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$Nd_2Ba_2CaZn_2Ti_3O_{14.4}$: A New High Dielectric Constant Oxide Having a Disordered (Cubic) Perovskite Structure

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A new oxide of the formula $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ has been successfully prepared by a high-temperature ceramic route at 1200 °C. The title compound crystallizes in a cubic structure with $a = 3.94263(7)$ Å (space group = $Pm\bar{3}m$, wRp = 0.0305, Rp = 0.0192) as obtained from Rietveld refinement of powder neutron diffraction data. X-ray and electron diffraction studies also confirm the absence of any ordering of the cations. The title compound has a high dielectric constant of 59 at 100 kHz and a very small frequency coefficient of the dielectric constant ($d\epsilon/dF = 1.26 \times 10^{-6}$ Hz^{-1}). The dielectric loss is 0.0047 at 100 kHz, which also shows very minor variation with frequency. The temperature-dependence studies show an increase in dielectric constant and dielectric loss over the temperature range 35−300 °C.

1. Introduction

Complex perovskite-related oxides have been of great importance since a number of materials exhibiting a wide range of unusual properties can be synthesized based on the perovskite structure. These include magnetic materials, superconductors, laser host materials, dielectric materials, and many others. The ability of the simple perovskite structure of the formula ABO_3 to give rise to intergrowth structures, oxygen-deficient ordered structures, and multiple perovskite structures (for example, double, triple, etc.) are well-known.[1−3] Several new families of complex metal oxides containing copper have been synthesized in the recent past, like $Gd_2Ba_2Ti_2Cu_2O_{11}$[4] and $La_2Ba_2Sn_2Cu_2O_{11}$,[5] other than those well-known as high T_c superconductors.[6] The rare-earth-based copper titanates of the formula $Ln_2Ba_2CaCu_2Ti_3O_{14}$ (Ln = La, Nd, Sm, Eu, Gd, etc.) have been synthesized recently[7,8] and have inspired us to carry out the present study. The structure of the above oxides can be conceived as the intergrowth of three TiO_6 (octahedral) and two CuO_5 (square pyramidal) layers in a repeat unit to form an ordered tetragonal structure, except in the case of lanthanum, where it gives a disordered cubic structure.

It is well-known that the presence of a partially filled d-band, as found in copper, gives rise to conducting (often superconducting) properties in copper-based materials. However, since our interest was to explore the possibility of formation of new dielectric materials, we have chosen the closed shell zinc to replace copper in the rare-earth-based titanates discussed above. Materials having ions with closed shell (d^0) electronic configuration are known to have interesting dielectric properties, for example, oxides of Ti^{4+}, Nb^{5+}, and Ta^{5+}. The electronic industry is highly dependent on new and better dielectric materials. Hence, there is tremendous activity toward discovering new dielectric materials.[9−13] Recently, there have been studies[14−16] on $CaCu_3Ti_4O_{12}$, which shows an unusually high dielectric constant (>1000) and is not a ferroelectric material.

In this paper we report a new oxide material, $Nd_2Ba_2CaZn_2Ti_3O_{14}$, whose dielectric properties appear promising. We discuss the synthesis, detailed structural analysis by combined X-ray, neutron, and electron diffraction studies, and also the frequency and temperature-dependent dielectric properties of $Nd_2Ba_2CaZn_2Ti_3O_{14}$.

2. Experimental Section

$Nd_2Ba_2CaZn_2Ti_3O_{14}$ was prepared by the ceramic method. Stoichiometric amounts of Nd_2O_3 (CDH, 99.9%), TiO_2 (Fluka,

