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Dielectric properties and phase transitions of $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type dielectrics

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Abstract

A study of $Bi_3Nb_{1-x}Ta_xO_7$ ceramics revealed that these solid solutions undergo an incommensurate-to-commensurate, $Fm3m \Leftrightarrow I\bar{4}m2$, phase transition. An analysis of the microwave dielectric properties showed that an increase of x for the $Bi_3Nb_{1-x}Ta_xO_7$ results in a slight decrease in the permittivity and an increase in the $Q \times f$ values for both crystal modifications. However, the order–disorder phase transition at temperatures below 900 °C reduces the dielectric losses: the $Q \times f$ values for the commensurate-tetragonal $Bi_3Nb_{1-x}Ta_xO_7$ samples are in the range 300–400 GHz higher than the values of the incommensurate-cubic analogues. In addition, the phase transition induces positive values of the temperature coefficient of resonant frequency (τ_f) for the commensurate-tetragonal $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type dielectrics.

Keywords: LTCC; Dielectric properties; Niobates

1. Introduction

Investigations of the stabilization by doping of the high-temperature δ-Bi_2O_3 (thermodynamically stable from 729 to 825 °C)[1] phase were initiated because it crystallizes in the face-centred-cubic (fcc) crystal structure, akin to the defect fluorite-type unit cell.[2] Due to a highly disordered defect fluorite structure with an oxygen sublattice that is 75% occupied[2] the interstitial vacancy transport[3] of oxygen leads to an exceptionally high conductivity. One of the best-known solid-state oxygen-ion conductors is found in the Bi_2O_3–Nb_2O_5 and Bi_2O_3–Ta_2O_5 systems.[4] Phase investigations showed that δ-Bi_2O_3 was found in the largest compositional range in each system.[5–7]

A study of the fluorite-like homogeneity region in the Bi_2O_3–Nb_2O_5 system revealed that it extends to 26 mol% Nb_2O_5.[8] Crystallographic studies determined this phase as being 3 + 3D incommensurately modulated,[9] with an underlying average fluorite unit cell that has the space-group symmetry $Fm3m$[7,9,10]; it is known in the literature as Type II. Our initial investigation of the formation characteristics of the incommensurate-cubic phase indicated that this phase undergoes a disorder–order phase transition to the commensurate-tetragonal phase at temperatures below 900 °C.[11] The structural model proposed for this lower-temperature modification is the tetragonal fluorite-based unit cell with the $I\bar{4}m2$ space group.[12] The tetragonal modification is described as an ordered 3 × 3 × 7 superstructure of the fluorite type δ-Bi_2O_3 and it is known as the Type III.

The δ-Bi_2O_3-related solid solution, labelled as Type II (extends from Bi_9TaO_{16} to Bi_3TaO_7)[6,7,13] in the Bi_2O_3–Ta_2O_5 system, is isomorphous with the analogue in the Bi_2O_3–Nb_2O_5 system. However, in contrast to Bi_3NbO_7, for the composition Bi_3TaO_7 only one temperature modification of the fluorite-like phase was found, the so-called Type II, with an incommensurate-cubic crystal structure. A refinement of structures in the Bi_2O_3–Ta_2O_5 system revealed that the labelled Type II* ($Bi_7Ta_3O_{18}$) and Type III ($Bi_4Ta_2O_{11}$) are not fluorite-related structures.[14] A recent synthesis involving mechanochemical activation showed that a fluorite-like solid solution of the cubic $Bi_3Nb_{1-x}Ta_xO_7$ exists across the whole range of compositions, $0 \leq x \leq 1$.[13]

In addition to the most frequently considered use of δ-Bi_2O_3 solid solutions, i.e., as a solid electrolyte, they were also proposed for use in low-temperature co-fired ceramic (LTCC) technology as a high-permittivity glass-free dielectric layer.[15]

On the basis of our initial investigations,[11] which indicated that the incommensurate-cubic Bi_3NbO_7 phase undergoes a phase transition to the commensurate-tetragonal, lower-temperature modification,[11] we began this investigation and

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proved that an order–disorder phase transition occurs for the incommensurate-cubic $Bi_3Nb_{1-x}Ta_xO_7$ solid solution. Therefore, the aim of this paper is to present a study of the dielectric properties of fluorite-type $Bi_3Nb_{1-x}Ta_xO_7$ phases as a function of the phase transition in the MW frequency range. In addition, we investigated the effect of partially substituting Nb with Ta on the dielectric properties of $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type dielectrics.

