering conditions were optimized to produce a highly dense (> 95%) thermodynamically stable monoclinic Nb$_2$O$_5$. The electrical properties of stable monoclinic Nb$_2$O$_5$ sample were thoroughly studied. The monoclinic Nb$_2$O$_5$ was found to have a dielectric constant of around 28 with a dielectric loss of 0.008 at room temperature and at 100 kHz. At low measurement frequencies, an anomalous increase in the effective dielectric permittivity with increasing temperature was observed. Large values of the ε’ are associated with polarization due to the accumulation of free electrons at the grain boundaries. An analysis of the dispersion curves of Nb$_2$O$_5$ revealed that two relaxation processes are responsible for the observed anomalies, and the temperature dependencies of their parameters (dielectric strength, relaxation time and spectrum broadening parameter) were determined. The low-frequency process (relaxation time τ$_0$ ~ 0.45 s), which makes the largest contribution to the dielectric constant, was apparently due to the inhomogeneous conductivity of ceramics. It was revealed that the DC conductivity of ceramics has thermoactivation character with activation energy of about 660 meV and was determined by the oxygen vacancies.

1. Introduction

Niobium oxides find its use in electronic applications, in particular niobium pentoxide (Nb$_2$O$_5$), which is the most stable oxide of niobium. Its physical properties include a high static dielectric constant (ε’) of 41 in the amorphous phase and a band gap of 3.4–5.3 eV [1]. Nb$_2$O$_5$ is also used in the preparation of alkaline metal niobates such as LiNbO$_3$, KNbO$_3$, and NaNbO$_3$ for its application in optoelectronic devices [2]. Belonging to VB group in the periodic table, niobium and tantalum have pentoxides with similar crystal structure. Niobium ore being more abundant than tantalum, in addition to the fact that Nb$_2$O$_5$ has a higher dielectric constant than Ta$_2$O$_5$, makes it an attractive candidate in capacitors [3,4]. Niobium pentoxide has many polymorphs, and a detailed understanding of the phase transitions is important for it to be considered for various applications. The most common phases of Nb$_2$O$_5$ are T-Nb$_2$O$_5$ and H–Nb$_2$O$_5$. The T phase is the low temperature phase with an orthorhombic crystal structure and the H phase is the thermodynamically stable high temperature phase with monoclinic structure [5]. The formation of other polymorphs such as B–Nb$_2$O$_5$, N–Nb$_2$O$_5$, R–Nb$_2$O$_5$, M – Nb$_2$O$_5$, P–Nb$_2$O$_5$ and TT–Nb$_2$O$_5$ strongly depends on the starting materials, synthesis route, and treatment temperatures [6].

The reported values of dielectric constant of Nb$_2$O$_5$ are rather limited and inconsistent. For amorphous films formed by anodization, the values vary from 41 to 120 [7,8]. Soares et al. [9] found that the dielectric constant of sintered Nb$_2$O$_5$ pellets varies from 38 to 165.
depending on the processing routes. Graca et al. [2] reported the dielectric constants of powder compacts of T-Nb₂O₅ and H-Nb₂O₅. For T phase, ε' value was found to be ~80, for H phase to be ~17, and for a mixture of T and H phases to be ~600. It is clear that the electrical properties of bulk Nb₂O₅ not only depend on the crystal structure, but also on the density and microstructures which vary with sintering conditions [2,9]. Variations in the transport property has also been attributed to the presence of oxygen vacancies. This dependence on vacancies is the basis for the technological application of this material. This refers to the reported photochromic properties of niobium oxides [10] and the synthesis of Nb₂O₅ thin films for its use as transparent conducting oxide (TCO) [11]. In addition, it should be emphasized that one of the most interesting and potential applications for niobium oxides are for memristors. In the case of niobium oxides, diffusion of oxygen and changes in conductivity may be a limitation for its use in solid-state electrolytic capacitors, but at the same time serve as a key factor for achieving a fully working memristor. Therefore, studies focused towards understanding the phase transformations, microstructure, oxidation state and oxygen vacancies are crucial.

