

**Permittivity Boosting in “Yellow” (Nb + In) Co-doped TiO₂**

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ARTICLE

Permittivity boosting in “yellow” (Nb + In) co-doped TiO₂

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Unusual effects of post annealing on optical and dielectric properties of (Nb_{0.5}In_{0.5})_{0.01}Ti_{0.99}O₂ (NITO-1.0%) are reported in the present study. The post-annealing performed under embedding in Al₂O₃ powder changes the color of a NITO-1.0% single crystal from black to yellow. Furthermore, the apparent increase in the relative permittivity due to the Maxwell-Wagner-Sillars effect, on the order of 10⁴, observed in the as-synthesized NITO-1.0% completely disappears after the post-annealing to reveal an intrinsic enhancement of dielectric response due to the co-doping of Nb and In. The relative permittivity of the post-annealed NITO-1.0% uniformly increases by approximately 120 from the original value of pure-TiO₂ over a wide temperature range from 4.2 K to room temperature. A temperature dependence of permittivity in the post-annealed NITO-1.0% shows behavior that is qualitatively identical to that of pure TiO₂, indicating that the co-doping gives rise to an additional dielectric response in TiO₂, probably through creation of defect complexes with large polarizability. The polarizability of the defect complex is estimated to be two hundred times greater than that of Ti⁴⁺, giving a new insight for the design of novel dielectric materials with large permittivity by means of complex defect engineering.

Introduction

To meet increasing demands for miniaturization, reliability improvement, and higher energy density of capacitors, much effort has been devoted to enhance dielectric permittivity of insulating materials.¹⁻⁶ A conventional approach to develop high-permittivity dielectric materials is to use a ferroelectric phase transition, around the transition temperature of which the dielectric permittivity divergently increases due to growth of polarization fluctuation. In BaTiO₃, a well-known perovskite-type ferroelectric material, for instance, relative permittivity ϵ' reaches approximately 10,000 around the transition temperature, thus leading to an opportunity to develop small capacitors with large capacitance.⁷ In ferroelectric materials, however, the dielectric response generally changes significantly by application of an electric field to limit stable operations of capacitors in electric devices. A strong temperature dependence of the permittivity in ferroelectric materials is disadvantageous for the development of capacitors with excellent temperature stability.

An alternative way to improve the dielectric response is via the Maxwell-Wagner-Sillars effect, in which extremely large permittivity can be obtained due to spatial inhomogeneity in electric conductivity.⁸ A typical example can be found in CaCu₃Ti₄O₁₂ (CCTO), whose relative permittivity reaches as high as an order of 10⁴.⁹⁻¹¹ In the case of CCTO, a special arrangement of insulating grains and conductive grain boundaries results in a situation like a barrier layer capacitor that induces an

apparently huge permittivity.¹² Depletion layers at interfaces between a semiconducting material and electrodes also give rise to the Maxwell-Wagner-Sillars-type apparent permittivity.¹³ In these cases, however, bias voltage exerts a serious influence on the dielectric response, and a dielectric relaxation takes place in a relatively low-frequency range, limiting their practical application.¹⁴

Hu et al. recently reported that co-doping of heterovalent Nb⁵⁺ and In³⁺ to a rutile-type TiO₂ creates unique defect complexes with large polarizability, termed electron-pinned defect-dipoles, which induce huge permittivity of the order of 10⁴.¹⁵ Although this result proposed a new concept to boost the permittivity with defect engineering, and thereby attracted considerable attention,¹⁶⁻²¹ follow-up studies have suggested an extrinsic contribution of the Maxwell-Wagner-Sillars effect due to grain boundaries and/or sample-electrode interfaces to allow the large permittivity.^{22,23} On the other hand, dielectric measurements on Nb+In co-doped TiO₂ single crystals at cryogenic temperatures have clarified that a severalfold enhancement of permittivity still remains, even when conductive carriers freeze at sufficiently low-temperatures to suppress the Maxwell-Wagner-Sillars effect.^{23,24} This discovery has suggested the possibility that the electron-pinned defect-dipole functions as an intrinsic "permittivity booster", even though the enhancement is not as great as initially expected.