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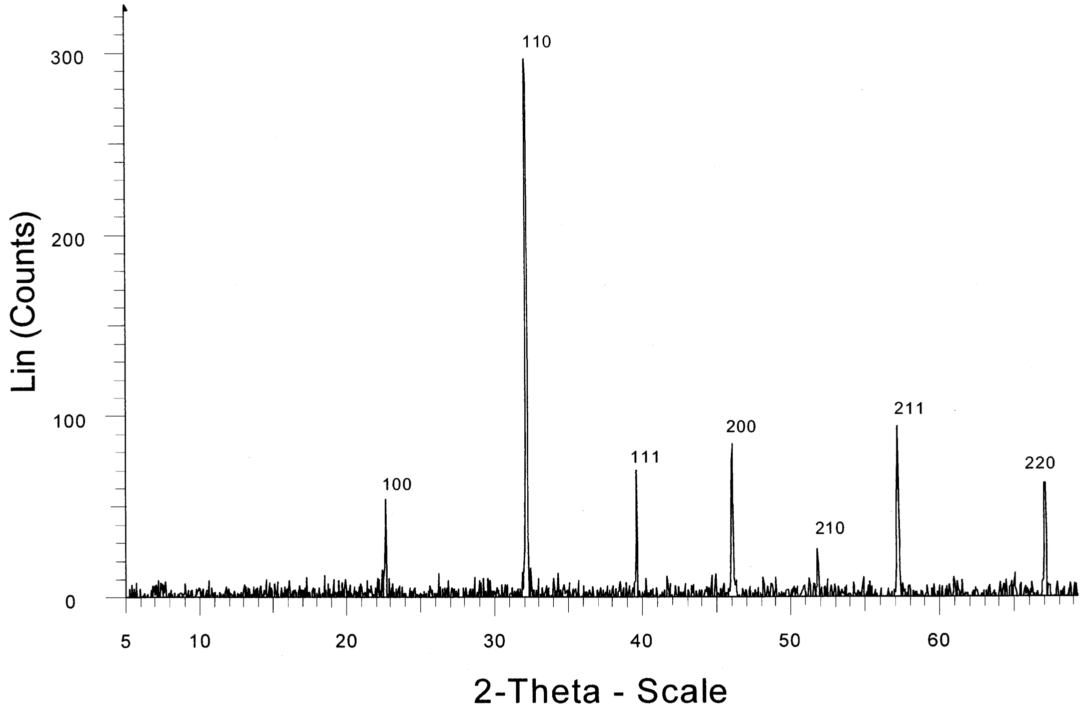

Figure 1. Powder X-ray diffraction pattern of $Nd_2Ba_2CaZn_2Ti_3O_{14}$.

99.99%), $CaCO_3$ (Aldrich, 98.5%), $BaCO_3$ (Loba Chemie, 99%), and ZnO (CDH, 99.5%) were taken. Nd_2O_3 was dried at 900 °C for 6 h before weighing, while the other oxides and carbonates were dried at 150 °C. The oxides and carbonates were thoroughly mixed in an agate mortar and pestle and loaded in alumina boats. The reactants were heated in an electrical muffle furnace at 1000 °C for 20 h followed by heating at 1100 °C for 10 h and 1200 °C for 5 h with intermittent grindings after each stage of heating. The resulting powder was ground, mixed with PVA (poly(vinyl alcohol)), and compacted into pellets at a pressure of 4 ton. The pellets were then sintered at 1200 °C for 14 h. Powder X-ray diffraction was obtained after each step with a Bruker D8 Advance diffractometer with Cu Kα radiation. A step size of 0.05 with a step time of 1 s was used for the 2θ range of 10−70°. The raw data was subjected to background correction and Kα_2 stripping.

The neutron diffraction experiment was carried out on the time-of-flight, high-pressure preferred orientation (HIPPO) neutron diffractometer at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos National Laboratory. The instrument uses chilled water as a moderator and has a short primary flight path (moderator to sample) distance of 9.0 m for the sake of higher neutron flux at the expense of resolution. Approximately 2 g of finely ground sample was loaded into a vanadium can and back-scattering data were collected at room temperature for roughly 2 h. The resolution and d-spacing range for the back-scattering detector banks are ~0.4% and 0.12 Å < d < 4.8 Å, respectively. Structure refinement was done using the GSAS software[17] for Rietveld refinement with default neutron scattering lengths and absorption cross sections. Standard procedure was followed for the refinement with a mixture of Nd, Ba, and Ca statistically allocated on the 1a site ($m\bar{3}m$ symmetry) with fixed ratio of 0.4:0.4:0.2 and a mixture of Ti and Zn statistically allocated on the 1b site ($m\bar{3}m$ symmetry) with a fixed ratio of 0.6:0.4, respectively. A single, refined temperature factor was used for both sites. Refinement cycles involved 16 parameters including background (shifted Chebyschev function with 8 terms), peak shape, scaling factor, unit cell, and isotropic thermal parameters. Oxygen site occupation factor was refined as well. However, since there were some weak shoulders, the possibility of impurity phases was considered and the final refinement included four phases (including three impurity phases; see Results and Discussion), fractions, lattice parameters, background and scaling coefficients, oxygen occupancy, and so forth.