In this work, Nb₂O₅ was synthesized through the liquid precursor route. Niobium ethoxide Nb₂(OC₂H₅)₁₀ was pyrolysed at varying temperatures to obtain various polymorphs of Nb₂O₅. The phase transitions were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dilatometry, and X-ray diffraction (XRD). The high temperature stable phase of Nb₂O₅ was compacted to produce dense pellets (95%) using pressureless sintering technique. The highly dense sample minimise the effects of porosity on dielectric loss, which is an issue seen in previous works. The microstructure of the samples were imaged using scanning electron microscopy (SEM). All the dielectric relaxation measurements were performed on dense pellets for a wide frequency and temperature range.

2. Experimental methods

2.1. Synthesis and characterization of Nb₂O₅ powders

The niobium ethoxide (Nb₂(OC₂H₅)₁₀) precursor (99.95% trace metal basis from Sigma Aldrich) was crosslinked at 473 K in air for 1 h. The thermal analysis of the crosslinked polymer was done using SDT Q600, TA Instruments, (USA) from room temperature to 973 K main- dium from Sigma Aldrich) was crosslinked at 473 K in air for 1 h. The sintered samples hereafter are referred to as N67, N85, and N95 indicating their percentage density. The apparent density of the sintered pellets was measured using the water displacement method (Table 1). The process to obtain dense pellets for dielectric measurements has been elucidated in Fig. 1. The sintered pellets were cut across the diameter using a diamond wafer blade and the cross sections were examined using field emission scanning electron microscopy (FEI Quanta 400, USA). The pellet with highest density was chosen and gold sputtered on both sides of pellet to act as electrodes. The dielectric measurements were done on a broadband dielectric spectrometer Novocontrol BDS80 (Germany) from room temperature to 673 K in the frequency range of 0.1 Hz–1 MHz.

3. Results and discussion

3.1. Phase evolution

The DSC and TGA of crosslinked Nb₂(OC₂H₅)₁₀ shown in Fig. 2, exemplify two prominent peaks at 373 K and 852 K on the DSC curves along with the corresponding weight loss shoulders. The first peak corresponds to the removal of entrapped moisture. The second peak indicates the crystallization of the phase that correspond to the pseudohexagonal crystal structure as observed in the XRD (Fig. 3).

The pyrolysed precursor was found to be amorphous till 723 K and further increase in temperature resulted in the crystallization of pseudohexagonal phase with the first three prominent peak angles (2θ) at 22.5°, 28.5°, and 36.6° [12]. The powder was a mix of black and white particles, indicating some remainder of carbon.

The dilatometry analysis (Fig. 4) shows a sharp contraction in length starting at 1003 K and ends at 1208 K. The change is associated a change in crystal structure of the material. It becomes evident from the
XRDs that the change is that of orthorhombic structure to monoclinic structure. The change from pseudohexagonal to orthorhombic is not observed because the powder used for dilatometry, obtained at 923 K, is already orthorhombic in structure. There are no other sharp length changes.

The X-ray diffractograms for Nb$_2$O$_5$ heat-treated at 923 K, 1023 K, 1123 K, 1223 K, 1323 K, 1423 K, and 1523 K are shown in Fig. 5. At 923 K it can be seen that the orthorhombic phase begins to crystallize and completes crystallization at 1023 K with the first three prominent peaks angles at 22.6°, 28.3°, and 36.6° (ICDD reference pattern 98-000-0955). At 1223 K, monoclinic Nb$_2$O$_5$ crystallizes, with the first three prominent peak angles at 23.6°, 24.4°, and 25.4° (ICDD reference pattern 98-000-0019). The transformation from pseudohexagonal to orthorhombic and orthorhombic to monoclinic are irreversible as evidenced by the XRDs taken at room temperature.

Raman spectra (Fig. 6) of the sample pyrolysed at 823 K show D & G peaks at 1345 cm$^{-1}$ and 1580 cm$^{-1}$ implying the presence of free carbon. The remaining peaks correspond to pseudohexagonal/orthorhombic Nb$_2$O$_5$ and can be seen in the more crystallized spectra of the sample heat-treated at 1023 K. The sample heat-treated at 1423 K indicate peaks which correspond to monoclinic Nb$_2$O$_5$.

