

The Order-Disorder Transition in Bi_2O_3 - Nb_2O_5 Fluorite-Like Dielectrics

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ABSTRACT

An analysis of the microwave dielectric properties showed that the cubic fluorite solid solutions $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Nb}_2\text{O}_5$ ($0.23 \leq x \leq 0.26$), the so-called $\delta\text{-BN}_{\text{SS}}$ Type II, exhibit a high permittivity of 100, but also high dielectric losses ($Q_{xf} = 300$ GHz) and a high temperature dependence of resonant frequency ($\tau_f = -200$ ppm/K). Investigations using x-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that the cubic incommensurate phase undergoes an order-disorder phase transition into a commensurate tetragonal phase at temperatures below 900°C (for $x = 0.25$). The higher degree of ordering in the tetragonal phase reduces the dielectric losses ($Q_{xf} = 1000$ GHz) and changes the sign of the temperature coefficient of resonant frequency ($\tau_f = 100 \cdot 10^{-6}/\text{K}$).

Keywords: Dielectric properties, Niobates, Bi_2O_3 , LTCC, Phase transition

I. INTRODUCTION

The high-temperature bismuth-oxide polymorph that is stable from 730°C up to its melting point at 825°C is known as the δ -modification.^(1,2) This $\delta\text{-Bi}_2\text{O}_3$ has a face-centered cubic (fcc) structure akin to a defect fluorite-type structure with an oxygen sublattice that is only 75% occupied.⁽²⁾ The high concentration of oxygen vacancies results in the high oxygen-ion conductivity of the cubic $\delta\text{-Bi}_2\text{O}_3$.⁽³⁾ In the order for these ceramic to have more applications as solid electrolytes it is necessary to broaden the thermodynamic stability to include lower

temperatures. It is known that the addition of several oxides, e.g., Nb₂O₅, Ta₂O₅, Y₂O₃ and rare-earth oxides, ⁽³⁾ can stabilize the cubic phase. This doping yields different solid solutions based on the δ -Bi₂O₃ crystal structure that have been reported as very good ionic conductors. ⁽⁴⁻⁶⁾ The highest oxide-ion conductivity was found for Bi₂O₃-Nb₂O₅ solid solutions, ⁽³⁾ for a composition that coincides with the minimum concentration of Nb₂O₅ necessary to stabilize the fluorite-type fcc structure. ⁽⁷⁾ Early studies reported the existence of two different cubic forms of δ -Bi₂O₃ solid solutions with Nb₂O₅, the so-called δ -BN_{SS}. The crystal structure of δ -BN_{SS} is much more complicated than its parent fluorite structure. An investigation of δ -BN_{SS} with electron diffraction and high-resolution electron microscopy revealed hitherto unknown superstructures (Type I to Type IV). ^(8, 9) A detailed characterization of the Type II superstructure showed that the modulation vectors of an incommensurately modulated structure as well as the cell parameters of the underlying unit cell vary as a function of the composition. ⁽⁹⁻¹¹⁾ Later studies revealed that δ -BN_{SS} Type II exists in the composition range from 7.6 to 25.0 mol % of Nb₂O₅. ^(8, 11, 12) The synthesis of a single-phase Type-III powder with 25 mol% of Nb₂O₅ was reported for the first time by Ling et al. ⁽¹¹⁾ Based on synchrotron x-ray diffraction and neutron powder diffraction they reported that the crystal structure of the Type-III compound synthesized at 900°C is a superstructure of the fluorite δ -Bi₂O₃ with a tetragonal unit cell ⁽¹³⁾

The sintering behavior, the thermo-mechanical properties and the chemical compatibility of cubic δ -BN_{SS} with silver suggests the possible use of these materials in LTCC (low-temperature co-fired ceramic) technology. LTCC technology is a developing technology for the production of integrated multifunctional electronic modules. Functional ceramic layers and chemically compatible electrodes are combined and co-fired to achieve a robust LTCC module. Because of the complexity of co-firing technology, the ceramic materials involved

must be well understood in terms of their chemical and physical characteristics. The synthesis, sintering and dielectric properties of the cubic δ -BN_{SS} in the microwave frequency (MW) and radio-frequency (RF) ranges were analyzed by Valant et al.⁽¹⁴⁾ The permittivity as well as the dielectric losses measured in the MW frequency range increased with Nb₂O₅ concentration. The temperature coefficient of resonant frequency was found to be highly negative. In the same study a tetragonal Bi₃NbO₇, the so-called Type III, was synthesized in the temperature range from 850 to 880°C. The authors also prepared dense, single-phase Type-III ceramics with 25 mol % of Nb₂O₅ and characterized their dielectric properties. The high permittivity in combination with modest dielectric losses and a low sintering temperature makes this material a candidate LTCC material. For this reason and because of the unusual phase-transformation sequence we engaged in a more detailed investigation of the synthesis and stability of this phase. We determined the temperature stability of the cubic and tetragonal phases for a composition with 25 mol % of Nb₂O₅ and characterized the influence of the phase transformation on the dielectric properties of the δ -BN_{SS}.