Herein, we demonstrate an intrinsic enhancement of permittivity in a post-annealed (Nb_{0.5}In_{0.5})_{0.01}Ti_{0.99}O₂ (NITO-1.0%) at elevated temperatures up to room temperature. The post annealing in Al₂O₃ powder has been found to change the color of as-synthesized samples from black to yellow, to indicate disappearance of thermally excited carriers that give rise to the Maxwell-Wagner-Sillars-type dielectric response. The post-

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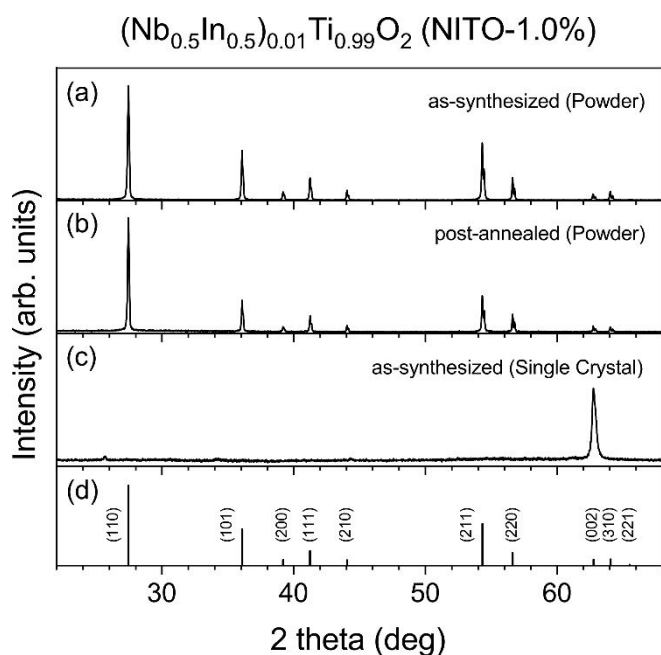


Figure 1. Powder x-ray diffraction patterns of (a) the as-synthesized and (b) the post-annealed NITO-1.0% crushed polycrystallines observed at room temperature. Panel (c) shows the x-ray diffraction patterns of the as-synthesized single crystal with (001) wide surfaces, which was used in the present experiments. The calculated pattern for the pure TiO_2 of rutile-type is presented in panel (d).

annealed NITO-1.0% still shows significantly enhanced permittivity, which is approximately two times larger than that of the pure TiO_2 , over a wide temperature range from 4.2 K to room temperature, although the Maxwell-Wagner-Sillars effect completely vanishes. Our work suggests that co-doping of Nb^{5+} and In^{3+} creates highly polarizable defect complexes in a matrix to improve the dielectric response of TiO_2 . The present discovery paves the way for boosting the dielectric permittivity through defect engineering.

Experimental

Single crystals of NITO-1.0% were grown by a floating zone method with an optical furnace FZ-T-4000-H-I-V (Crystal Systems) equipped with a single ellipsoidal gold-plated mirror. Polycrystalline rods used for the crystal growth were synthesized by sintering a pressed stoichiometric mixture of TiO_2 (99.99%, Furuuchi Chemical), In_2O_3 (99.9%, Furuuchi Chemical), and Nb_2O_5 (99.99%, Sigma-Aldrich) powders at 1673 K for 10 h. The single crystals were then sliced into the shape of a disk. A crystallographic plane of disk surfaces was confirmed to be of (001). The same synthesis procedure as applied for the rods was also used to prepare polycrystalline pellets of NITO-1.0%. Some of the synthesized single crystals and polycrystalline pellets were subjected to post-annealing in Al_2O_3 powder at 1673 K for 10 h in air. Crystal phases of the as-synthesized NITO-1.0% and the post-annealed NITO-1.0% were examined by powder x-ray diffraction measurements on crushed samples with an x-ray diffractometer Miniflex600 (Rigaku). Diffuse