### 3.2. Sintering optimisation

N95 was shown to have the maximum apparent density 4.31 g/cm$^3$ which was 95% of the theoretical density (4.55 g/cm$^3$) [13]. The sintered samples were also found to be monoclinic. The scanning electron micrographs of N67, N85, and N95 are shown in Fig. 7. N67 and N85
shows considerable amount of porosity, unlike N95. All further studies were carried out on sample N95.

3.3. Conductivity and dielectric properties

As it was previously shown [14, 15], the conductivity of niobium oxide is mainly determined by electrons generated by oxygen vacancies, which in turn is determined by the preparation method and the presence of oxygen on the surface. Thus, the electrical properties of sample can vary greatly depending on the conditions of experiment.

Fig. 8 a shows experimental temperature dependency of the AC conductivity of N95 Nb₂O₅ ceramic at the measuring frequency of 250 kHz for several measurement modes (a) heating in a nitrogen atmosphere and in air, and (b) two heating-cooling cycles in an air atmosphere.

Fig. 9. Frequency dependencies of the dielectric permittivity and loss tangent of N95 Nb₂O₅ ceramic for several temperatures near RT.

Fig. 10. Temperature dependency of the real part of the dielectric response (a) and conductivity (b) of N95 Nb₂O₅ ceramic at several measuring frequencies.


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conductivity monotonously reduced. Upon second heating, the peak almost disappeared, and upon cooling, the behavior of the conductivity does not depend on the number of measurement cycles (Fig. 8 b). In order to avoid similar effects and to achieve reproducible results, all further studies were carried out during cooling in ambient air atmosphere after durable annealing in air.

The frequency dependencies of the dielectric permittivity and loss tangent of the studied ceramics near room temperature are shown in Fig. 9. The epsilon value is of the order of 28 at frequencies above 1 kHz and the loss tangent is less than 0.01. At low measurement frequencies a sharp increase in epsilon and losses were observed that can be attributed to the polarization due to the accumulation of free electrons at the grain boundaries.

In Fig. 10 the temperature dependencies of the dielectric constant and conductivity of Nb_2O_5 for several measurement frequencies are shown. On heating, \( \varepsilon \) and \( \sigma \) increased exponentially and this increase seems to be much stronger at low measurement frequencies. The effective dielectric constant of the ceramic reaches \( 10^5 \) at 600 K at a frequency of 0.1 Hz, which indicates the dominant contribution of the inhomogeneous conductivity to \( \varepsilon \) [16,17].

To clarify the nature of the observed dielectric response, the spectra was analyzed within the framework of existing theoretical models. The frequency dependencies of the real and imaginary parts of the dielectric constant of Nb_2O_5 ceramic for several temperatures are presented in Fig. 11. As a model function, we have used the sum of high-frequency dielectric constant \( \varepsilon_\infty \), DC conductivity \( \sigma_0 \) and relaxation terms, which have been described using the Cole – Cole function [18]:

![Fig. 11. Frequency dependencies of the real and imaginary parts of the dielectric permittivity of N95 Nb_2O_5 ceramics for several temperatures.](image)

\( \varepsilon_\infty \) is the high-frequency dielectric constant, \( \sigma_0 \) is the DC conductivity, and \( \tau \) is the relaxation time.

![Fig. 12. Temperature dependencies of the parameters of relaxation processes \( \Delta \varepsilon \), \( \alpha \), and \( \tau \) (in Arrhenius coordinates for clarity).](image)

![Fig. 13. DC conductivity versus 1/T of N95 Nb_2O_5.](image)
\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0}{\varepsilon_\infty \omega} + \sum_j \Delta \varepsilon_j \left( 1 + (i \omega \tau_j)^\alpha \right) \]  

(1)

Summation was made over several relaxation processes enumerated by the index \( j \). Here, \( \Delta \varepsilon_j, \tau_j, \alpha, \varepsilon_0 \) refer to dielectric strength, relaxation time, parameter describing the broadening of the spectrum as compared to the Debye spectrum of the \( j \)-s process and electric constant respectively.

The real and imaginary parts of the complex dielectric permittivity were fitted simultaneously, which permitted significant improvement in the accuracy of calculations. For this purpose, a special C program was written using the Levenberg-Marquardt algorithm.