II. EXPERIMENTAL

We prepared polycrystalline specimens of the $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Nb}_2\text{O}_5$ composition in the range $0.230 < x < 0.260$ using a solid-state reaction technique. Stoichiometric mixtures of dried reagent-grade oxides (Bi₂O₃, 99.975 %, Alfa Aesar; and Nb₂O₅, 99.9+ %, Alfa Aesar) were homogenized in a mortar with acetone. To ensure accurate heat treatments the furnaces were repeatedly calibrated with an external Pt-Rh thermocouple. The powders were first preheated at 700°C for 10h, and then ground and reheated at 750°C for 5 h. During the low-temperature heat treatment the Bi₂O₃ reacts to form less-volatile Nb compounds and permits additional firing at higher temperatures without significant losses of Bi. The ground and milled powders

were then uniaxially pressed into pellets at ~ 150 MPa and sintered at different temperatures (840, 860 and 950°C) for 10h. The homogeneities of the specimens were examined using XRD and later confirmed with energy-dispersive X-ray microanalysis. The level of porosity was visually estimated from the microstructural images. The x-ray powder diffraction (XRD) was performed with a Bruker AXS D4 Endeavor diffractometer using $\text{Cu}_{K\alpha}$ radiation. The data were collected from $2^\circ < 2\theta < 90^\circ$ with a step of 0.02, a counting time of 4s and variable V12 slits. The microstructural and energy-dispersive x-ray (EDS) analyses of the ceramics were made using a JEOL JXA 840A scanning electron microscope (SEM). The selected-area electron diffraction (SAED) patterns and high-resolution transmission electron microscope (HRTEM) images were obtained using a JEOL 2010F transmission electron microscope (TEM).

The MW dielectric properties were characterized using the closed air-cavity method with a network analyzer (HP 8719C). The permittivity and Q -values were calculated at the resonant conditions (TE_{018} mode) from the S_{11} -reflection coefficients, as proposed by Kajfez et al.⁽¹⁵⁾ To measure the temperature dependence of resonant frequency the test cavities were placed into a temperature-controlled chamber and the dielectric properties were analyzed in the temperature range from 20 to 60°C. The RF measurements were made from 1 kHz to 1MHz on In-Ga plated pellets using a high-precision LCR meter (Agilent 4824A). The temperature dependence of the dielectric properties was measured in the range from -130 to 150°C in a temperature-controlled (with copper-constantan; T-type thermocouple) chamber (Delta Design, Delta 9039).

III. RESULTS

Preliminary experiments involved the firing of the reaction mixture with 25 mol % of Nb₂O₅ at three different temperatures: 700, 860 and 950°C. The x-ray powder diffraction pattern of the sample fired at 950°C for 10h is shown in **Fig 1**. The intense peaks correspond to those of the cubic fluorite-like phase obtained by Zhou et al. ⁽⁸⁾ for the same composition. The additional, i.e., satellite, reflection of low intensity in **Fig 2** indicate a superstructure. The satellite reflections are present at the same positions as those reported in the literature, which confirms the similar incommensurate modulation of Type II, as described by Miida et al. ⁽¹⁰⁾

The firing of the same composition at a lower temperature (860°C) also resulted in a single-phase sample. However, a comparison of the x-ray patterns reveals significant differences between the samples fired at 860°C and those fired at 950°C. It is clear from **Fig 1** that the most intense diffraction peaks appear at approximately the same 2θ angles, but in the case of the sample fired at 860°C they exhibit a very noticeable tetragonal splitting, as already reported by Valant et al. ⁽¹⁵⁾ In addition, as it is clear from **Fig 2**, a whole new set of satellite reflections is found at positions that are different to those in the cubic phase previously described. The low-temperature firing (700°C) of the oxides resulted in a cubic phase, which according to the x-ray pattern is identical to that obtained after firing at 950°C.