2. Experimental

We prepared polycrystalline specimens of the $Bi_3Nb_{1-x}Ta_xO_7$ compositions, for $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, using a solid-state reaction technique. Stoichiometric mixtures of dried reagent-grade oxides (Bi_2O_3, 99.975%, and Nb_2O_5, >99.9%, Alfa Aesar) were homogenized in a mortar with ethanol. The powders were first preheated at 750 °C for 10 h, and then ground and reheated twice at 800 °C for 5 h. During this heat treatment the Bi_2O_3 reacts to form Nb compounds and this permits additional firing at higher temperatures without significant losses of Bi. The calcinated powders were milled and then uniaxially pressed (at ~150 MPa) into pellets with a diameter of 10 mm and thickness varying from 3 to 4 mm. The sintering temperatures used were 880 and 950 °C, selected according to the thermal stability of the phases.[8] The sintering times were chosen as 15, 80 and 250 h, after a consideration of the kinetics,[8] in order to achieve single-phase materials. The relative density of all the samples was estimated from the microstructure to be >97%. X-ray powder diffraction (XRD) (Bruker AXS D4 Endeavor) was used to determine the phase purity and the homogeneities of the specimens.

The MW dielectric properties were characterized using a network analyzer (HP 8719C) and the closed air-cavity method. The permittivities and Q-values were calculated at the resonant conditions ($TE_{01\delta}$ mode at around 4 GHz) from the S_{11}-reflection coefficients, as proposed by Kajfez and Hwan.[16]

3. Results

Solid-state synthesis of the compositions $Bi_3Nb_{1-x}Ta_xO_7$, where $x = 0$, 0.2, 0.4 and 0.6 at 950 °C for 15 h resulted in single-phase materials. The XRD powder-diffraction patterns shown in Fig. 1 for the samples with $x = 0.2$, 0.4, fired at 950 °C for 15 h revealed an isostructural symmetry with the pattern of a fluorite-type Bi_3NbO_7 ($x = 0$), which crystallizes in the cubic $Fm3m$ space group.[10] These experimental results from Fig. 1 are in accordance with literature claims about the existence of the $Bi_3Nb_{1-x}Ta_xO_7$ solid solution.[10]Solid-state synthesis of the same compositions $Bi_3Nb_{1-x}Ta_xO_7$, $x = 0$, 0.2, 0.4, and 0.6, at the lower temperature of 880 °C and the sintering time of 80 h also resulted in a single-phase sample. However, as shown in Fig. 1, XRD patterns of $Bi_3Nb_{1-x}Ta_xO_7$, $x = 0.2$, 0.4, sintered at 880 °C have a completely different form than the one resulting from the treatment at 950 °C. The intense diffraction lines of these samples match the indexing of an isostructural Bi_3NbO_7 compound that crystallizes in the tetragonal $I\bar{4}m2$ space group.[12]

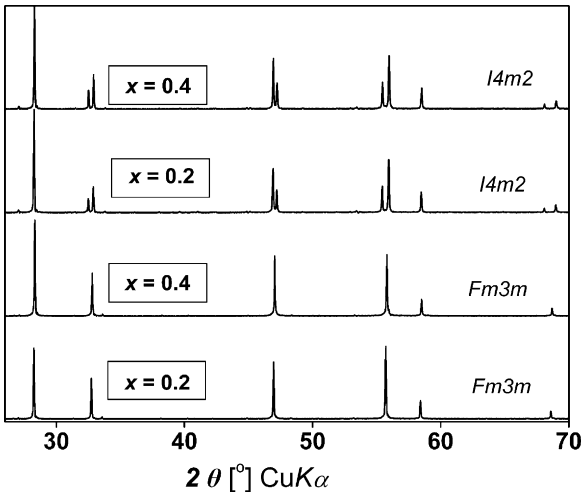

Fig. 1. X-ray powder-diffraction pattern comparison on the level of the prototype cell. $Bi_3Nb_{1-x}Ta_xO_7$ compositions with $x = 0.2$, 0.4, fired at 950 °C for 15 h with the cubic fluorite-like form in contrast to the same compositions fired at 880 °C for 80 h with tetragonal fluorite-like form.