As a result of the fitting, two relaxation processes were distinguished and their parameters were obtained. The temperature dependences of the parameters of these relaxation processes are shown in Fig. 12. It can be seen that all processes possess a substantially broadened spectra in comparison to Debye spectrum, therefore there seems to be a wide range of relaxation times in this system. The main contribution into the response comes from the low-frequency process, apparently related to the polarization of the grains due to the accumulation of charges at their boundaries. The \( \Delta \varepsilon \) of this process grew exponentially on heating. The behavior of the characteristic relaxation time can be described by the Vogel-Fulcher law with the freezing temperature 380 K and \( \tau_0 \sim 0.45 \) s since a simple Arrhenius approximation does not provide good agreement with the data. The second process was characterized by higher frequency and its contribution seems to be rather weak. The temperature dependence of the characteristic relaxation time was non-monotonic, but in the temperature range above 470 K it was well described by the Arrhenius law with \( E_a = 870 \text{ meV} \) and \( \tau_0 \sim 10^{-13} \text{ s} \). The \( \Delta \varepsilon \) has the maximum near 490 K.

The conductivity activation energy (Fig. 13) of the ceramic determined was 0.66 eV, which seems to be consistent with the literature data. In literature, it was found that the conductivity of Nb_{2}O_{5} single crystals depends exponentially on the temperature with an activation energy of 0.9 eV in the range from 1150 to 650 K and 0.2 eV in the range from 650 to 350 K [13,14]. It was also found that the electrical conductivity of ceramic samples depends exponentially on temperature, but in the entire temperature range only one activation energy was obtained. This activation energy depended on the concentration of defects and ranged from 1.0 eV for the highest to almost zero for the lowest concentration at which the behavior of ceramics was similar to that of a degenerate semiconductor.

The comparison of room temperature dielectric constant and loss at 100 kHz with previously reported literature are shown in Table 2. Commercially available Nb_{2}O_{5} powders, when sintered at 800 °C, 1000 °C and 1200 °C resulted in pellets that were not completely dense [9]. However, preferentially oriented grains were observed at 1000 °C which increased the dipole moment and the dielectric permittivity. Nb_{2}O_{5} produced through sol-gel route and calcined at 600 °C, 800 °C, 900 °C and 1200 °C were powder compacted without sintering, for dielectric measurement [2]. Table 2 provides the comparison of dielectric permittivity values of present study with these previously reported values. The difference in values between the dielectric permittivity and loss of current work and previous works could be attributed to the differences in crystal structure, density, microstructure, presence of a coated electrode, and the thermal history of the samples.

### 4. Conclusions

Niobium ethoxide precursor (\( \text{Nb}_2(\text{OC}_{2}\text{H}_5)_{10} \)) was transformed to various forms of crystalline oxides of niobium at various temperatures and the phase transitions were analyzed using diffraction, spectroscopy and dilatometry. The crystalline Nb_{2}O_{5} changes crystal structure from pseudohexagonal to orthorhombic at 1023 K and finally to monoclinic at 1223 K with increase in crystallinity at 1423 K. The optimisation of sintering conditions resulted in achieving a density close to 95% of the theoretical density resulting in a stable monoclinic crystal structure of Nb_{2}O_{5}. For the first time, the electrical properties of ceramics of the dense monoclinic Nb_{2}O_{5} in a wide frequency and temperature ranges were studied by broadband dielectric spectroscopy. The dielectric constant was found to be around 28 at room temperature and 100 kHz with a minimal loss value of 0.008. It was shown that the electrical properties of Nb_{2}O_{5} ceramics depend on the thermal history of the sample and experimental conditions. The giant increase in the effective dielectric permittivity at low measuring frequencies was attributed to the accumulation of charges at the grain boundaries. The DC conductivity of the ceramic has thermoactivation behavior with an activation energy of 660 meV. Two relaxation processes were revealed, of which the lower-frequency one makes the main contribution to the dielectric response and is connected apparently with inhomogeneous oxygen vacancy conductivity. This relaxation process was described by the Vogel-Fulcher law with a freezing temperature of 380 K.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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