A further comparison of the samples obtained after firing at three different temperatures was made with SAED. Apart from the tetragonal distortion (not visible to the naked eye) **Fig 3** reveals additional differences between the cubic and tetragonal phases. The satellite reflections at $\sim 0.37[220]$ that indicate the incommensurate modulation of the cubic phase are not present in the SAED patterns of the sample fired at 860°C. Instead, additional reflections

are visible at $1/3[200]$, $1/3[020]$ and $1/7[002]$, which reveal the presence of the $3 \times 3 \times 7$ -type commensurate superstructure, the existence of which was already reported by Ling et al.⁽¹³⁾

Another detailed investigation of the phase formation was performed by firing the reaction mixture at various temperatures between 700 and 950°C for different lengths of time up to 120h. The experiments showed that the tetragonal phase with the $3 \times 3 \times 7$ superstructure appears below 900°C and above 780°C. The firing time to obtain the single-phase tetragonal sample, however, varies significantly with the temperature. Firing at 800°C for 15h, for instance, yields a sample in which both cubic and tetragonal phases were detected. In order to achieve equilibrium, i.e., a single-phase tetragonal sample, a prolonged annealing time of 60h is required. From experiments performed to determine the thermal stability of the tetragonal Bi_3NbO_7 we noticed that during the synthesis from the reagent powders the cubic phase is formed first, and then if the right annealing conditions are used it transforms into the tetragonal phase.

The previously described SAED patterns and the phase contrast visible on the HRTEM images shown in **Fig 4** reveal periodicity in the tetragonal phase that is a rational multiple of the unit cell of the underlying fluorite structure. This indicates that the tetragonal phase in contrast to the cubic phase, exhibits a commensurate superstructural ordering. This means that the transition from cubic to tetragonal phase in the case of Bi_3NbO_7 is a certain kind of disorder-order or incommensurate-commensurate phase transition. Such a phase transition exhibits kinetics that is temperature dependent. Therefore, at higher temperatures, closer to the upper temperature limit (900°C) of its thermodynamic stability, the formation of the tetragonal (ordered) phase is much more rapid than at the lower temperatures (700°C), where even annealing for 120 h was not sufficient to obtain ordering. However, due to the

thermodynamic facts governing disorder-order transitions ⁽¹⁶⁾ we assume that the ordered tetragonal Bi_3NbO_7 , the so-called Type III, is also thermodynamically stable at lower temperatures, but its formation is hindered by slow kinetics.

Furthermore, on the basis of our experimental work we established that the tetragonal (ordered) Type-III structure is not limited to the composition with 25 mol % of Nb_2O_5 . Using XRD analysis we found that the tetragonal-ordered phase exists in an extended concentration range around Bi_3NbO_7 . A detailed investigation of the homogeneity range of the Type III is beyond the scope of this paper and will be published elsewhere. However, the analysis of the dielectric properties of the whole homogeneity range will be reported here.

In the scope of this investigation we compared the dielectric properties of densely sintered ceramics (**Fig. 5**) of the cubic and tetragonal BN_{ss} modifications in the compositional range from 23 to 26 mol % of Nb_2O_5 . As can be seen from the measured data in the MW frequency range plotted in **Fig. 6a** the permittivities of the tetragonal samples are around 90, but they increase slightly with an increase in the Nb_2O_5 concentration, which is typical for BN_{ss} ¹⁴. The same trend can be seen for the cubic modification. Somewhat higher permittivities around 100, can be attributed to the slightly lower degree of residual porosity due to the higher sintering temperature. According to these results, superstructural ordering does not significantly affect the values of the permittivities. These results are to be expected since the ion polarizability and the mole volume of the tetragonal and cubic crystal structures do not change significantly during the order-disorder phase transition.

However, we found that the ordering profoundly affects the dielectric losses in these fluorite-based structures, in accordance with the studies reported for other crystal-structure

families.⁽¹⁶⁾ In the case of the cubic samples the Q_{xf} values are low, around 300 GHz, and a slight decrease is observed with the increase in Nb_2O_5 concentration, which is consistent with previous observations.⁽¹⁴⁾ A higher degree of ordering in the samples with the tetragonal-ordered crystal structure causes a significant decrease in the dielectric losses. The Q_{xf} values increase with Nb_2O_5 concentration from 550 GHz for the composition with 23 mol % of Nb_2O_5 , until it reaches a maximum value of 1000 GHz at 26 mol% of Nb_2O_5 .

Superstructural ordering has the most profound effect on the temperature coefficient of resonant frequency (τ_f). The cubic phase exhibits a negative τ_f , which with the increase in the concentration of Nb_2O_5 continues the trend from $\delta\text{-BN}_{\text{SS}}$ Type II.⁽¹⁴⁾ With the phase transition from the cubic structure to the ordered tetragonal structure the τ_f becomes positive and further increases with the increase in Nb_2O_5 concentration within the homogeneity range of the tetragonal structure. The maximum value of +125 ppm/K was measured for the composition with 26 mol % of Nb_2O_5 . We believe that such an abrupt change in the τ_f caused by the structural phase transition can be attributed to the changes in the oxygen sublattice that accompany the superstructural ordering. In this system the changes in the oxygen sublattice during the formation of the superstructure can be associated with the redistribution of the oxygen vacancies. The redistribution or the change in the modulation of the oxygen sublattice can be induced by the changes in the charge distribution and the chemical potentials due to the cation ordering.⁽¹⁷⁾ This reasoning is supported by the RF measurements of the frequency and the temperature dependence of the permittivity. The tetragonal phase shows a significantly higher high-temperature permittivity at 1 kHz than the cubic phase of the same composition. Because the concentration of vacancies is in both cases the same the increase is due to the increased mobility of free charge carriers, which in the fluorite-like structure is related to the oxygen-vacancy distribution or the modulation of the oxygen sublattice.

