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New perovskite-related oxides having high dielectric constant: $Ln_2Ba_2CaZn_2Ti_3O_{14}$ (Ln = La and Pr)[¶]

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Abstract. Two new oxides, $La_2Ba_2CaZn_2Ti_3O_{14}$ and $Pr_2Ba_2CaZn_2Ti_3O_{14}$, have been synthesized by the ceramic route at 1100°C. These oxides crystallize in the disordered cubic structure with an '**a**' lattice parameter of 3·9728 (2) and 3·9448 (5) respectively. These oxides show high dielectric constant (70 and 57) and low loss (0·003 and 0·013 at 100 kHz) for $La_2Ba_2CaZn_2Ti_3O_{14}$ and $Pr_2Ba_2CaZn_2Ti_3O_{14}$ respectively. The dielectric constant is highly stable with frequency and temperature.

Keywords. Perovskite structure; oxides; dielectric material.

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 and dielectric materials.[1] The ability of the simple perovskite structure (ABO_3) to give rise to intergrowth structures, oxygen deficient structures and ordered perovskite structures are well known.[2–5] The design of new materials with copper due to the extensive research in high *Tc* superconductors[6–8] has lead to several new families of complex metal oxides like $LnBa_2Cu_3O_7$, $Bi_2Ca_{n-1}Sr_2Cu_nO_{2n+4}$, $Tl_mCa_{n-1}Ba_2Cu_nO_{n+m+2}$, and $Hg_2Ca_{n-1}Ba_2Cu_nO_{2n+3}$. Search for new copper based materials also lead to the synthesis of non-superconducting oxides like $Gd_2Ba_2Ti_2Cu_2O_{11}$,[9] $La_2Ba_2Sn_2Cu_2O_{11}$[10] etc. The rare earth-based copper titanates of the formula $Ln_2Ba_2CaCu_2Ti_3O_{14}$ (Ln = La, Nd, Sm, Eu, Gd etc.) have been synthesised recently.[11,12] The structure of these oxides can be conceived of 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 (figure 1b), except in the case of lanthanum where it gives a disordered cubic structure (figure 1a). The ordered structure can be considered to be a five-layered perovskite oxide.

Dielectric oxides constitute a large proportion of materials, which have large-scale technological applications. There is an increasing demand on dielectric materials to surpass their present abilities to be of use in the fast changing world of electronic devices. Microelectronics thrives on an insatiable urge to design smaller and faster devices. At the root of all devices lie the bulk dielectric materials, on whose basic properties further progress may be made. In memory devices based on capacitive components, such as static and dynamic random access memories, the static dielectric constant of the material

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[¶] Dedicated to Professor C N R Rao on his 70th birthday

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will ultimately decide the degree of miniaturization. Hence, search for new materials with unusual properties is of great importance. Most of the insulating oxide materials have dielectric constant in the range of 10–30. Ferroelectric oxides have very high dielectric constant (~ 10,000) but have a high dielectric loss. Materials with reasonably high dielectric constant (> 40) and low loss are rare. This has led chemists to take up the challenge to search for novel materials[13–20] or search for novel properties in known materials e.g. $CaCu_3Ti_4O_{12}$.[21–23] Table 1 lists some of the materials with high dielectric constant (> 40).

Recently, the structural characterization and dielectric properties of the oxide $Nd_2Ba_2CaZn_2Ti_3O_{14}$ has been reported[24] by us, where the closed shell electronic configuration of ‘Zn’ instead of ‘Cu’ permits for a high value of dielectric constant in $Nd_2Ba_2CaZn_2Ti_3O_{14}$. This ‘Zn’ substituted compound is related to the earlier Cu-based family of $Ln_2Ba_2CaCu_2Ti_3O_{14}$.[11,12] In this paper we report the synthesis, X-ray diffraction studies and the dielectric properties of two new similar perovskite oxides $La_2Ba_2CaZn_2Ti_3O_{14}$ and $Pr_2Ba_2CaZn_2Ti_3O_{14}$ which appear to have promising dielectric properties.