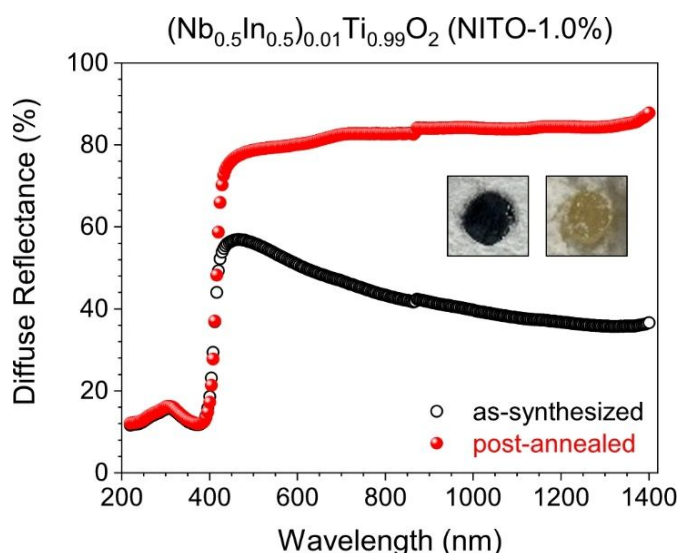


Figure 2. Diffuse reflectance spectra of the as-synthesized (open symbols) and the post-annealed (closed symbols) NITO-1.0% crushed polycrystallines. The insets show the as-synthesized (left) and the post-annealed (right) single crystals.

reflectance measurements were performed also on crushed samples using a spectrometer UV-2600 equipped with an integrating sphere (Shimadzu). Dielectric properties were investigated with a Keysight 4284A Precision LCR meter over the temperature range from 4.2 K to room temperature. The temperature of samples was controlled in a liquid He cryostat with a home-made station.

Results and discussion

Figures 1(a) and 1(b) show x-ray powder diffraction patterns of the as-synthesized and the post-annealed NITO-1.0%, respectively. Figure 1(c), on the other hand, presents the x-ray diffraction pattern of an as-synthesized single crystal of NITO-1.0%, which was used in the present study. A calculated pattern of the rutile-type TiO_2 was additionally plotted in the panel (d) for comparison. The powder diffraction patterns for both samples agreed with the calculated one, confirming their rutile-type phase (see also the supplemental figure Fig. S1). The 002 diffraction peak around 63° , Fig. 1(c), indicated that the single crystal with (001) wide surfaces was successfully prepared for the present measurements. A remarkable post-annealing effect was observed by a color change; the black color of the as-synthesized sample turned completely yellow, suggesting qualitative variation of electric properties. Figure 2 presents a change in the diffuse reflectance across the post-annealing, which was examined in the crushed samples of as-synthesized and post-annealed NITO-1.0% polycrystallines. A broad sub-bandgap reflectance was observed in the as-synthesized sample in the wavelength range longer than approximately 400 nm, the absorption edge due to an interband excitation. This sub-bandgap reflectance resembled that observed in a reduced TiO_2 ,²⁵ indicating that Ti^{3+} and concomitant oxygen vacancies exist in the as-synthesized NITO-1.0%. Note that little Ti^{3+} generation is to be expected in NITO-1.0% as the average

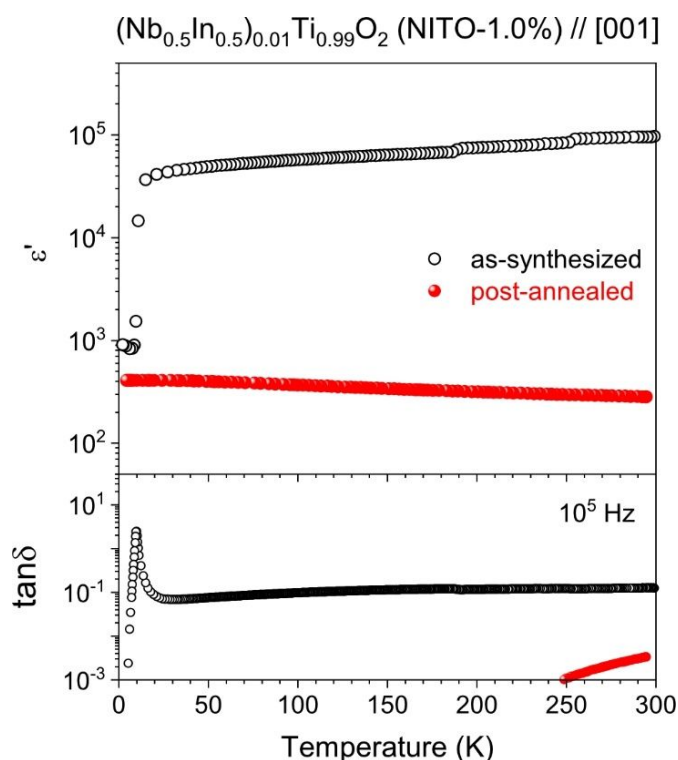


Figure 3. Relative permittivity ϵ' (top panel) and loss tangent $\tan \delta$ (bottom panel) of the NITO-1.0% single crystals, measured over a temperature range from 4.2 K to room temperature. The dielectric measurements were performed with a test frequency of 10^5 Hz applied along the crystallographic [001] direction. Results for the as-synthesized and the post-annealed samples are plotted with open and closed symbols, respectively.