IV. CONCLUSIONS

Our investigations of the microwave dielectric properties of the high-temperature cubic modification (Type II) showed that these ceramics exhibit a high permittivity (100); however, due to the incommensurate, modulated structure the dielectric losses are too high and the temperature coefficient of the resonant frequency is too negative for dielectric applications. We have shown that the incommensurate phase undergoes an order-disorder phase transition into a commensurately modulated crystal structure (Type III) at temperatures below 900°C. Studies of the influence of the superstructural ordering showed that in the tetragonal modification the dielectric losses are reduced due to a higher level of ordering, and the temperature coefficient of the resonant frequency gains a positive value, most probably due to the modifications in the oxygen sublattice. The investigations showed that the tetragonal modification exhibits good dielectric properties and that it is stable and can be sintered in a temperature range below 900°C, which is in accordance with the requirements for LTCC modules. This means that the tetragonal phase represents an interesting candidate for high-permittivity glass-free LTCC dielectrics.

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FIGURE CAPTIONS

Fig. 1. X-ray powder-diffraction pattern of the cubic fluorite-like and tetragonal fluorite-like forms with the composition of 25mol % of Nb₂O₅ fired at 950 °C for 10 h and 860 °C for 10 h.

Fig. 2. X-ray powder superstructural diffraction peaks on a larger scale with the composition of 25 mol % of Nb₂O₅ fired at 950 °C and 860 °C for 10 h.

Fig. 3. SAED patterns collected from the sample with 25mol % of Nb₂O₅ fired at a) 950 °C and b) and c) 860°C.

Fig. 4. HRTEM images of the sample with 25mol% of Nb₂O₅ a) cubic phase and b) ordered tetragonal phase.

Fig. 5. SEM image of chemically etched microstructure of the composition with 25 mol % of Nb₂O₅ fired at 860 °C.

Fig. 6 Microwave dielectric properties of the tetragonal-ordered phase (●) and cubic-incommensurate phase (▲): (a) permittivity; (b) dielectric losses; (c) temperature coefficient of resonant frequency

Fig. 7. RF temperature dependence of permittivity and dielectric losses of the tetragonal-ordered phase (—) and cubic-incommensurate phase (—) of the composition with 26 mol % of Nb₂O₅ (measured at 1kHz).