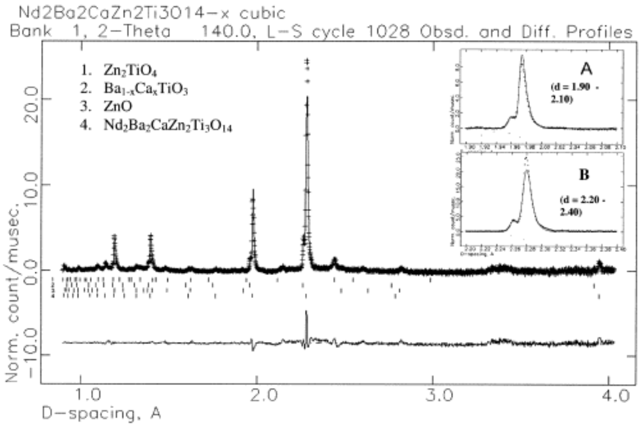

Figure 2. Observed, calculated, and difference plot of the powder neutron diffraction data of $Nd_2Ba_2CaZn_2Ti_3O_{14}$ (inset shows the fitting of the two most intense peaks).

Electron diffraction studies were performed using a JEOL 200CX transmission electron microscope operating at 200 kV. Scanning electron micrographs (SEM) were obtained on a Cambridge Stereoscan 360 electron microscope. The dielectric constant was measured on pellets coated with silver using a HP 4284L LCR meter in the frequency range of 50−500 kHz. Temperature variation studies of the dielectric constant and dielectric loss were carried out in the range of 35−300 °C. The density of the sintered disks was obtained by the Archimedes principle using carbon tetrachloride as a solvent and was found to be 95% of the theoretical density.

3. Results and Discussion

The X-ray diffraction pattern of the sample of $Nd_2Ba_2CaZn_2Ti_3O_{14}$ prepared by heating at 1200 °C shows a pure cubic phase (Figure 1). The X- ray

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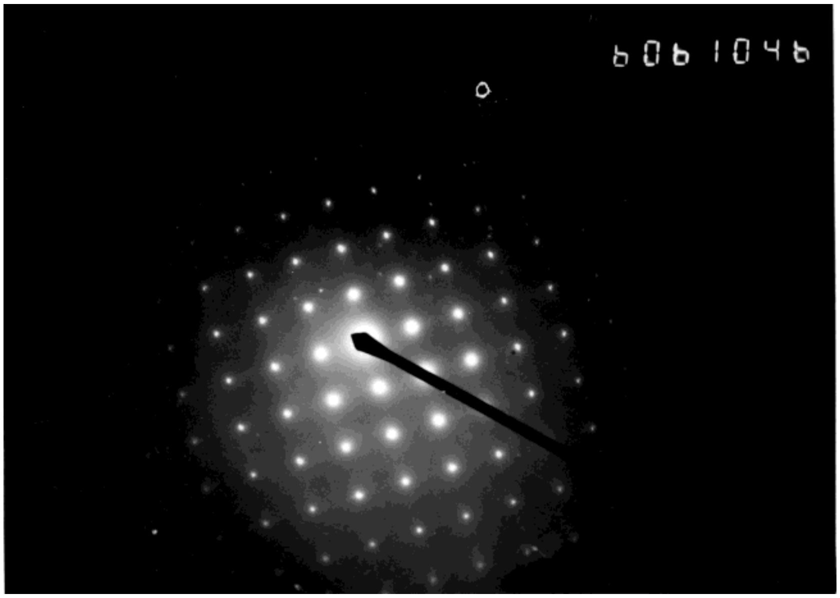

Figure 3. Electron diffraction pattern of $Nd_2Ba_2CaZn_2Ti_3O_{14}$ showing the reciprocal lattice of a typical cubic cell.