valence between Nb^{5+} and In^{3+} is equivalent to Ti^{4+} . However, unavoidable non-stoichiometry and/or inhomogeneous distribution of the co-dopants would induce Ti^{3+} in the matrix. Supplemental Seebeck measurements indicated a negative sign of the charge carrier in the as-synthesized NITO-1.0%, suggesting the existence of Ti^{3+} in the matrix (Fig. S2). In contrast, after the post-annealing, the sub-bandgap absorption disappeared (solid circles in Fig. 2), indicating variations of the in-gap states. Possibly, the oxygen vacancies were considerably reduced to recover the valence state of Ti from 3+ to 4+. Surprisingly, the post-annealing was effective not only for the polycrystalline pellet with many grain boundaries, but also for the bulk single crystal of NITO-1.0%. Once the as-synthesized black single crystal was subjected to the post-annealing in Al_2O_3 powder, its color homogeneously changed to yellow (insets of Fig. 2). Note that the homogeneous color change was never observed when the sample was embedded in TiO_2 powder during the post-annealing. The post-annealing in an O_2 atmosphere at 1673 K for 10 h was not successful too.

Simultaneously with the color change, marked variations due to the post-annealing were found in the dielectric response. Figure 3 shows the temperature dependence of dielectric properties observed in the as-synthesized (open symbols) and the post-annealed (solid symbols) NITO-1.0% single crystals

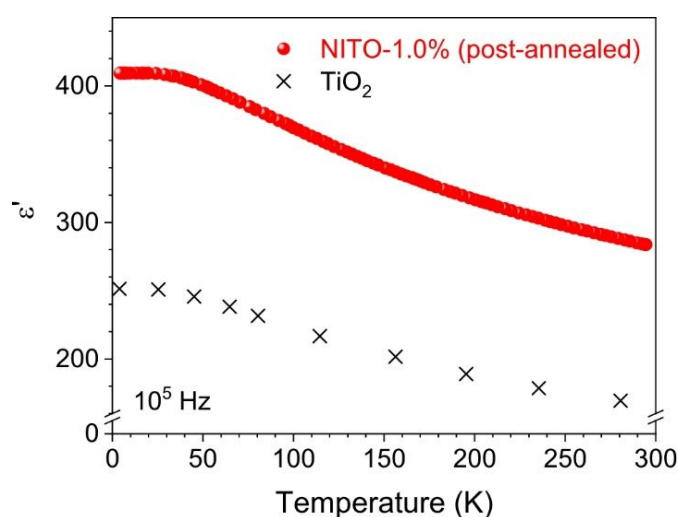


Figure 4. Temperature dependence of relative permittivity ϵ' , which was measured in the post-annealed single crystal of NITO-1.0% with a test frequency of 10^5 Hz applied along the crystallographic [001] direction. The relative permittivity ϵ' along the [001] direction of the pure TiO_2 single crystal (\times), which was reported in a previous study, is also plotted for comparison.²⁶

over the temperature range from 4.2 K to room temperature. Top and bottom panels present the relative permittivity ϵ' and loss tangent $\tan \delta$, which were each measured at a test frequency of 10^5 Hz, where the ac voltage was applied along the crystallographic [001] direction. The as-synthesized sample showed a huge permittivity of the order of 10^4 over a wide temperature range with a relatively large value of $\tan \delta$. This trend is consistent with the results of previous studies,^{23,24} and stems from the Maxwell-Wagner-Sillars effect due to conductive carriers, which would be thermally excited to the defect-states that cause the sub-bandgap reflectance presented in Fig. 2. In a low-temperature region where the conductive carriers are expected to be frozen, the permittivity steeply decreased to a value of approximately 1,000. Along with this dielectric relaxation, a peak anomaly of $\tan \delta$ appeared to exhibit typical behavior of the Maxwell-Wagner-Sillars-type dielectric response.^{12,13} Notably, the permittivity at the lowest temperature was still several times greater than the original value of the pure TiO_2 . This substantial enhancement observed in the lowest temperature region may reflect the intrinsic effect due to the electron-pinned defect-dipoles, as also claimed in previous studies.^{23,24} In marked contrast to the as-synthesized sample, relative permittivity of the post-annealed sample stayed in the order of 10^2 over the entire temperature region in the present study (top panel, Fig. 3). Furthermore, the dielectric relaxation completely disappeared after the post-annealing, demonstrating that conductive carriers disappear, quenching the Maxwell-Wagner-Sillars effect. The magnitude of $\tan \delta$, on the other hand, markedly decreased through the post annealing, indicating significant improvement of an insulating property of the sample. Note that at low temperatures below 210 K, the imaginary part of permittivity fell below the lowest