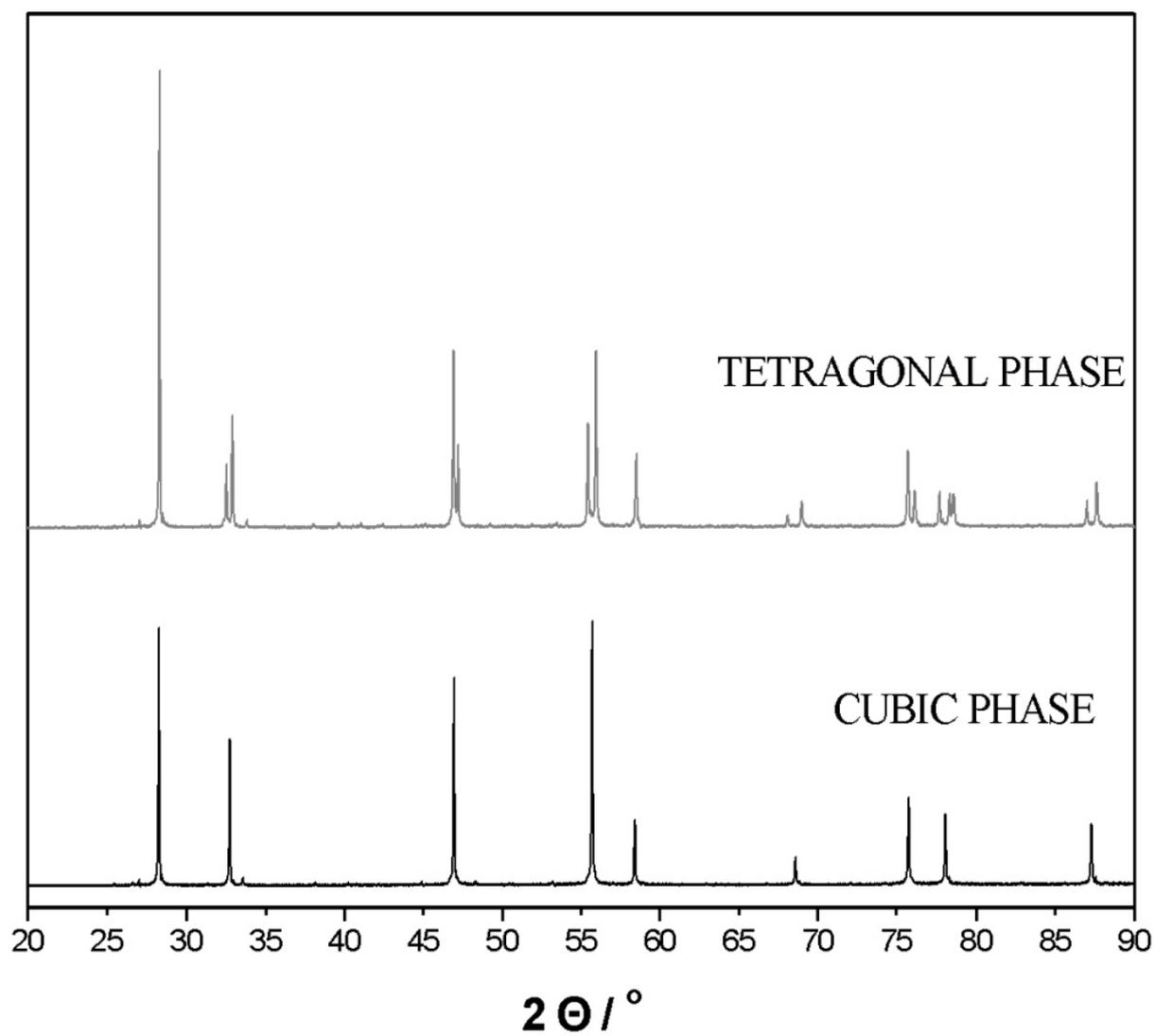


Fig. 1.