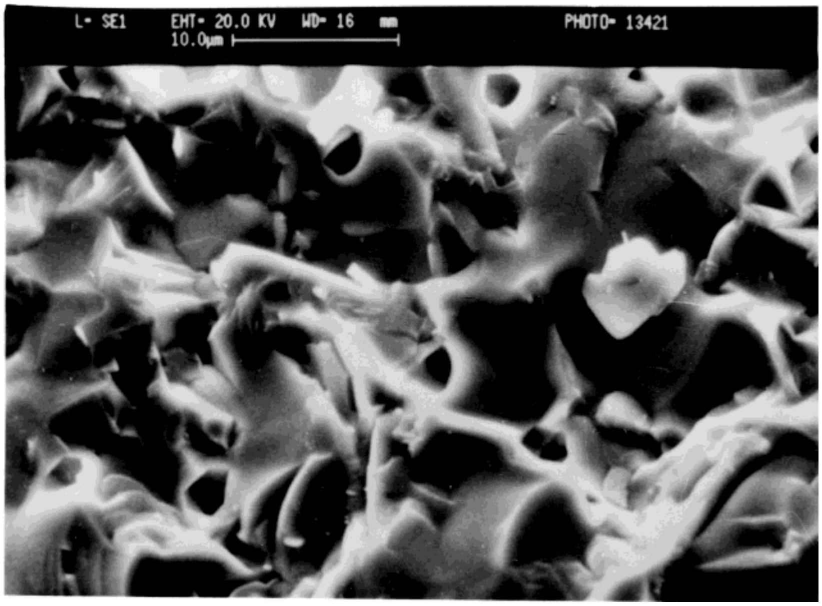

Figure 4. Scanning electron micrograph of $Nd_2Ba_2CaZn_2Ti_3O_{14}$.

Table 1. Positional, Thermal, and Occupancy Factors of $Nd_2Ba_2CaZn_2Ti_3O_{14.49}$ as Obtained by Refinement of Neutron Diffraction Data[a]

atom	Wyckoff position	*x*	*y*	*z*	fraction	100 × $U_{(iso)}$
Nd	1a	0.0	0.0	0.0	0.4	1.538(14)
Ba	1a	0.0	0.0	0.0	0.4	1.538(15)
Ca	1a	0.0	0.0	0.0	0.2	1.538(2)
Zn	1b	0.5	0.5	0.5	0.4	1.000(2)
Ti	1b	0.5	0.5	0.5	0.6	1.000(2)
O	3c	0.0	0.5	0.5	0.966(24)	4.166(145)

[a] Space group = $Pm\bar{3}m$, $a = 3.94263$ (7), wRp = 0.0305, and Rp = 0.0192.

diffractionpattern could be satisfactorily indexed on a cubic cell with $a \sim 3.937$ Å. The refined lattice parameter from neutron studies was found to be 3.94263(7) Å(space group, $Pm\bar{3}m$). Note that cubic $BaTiO_3$ has a lattice parameter of ~4.00 Å, which is much larger than that obtained for the $Nd_2Ba_2CaZn_2Ti_3O_{14}$ phase. This is possible due to the smaller size of the Nd^{3+} and Ca^{2+}-ions substituting the Ba^{2+} sites. Thus, the formula of $Nd_2Ba_2CaZn_2Ti_3O_{14}$ may also be represented as $(Nd_{0.4}Ba_{0.4}Ca_{0.2})(Zn_{0.4}Ti_{0.6})O_{2.9}$, where the A and B sites of the cubic perovskite structure (ABO_3) are occupied by more than one type of atom. However, from the neutron studies it seems that all the major reflections at lower *d* spacings have a shoulder and all the observed reflections cannot be assigned on the basis of one cubic phase. Using other models to refine the data yielded no positive results. Hence, we checked for impurity phases that may be present in the sample (and are not seen in the XRD patterns). We found the presence of a cubic perovskite phase, $Ca_xBa_{1-x}TiO_3$ (2−3%), with lattice parameter 3.9133(2), which explained the presence of shoulders at reflections observed at lower *d* values. The reflections that could not be refined satisfactorily with the above two cubic phases could be accounted for by using the spinel phase Zn_2TiO_4 (1%) with lattice parameter 8.4444(5) and the hexagonal ZnO (1%) with lattice

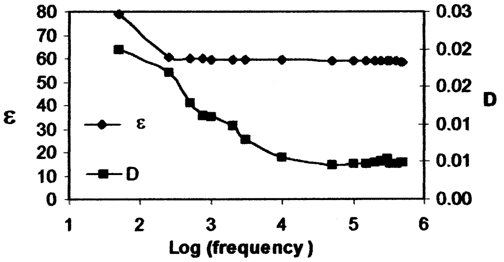

Figure 5. Plot of the variation of the dielectric constant (ϵ) and dielectric loss (*D*) with frequency at room temperature.