measurement limit of our facility to estimate an accurate value of $\tan \delta$.

The relative permittivity of the post-annealed NITO-1.0% single crystal is plotted in Fig. 4 on a magnified scale, along with the relative permittivity of the pure TiO_2 at several temperatures, which was reported in a previous study.²⁶ Rutile TiO_2 is known to show an incipient ferroelectricity, the permittivity of which gradually increases on cooling to saturate in the vicinity of 0 K. The temperature dependence of permittivity observed in the post-annealed NITO-1.0% was qualitatively the same as that of pure TiO_2 (Fig. 4). Therefore, the bulk property would remain almost intact through the co-doping of Nb^{5+} and In^{3+} . On the other hand, the value of permittivity was uniformly raised by the co-doping over the entire temperature region observed in the present study. This result indicates that the co-doping affords some sort of temperature independent polarizable agents to the matrix, increasing the total permittivity. Since the boost in permittivity was obtained in the single crystal, we can first rule out the contribution of free charges accumulated in the grain boundary to the additional dielectric response superimposed upon that of the pure TiO_2 alone. The most plausible candidate for the origin of enhanced permittivity is thus the complex defects introduced in the matrix as originally proposed as the electron-pinned defect-dipole.¹⁵ According to Ref. 15, the triangular $\text{In}^{3+}_2\text{V}_\text{o} \cdot \text{Ti}^{3+}$ and the diamond-shaped $\text{Nb}^{5+}_2\text{Ti}^{3+}\text{A}_\text{Ti}$ (A_Ti : Ti^{3+} , Ti^{4+} or In^{3+}) complex defects are formed in the matrix and mutually correlate to give rise to large clusters. The electrons loosely trapped to such clusters are expected to shift considerably under the application of an electric field, resulting in the great polarizability. Although stability of the triangular and the diamond-shaped defects was confirmed by the calculations, there is no guarantee that the equivalent defect structures are realized in the present post-annealed NITO-1.0% because the defect formation strongly depends on the synthesis process. Future comprehensive investigations will elucidate the defect structures formed in the post-annealed NITO-1.0%.

Finally, the absolute increment of permittivity was found to be around 120 at room temperature. Given that NITO-1.0% contains one defect complex for every hundred unit-cells, the relative permittivity of 120 estimates a polarizability of approximately 600 \AA^3 for the single defect-complex. This polarizability is two hundred times greater than that of Ti^{4+} ,²⁷ suggesting the great potential of defect engineering to boost the permittivity of dielectric materials.

Conclusions

Significant permittivity boosting has been demonstrated in $(\text{Nb}_{0.5}\text{In}_{0.5})_{0.01}\text{Ti}_{0.99}\text{O}_2$, which was subjected to a special post-annealing process with Al_2O_3 powder. The post-annealing markedly modified the defect states of the as-synthesized "black" sample to suppress the Maxwell-Wagner-Sillars-type extrinsic dielectric response due to thermally excited carriers. This work shows that the relative permittivity of the post-annealed "yellow" $(\text{Nb}_{0.5}\text{In}_{0.5})_{0.01}\text{Ti}_{0.99}\text{O}_2$ increases uniformly from the initial value of pure TiO_2 by 120 over the temperature

range from 4.2 k to room temperature. Given that the co-doping creates polarizable defect complexes in the matrix to improve the dielectric response of TiO_2 , the individual defect complex is expected to have the polarizability of approximately 600 \AA^3 , which is two hundred times greater than that of Ti^{4+} . Such a remarkable estimated polarizability for the defect complex indicates a great potential of the defect engineering in the development of dielectric materials with large permittivity.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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