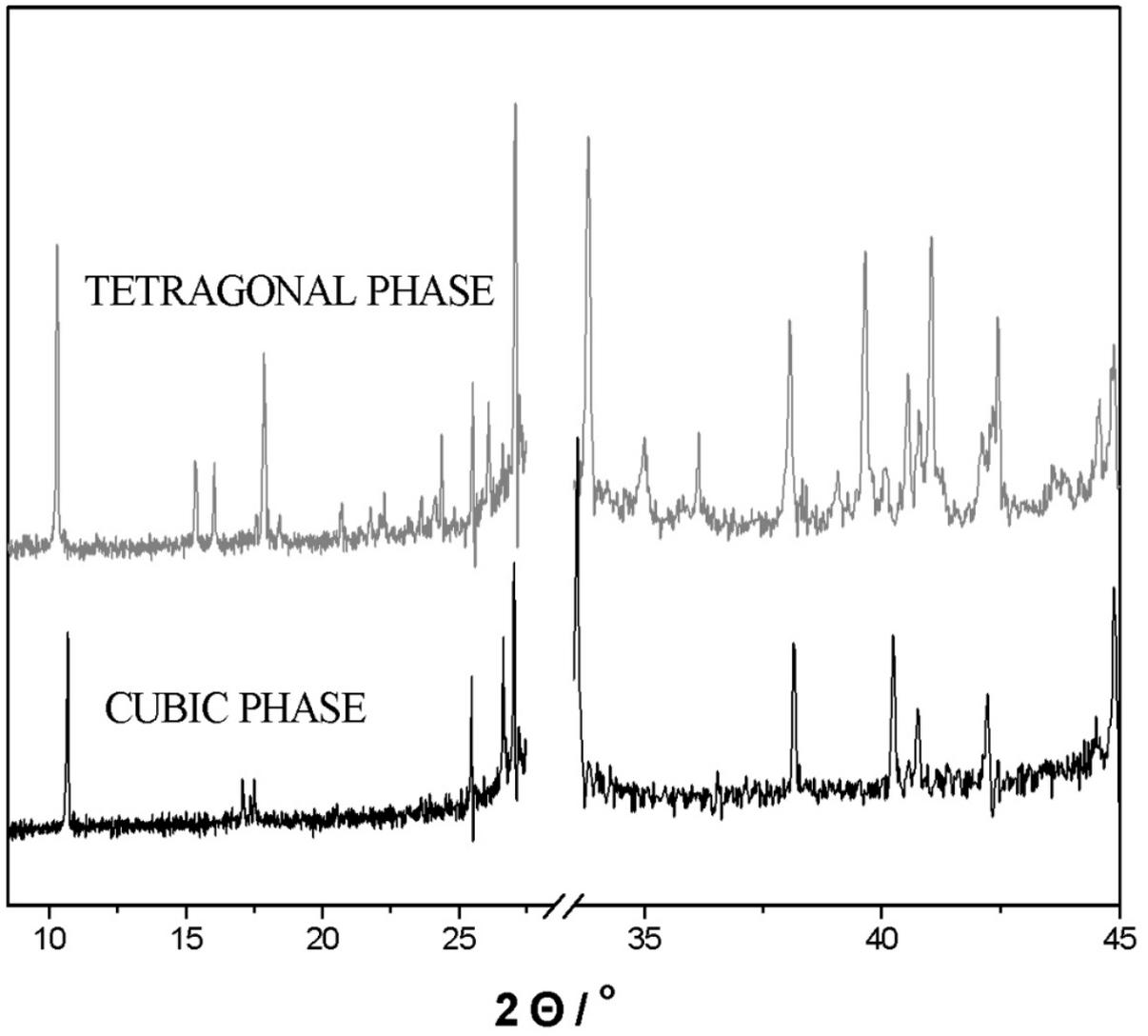


Fig. 2

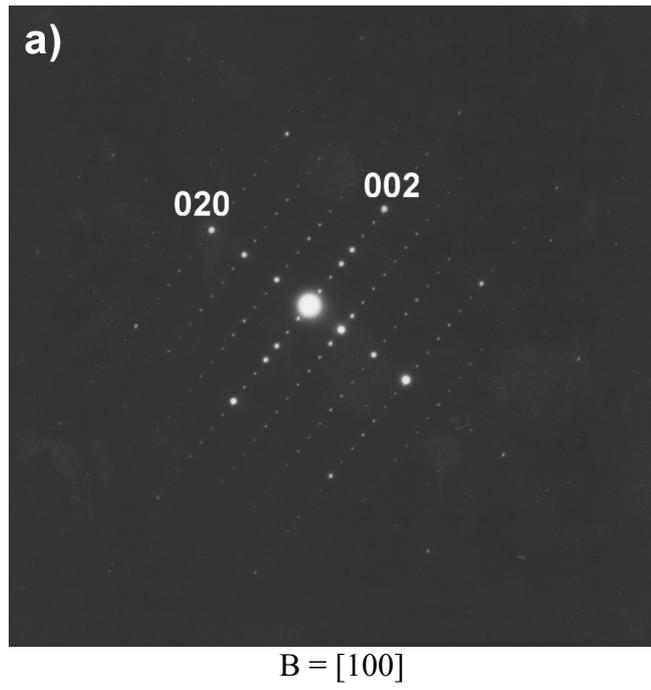
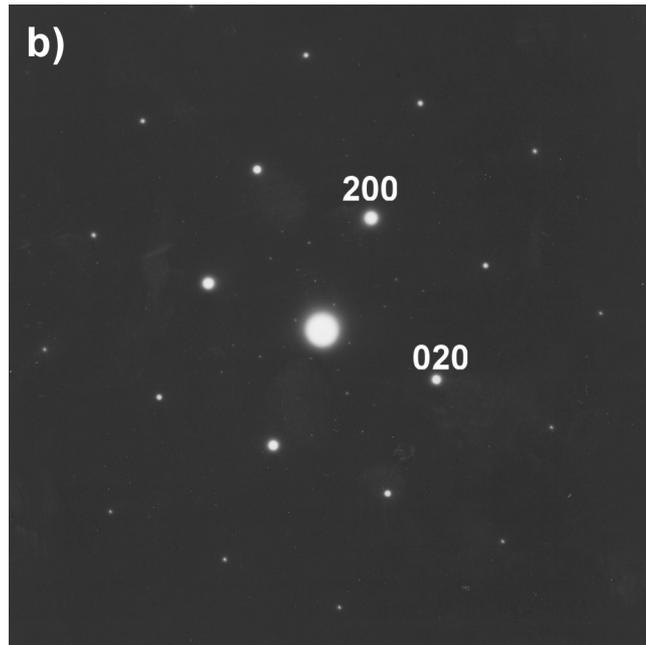


Fig 3a.



$B = [001]$

Fig. 3b.