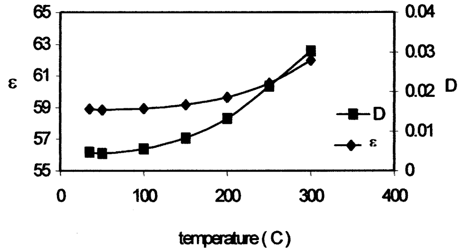

Figure 6. Plot of the variation of the dielectric constant (ϵ) and dielectric loss (*D*) with temperature (at 100 kHz).

parameters 3.2445(3) and 5.2627(7). All these minor impurity phases (<3%) have been indicated in Figure 2. The two strongest reflections (enlarged) are also shown to support the quality of the fit (inset of Figure 2). Hence, by changing the model from a single phase to a model where the impurities have been refined, all the reflections could be accounted for. However, there is still some discrepancy between the observed and the calculated intensity of the two strongest reflections. This is due to the fact that we have refined four phases (three impurity phases with very weak reflections) in the final refinement along with other parameters such as fractional occupancy, background and scaling coefficients, and oxygen occupancy. The large number of parameters makes it difficult to refine the anisotropic thermal parameters. The lattice parameters, thermal factors, and the occupancy of oxygen were refined together in the final cycle. The positions, occupancies, and thermal parameters are given in Table 1. The final refined composition is $Nd_2Ba_2CaZn_2Ti_3O_{14.4(3)}$. Both the X-ray and neutron studies clearly show the absence of an ordered perovskite structure. We have also done careful electron diffraction studies to look for ordering of the A (Nd/Ba/Ca) and/or B (Zn/Ti) cations in the "ABO_3" perovskite structure. However, we could observe only the simple cubic reciprocal cell (Figure 3) in our electron diffraction studies, confirming the X-ray and neutron structural refinement. Our loaded composition corresponds to the five layered (copper-containing) perovskite oxide, $Nd_2Ba_2CaCu_2Ti_3O_{14}$, reported earlier,[8] where the "*c*" parameter is roughly 5 times the "*a*" parameter ($a = 3.9036(1)$ and $c = 19.619(1)$ Å). However, we could not find any evidence for the tetragonal cell either in the X-ray, neutron, or electron diffraction studies. Figure 3 clearly shows a reciprocal lattice for a cubic (disordered perovskite) structure. All attempts to find any weak reflections in the electron diffraction (to suggest ordering) have been negative. Hence, it appears that $Nd_2Ba_2CaZn_2Ti_3O_{14}$ crystallizes as a disordered perovskite. It may be noted that in analogous copper-based oxides the Nd compound ($Nd_2Ba_2CaCu_2Ti_3O_{14}$) shows an ordered five-layer perovskite structure whereas the La compound, $La_2Ba_2CaCu_2Ti_3O_{14}$, has been reported[8] to have the disordered perovskite structure.