Furthermore, a detailed comparison (Fig. 2) of the X-ray superstructural diffraction-peak patterns of cubic $Bi_3Nb_{1-x}Ta_xO_7$ samples, $x = 0.2$, 0.4, fired at 950 °C for 15 h, reveals that satellite reflections of low intensity are present at the same positions as those reported for the composition $x = 0$. This confirms similar incommensurate modulations of the cubic $Bi_3Nb_{1-x}Ta_xO_7$, $x = 0.2$, 0.4, samples, as described by Miida and Tanaka.[9] An analogous situation is presented in the same Fig. 2 for the commensurate $3 \times 3 \times 7$ superstructural identity of the tetragonal $Bi_3Nb_{1-x}Ta_xO_7$, $x = 0.2$, 0.4 samples, which were obtained at 880 °C with the composition of $x = 0$.[12]

Since Figs. 1 and 2 reveal structural identity on the level of the prototype cell and on the level of the superstructure modulation it is evident that the incommensurate-cubic

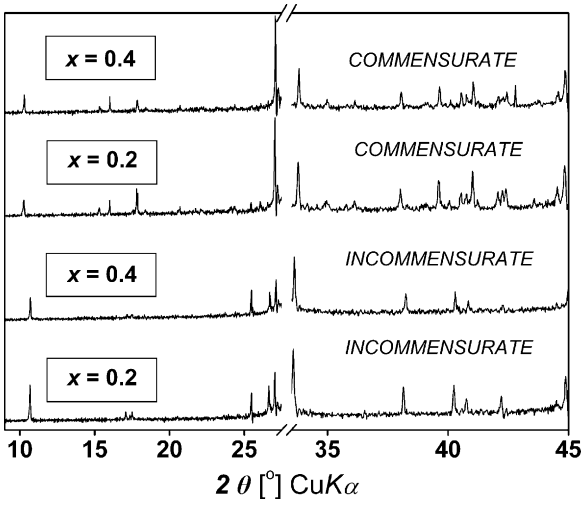

Fig. 2. X-ray powder superstructural diffraction pattern comparison of $Bi_3Nb_{1-x}Ta_xO_7$ compositions with $x = 0.2$, 0.4, fired at 950 °C for 15 h with the incommensurate-cubic fluorite-like form with the same compositions fired at 880 °C for 80 h with the commensurate-tetragonal fluorite-like form.

$Bi_3Nb_{1-x}Ta_xO_7$ undergoes a certain kind of disorder–order phase transition below 900 °C to the commensurate-tetragonal $Bi_3Nb_{1-x}Ta_xO_7$. Furthermore, on the basis of the experimental work we established that the commensurate-tetragonal $Bi_3Nb_{1-x}Ta_xO_7$ homogeneity range exists and it is thermodynamically stable below 900 °C. A detailed investigation of the synthesis and stability of the commensurate, tetragonal $Bi_3Nb_{1-x}Ta_xO_7$ homogeneity range as well the crystallographic and kinetic aspects of the phase transition will be the focus of a special study. However, the analysis of the dielectric properties as a function of the disordered–order phase transition of $Bi_3Nb_{1-x}Ta_xO_7$ will be reported here.

As can be seen from the measured data in the MW frequency range plotted in Fig. 3(A) the permittivities of the incommensurate-cubic phase (▲) and the commensurate-tetragonal phase (●) show a slight decrease with the increase in x of the $Bi_3Nb_{1-x}Ta_xO_7$. The permittivities of the incommensurate-cubic phases (▲) decrease from a value of 102 for the composition with $x=0$, to 74 for the composition with $x=0.6$. The effect of decreasing the permittivity with increasing x can also be seen in the case of the commensurate-tetragonal phases (●), where the values change from 89 for the composition with $x=0$, to 65 for the composition with $x=0.6$.

As the processing of both modifications yielded dense ceramics, the $Q\times f$ values can therefore be ascribed to changes in the intrinsic dielectric losses. The possibility of achieving higher $Q\times f$ values, comparable to Bi_2O_3–Nb_2O fluorite-like dielectrics, was the part of the study involving tailoring of the dielectric properties, and also the reason for studying the influence of a partial substitution of Nb with Ta. The trend for both phases can be seen in Fig. 3(B). In the case of the incommensurate-cubic (▲) samples the $Q\times f$ values increase from a value of 300 GHz for the composition with $x=0$ up to 663 GHz for the composition with $x=0.6$. As in the case with Bi_2O_3–Nb_2O fluorite dielectrics, where an incommensurate-commensurate phase transition profoundly affects the dielectric losses,[11] we found the same trend for Nb with Ta-substituted phase analogues. The $Q\times f$ values of the $Bi_3Nb_{1-x}Ta_xO_7$ samples for the incommensurate-cubic phase (▲) are much lower compared to the commensurate-tetragonal phase (●) (Fig. 3(B) samples. The $Q\times f$ values for the commensurate-tetragonal phase (●) samples increase from 676 GHz, for the composition with $x=0$, up to 1150 GHz, for the composition with $x=0.6$, which is consistent with previous observations in similar systems.[11,15]

The phase transition of the $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type dielectrics has a most profound effect on the temperature coefficient of resonant frequency (τ_f). The incommensurate-cubic phase (▲) samples have negative values of τ_f, which are found around $-100\,ppm\,K^{-1}$ (Fig. 3(C)). These negative values change with the phase transition into the commensurate-tetragonal phase to become positive values. The values of τ_f for the commensurate-tetragonal phase (●) samples vary with x from 88 to 2 $ppm\,K^{-1}$. These values can be useful for LTCC applications and a detailed optimisation of τ_f as a function of processing conditions is currently in progress.