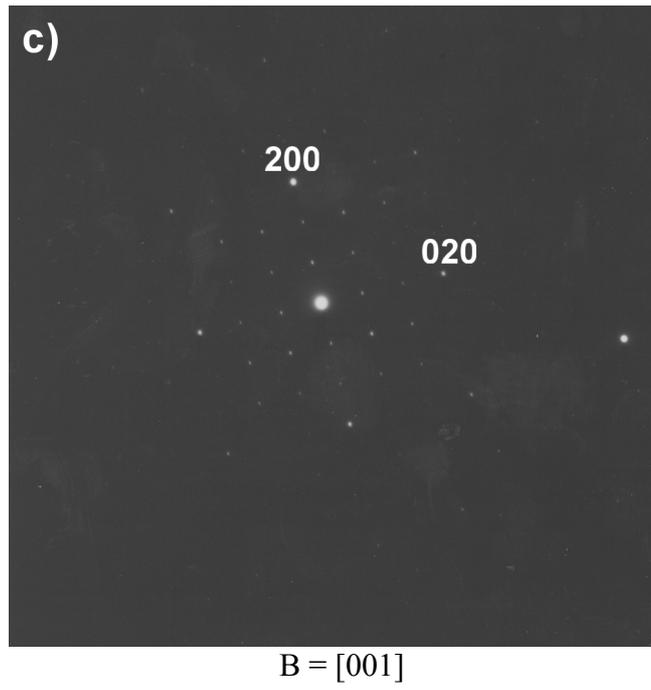


Fig. 3c.

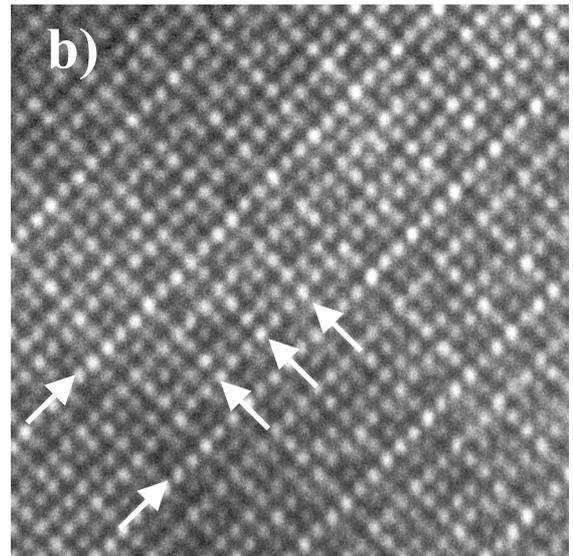
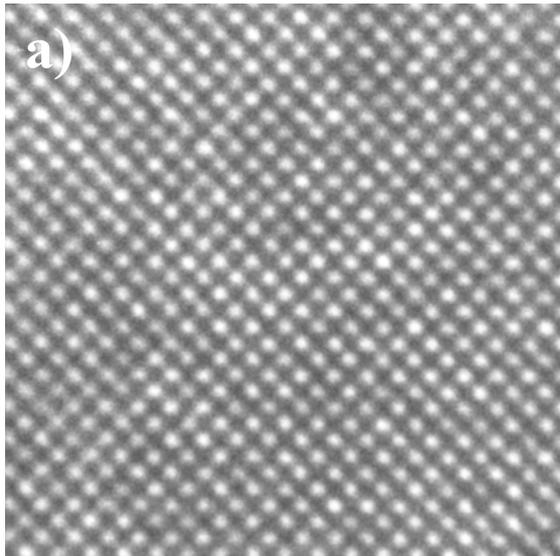


Fig. 4.

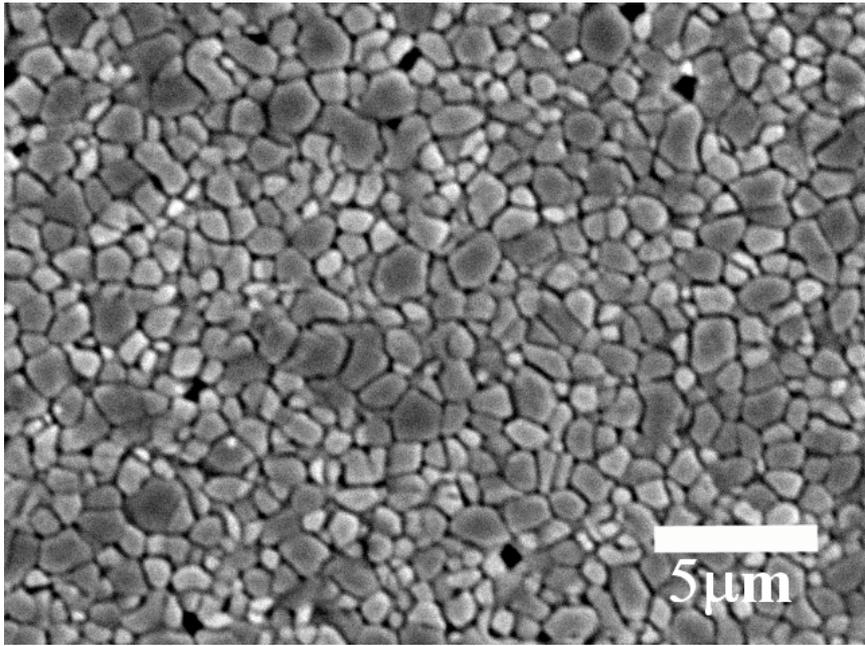


Fig.5.