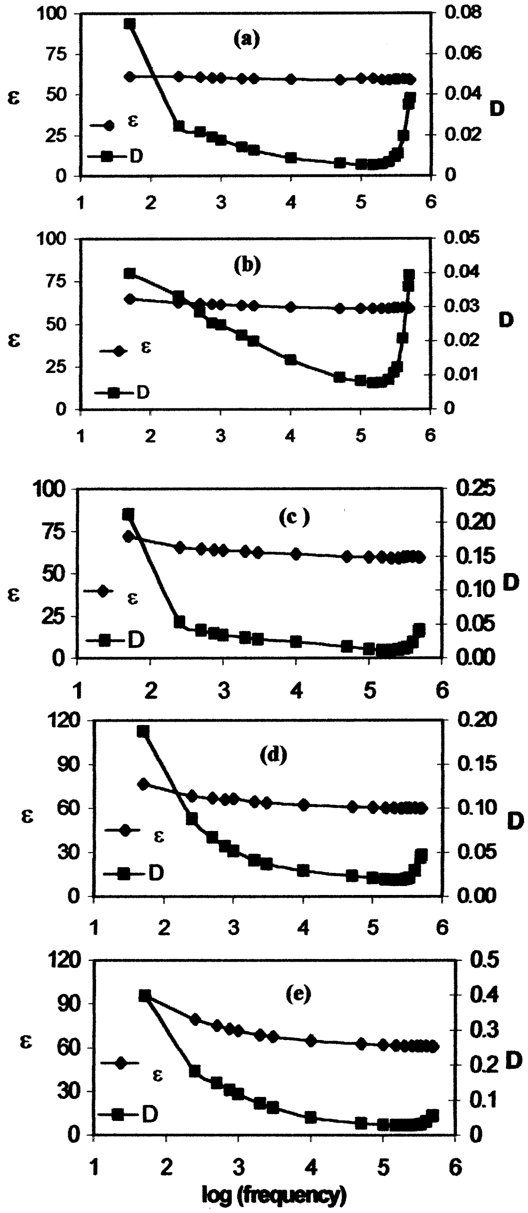

Figure 7. Plot of the variation of the dielectric constant (ϵ) and dielectric loss (*D*) with frequency at different temperatures: (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 °C.

We have carried out the dielectric properties on dense ceramics (95% of the theoretical density). Scanning electron micrographs (SEM) also show (Figure 4) that the material is highly dense. The grain size obtained from the SEM photographs (using the diagonal intercept method) show an average grain size of 7 μm (Figure 4).

The dielectric property of $Nd_2Ba_2CaZn_2Ti_3O_{14}$ has been found to be very interesting. The plot of the dielectric constant and dielectric loss vs frequencies at different temperatures is given in Figure 5. It is found that the dielectric constant (ϵ) has a high value of 59 at 100 kHz and remains nearly constant over a large range of frequency (0.5−500 kHz). The frequency coefficient of the dielectric constant ($d\epsilon/dF$) has a value of 1.26×10^{-6} Hz^{-1}. We have also studied the temperature dependence of the dielectric properties (Figure 6). We find a steady increase in the dielectric constant (ϵ) with an increase in temperature. The dielectric constant (ϵ) for this compound varied from 59 around 35 °C to 62 at 300 °C and the dielectric loss (D) varied from 0.0047 (35 °C) to 0.03033 (300 °C) measured at a frequency of 100 kHz. The dielectric constant has been found to be stable with frequency at all the temperatures at which measurements have been carried out (Figure 7). The dielectric loss however shows (Figure 7) a decrease with an increase in frequency up to 200 kHz, beyond which the loss increases. It appears that there is a loss peak beyond (but close to) 500 kHz and its signature is seen clearly in the plots for samples which were heated at 100 and 150 °C (Figure 7a,b). Normally, such a peak in the dielectric loss would be associated with a change in the modes of polarization of the dielectric.

The oxide $Nd_2Ba_2CaZn_2Ti_3O_{14}$ is a novel dielectric material since there are very few materials with low dielectric loss and having a dielectric constant above 30. Among them oxides of the type $BaLn_2Ti_4O_{12}$ and $BaLn_2Ti_5O_{14}$ (Ln = La, Nd, Sm, Eu, Gd) are known[18] to have high dielectric constants of 70−90. Some of them have the problem of high dielectric loss. Therefore, attempts are being made to obtain new materials of high dielectric constant but with low loss that would be very attractive to applied physicists and material scientists. We feel that the new oxide discussed in this paper merits attention for its viability as an efficient dielectric oxide especially in the microwave region. However, other aspects such as low thermal expansion, high mechanical strength, and ease of thin film fabrication are necessary for any new material (with high dielectric constant) to be of use in the electronic industry.

Conclusions

A new oxide of the formula $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ having the disordered perovskite structure has been successfully prepared by the ceramic method. We have not found any indication of an ordered structure by X-ray, neutron, and electron diffraction studies. This oxide has an unusually high dielectric constant compared to most oxides. The dielectric constant varies between 59 and 62 depending on temperature and is frequency-stable over a large range (0.5−500 kHz at room temperature) of frequencies. The high dielectric constant and low loss along with the stability of the dielectric constant with frequency makes this material interesting for further studies and applications.

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