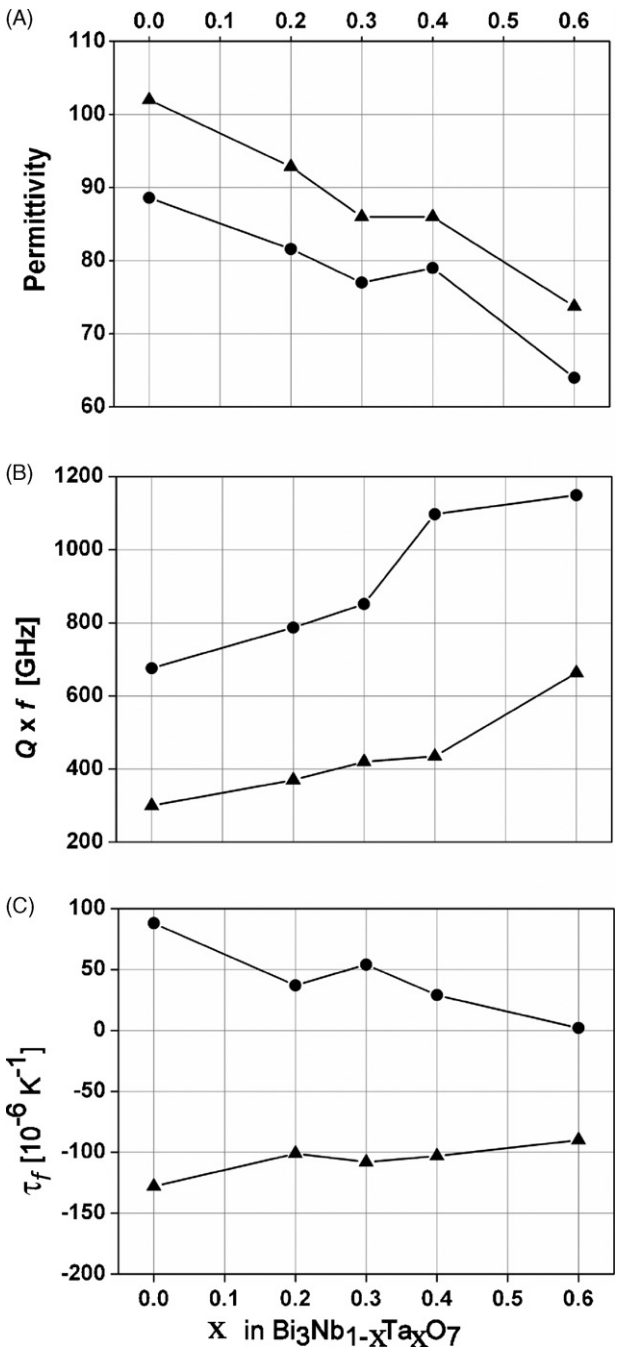

Fig. 3. Microwave dielectric properties of the commensurate-tetragonal phase (●) and incommensurate-cubic phase (▲): (A) permittivity; (B) dielectric losses; (C) temperature coefficient of resonant frequency.

4. Conclusions

Our measurements performed in the microwave frequency region for the high-temperature incommensurate-cubic $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type modification showed that an increase in x results in a slight decrease in the permittivity (values around 90) and an increase in the $Q\times f$ values. However, due to the incommensurately modulated structure the temperature coefficient of resonant frequency (τ_f) values of these samples were negative. We have furthermore shown that at a temper-

ature of 880 °C the low-temperature commensurate-tetragonal form of the $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type modification is stable.

Studies of the influence of the superstructural ordering showed that in the commensurate-tetragonal modification the dielectric losses are reduced due to a higher degree of ordering and the temperature coefficient of resonant frequency has positive values, most probably due to modifications of the oxygen sublattice. Furthermore, it was shown that the commensurate-tetragonal modification exhibits interesting dielectric properties and can be sintered to form dense ceramics below 900 °C, which is in accordance with the requirements for LTCC modules. This makes the commensurate-tetragonal $Bi_3Nb_{1-x}Ta_xO_7$ fluorite-type material an interesting candidate for high-permittivity glass-free LTCC dielectrics.

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