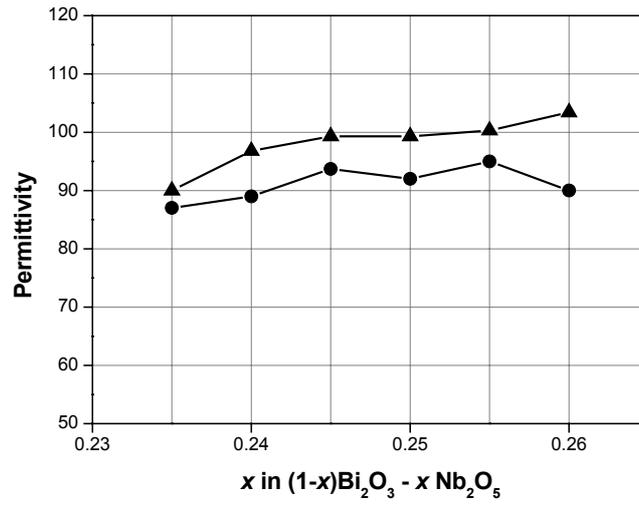


Fig. 6a.

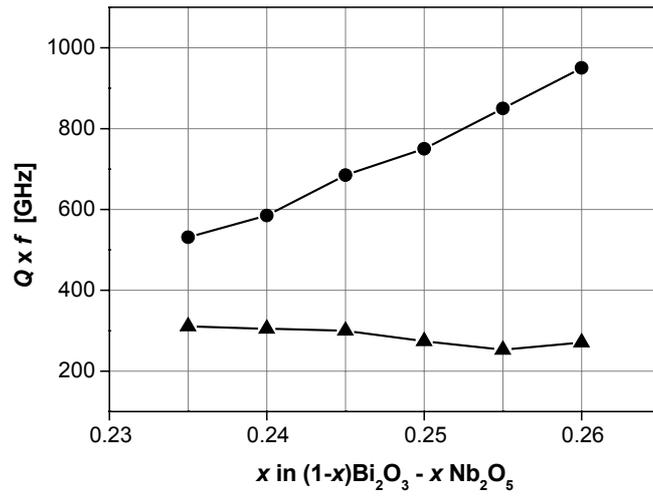


Fig. 6b.

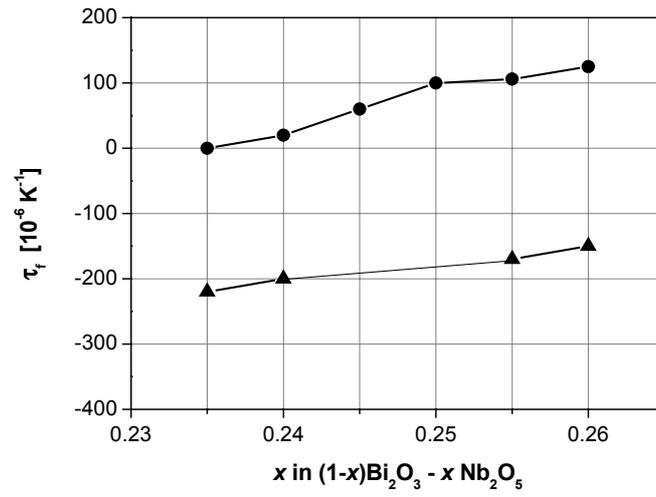


Fig. 6c.

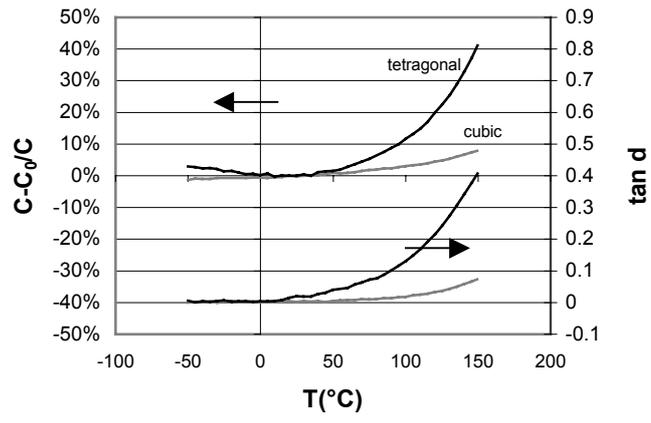


Fig. 7.