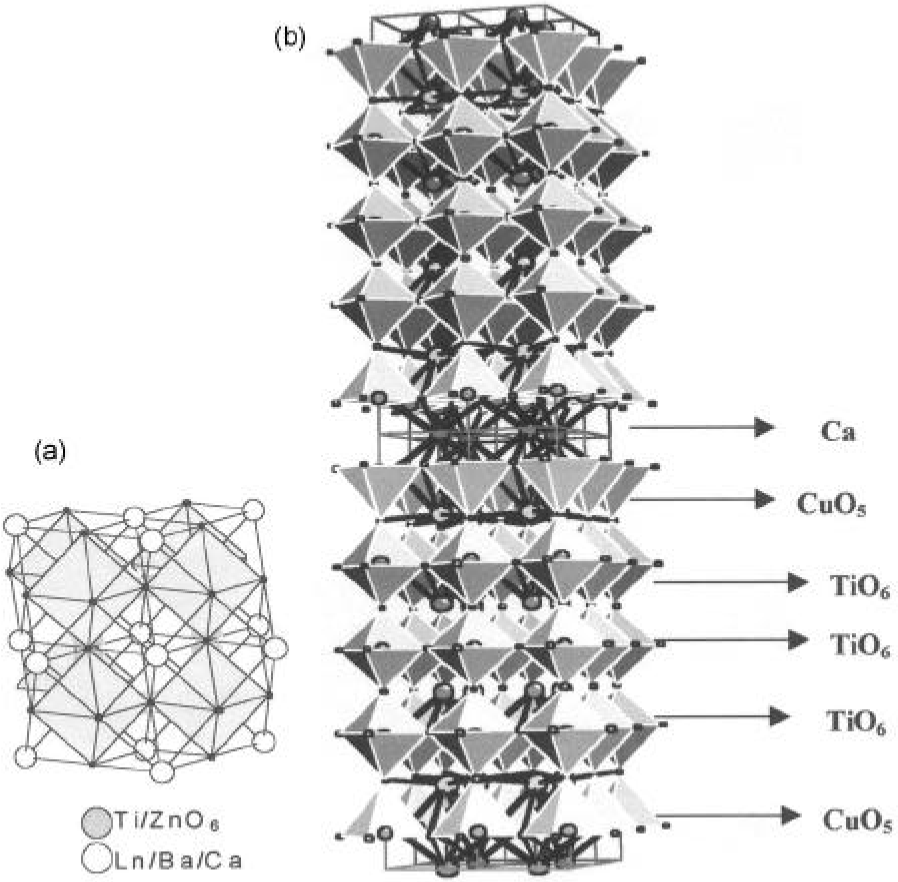

Figure 1. Schematic diagram of (**a**) disordered perovskite structure, (**b**) ordered five layer perovskite structure.

Table 1. Oxides having high dielectric constant ($e > 40$).

Composition	e	D	Reference
$Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$)	86·4 (GHz)	–	20
$Ba_{6-3x}(Nd, Bi_y)8_{+2x}Ti_{18}O_{54}$ ($x = 2/3, y = 0{\cdot}2$)	102·4 (GHz)	–	20
$CaCu_3Ti_4O_{12}$	10,286 (1 kHz)	0·067	22
$BaLa_2Ti_4O_{12}$	110 (1 MHz)	–	13
$BaPr_2Ti_4O_{12}$	91 (1 MHz)	–	13
$BaSm_2Ti_4O_{12}$	80 (1 MHz)	–	13
$Nd_2Ba_2CaZn_2Ti_3O_{14}$	59 (100 kHz)	0·005	24

2. Experimental

The oxides were prepared by the ceramic method. Stoichiometric amounts of La_2O_3 and Pr_6O_{11} (CDH, 99·9%), TiO_2 (CDH, 99·99%), $CaCO_3$ (Merck, 98·5%), $BaCO_3$ (Loba Chemie, 99%) and ZnO (CDH, 99·5%) were taken. The rare earth oxides were 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 loaded in alumina boats. The reactants were heated in an electrical muffle furnace at 900°C for 12 h and 1000°C for 24 h followed by heating at 1050°C for 40 h with two intermittent grindings. The resulting powder was ground, mixed with PVA (polyvinyl alcohol) and compacted into pellets at a pressure of 8 tons. The pellets were then sintered at 1100°C for 16 h. Powder X-ray diffraction patterns were obtained after each reaction step with a Bruker D8 Advance diffractometer with Cu-Kα radiation. A step size of 0·05 with step time of 1 s was used in the 2-theta range of 10 to 70°. The raw data was subjected to background correction and to Kα_2 stripping. 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 to 500 kHz. Measurements of the dielectric constant and dielectric loss was also carried out by varying the temperature in the range of 35 to 300°C. The density of the sintered disks was obtained by the Archimedes method using CCl_4. The disks were soaked in the organic medium for sufficiently long time and weights were taken till a constant weight was observed. For consistency, three different density measurements were carried out for each sample. The density was found to vary between 92 to 94% of theoretical density.

3. Results and discussions

Powder X-ray diffraction patterns of the samples show the formation of the perovskite phase along with major impurity phases at 900°C, which decreased with treatment at higher temperatures. At 1050°C around 2–3% of ZnO remained unreacted as shown by XRD taken after the first grinding and this was eliminated with further heating at this temperature. After heating at 1050°C for 40 h a pure cubic phase was obtained with lattice parameter **a** = 3·9728 (2) for the 'La' based compound (figure 2a) and 3·9448 (5) for the 'Pr' based oxide (figure 2b). The lattice parameters are in accordance with expectation as the atomic radius of La is greater than that of Pr. However for the oxide containing Pr, some amount of impurities of $Ba_2Ti_6O_{13}$ and ZnO (around 5–6%) were observed. Attempts were made to remove these minor phases by varying the reaction conditions but they were unsuccessful. Detailed structural characterization carried out by us on the oxide of formula $Nd_2Ba_2CaZn_2Ti_3O_{14}$,[24] shows that it has a disordered cubic structure with space group $Pm\overline{3}m$. The copper, and lanthanum-based oxide $La_2Ba_2CaCu_2Ti_3O_{14}$ was also reported to have the same[12] (disordered cubic) structure. The disordered structure of the above oxide may also be written as $(Pr_{0.4}Ba_{0.4}Ca_{0.2})(Zn_{0.4}Ti_{0.6})O_{3-\partial}$, where the Pr, Ba and Ca occupy the A-site while Zn and Ti occupy the B-site of the perovskite ABO_3 structure (figure 1a). We have attempted to promote ordering of the cations in the zinc-based complex oxides containing La, Pr and Nd having the disordered perovskite structure. Annealing at temperatures varying from 700 to 950°C for several days followed by slow cooling has not yet resulted in any ordering of

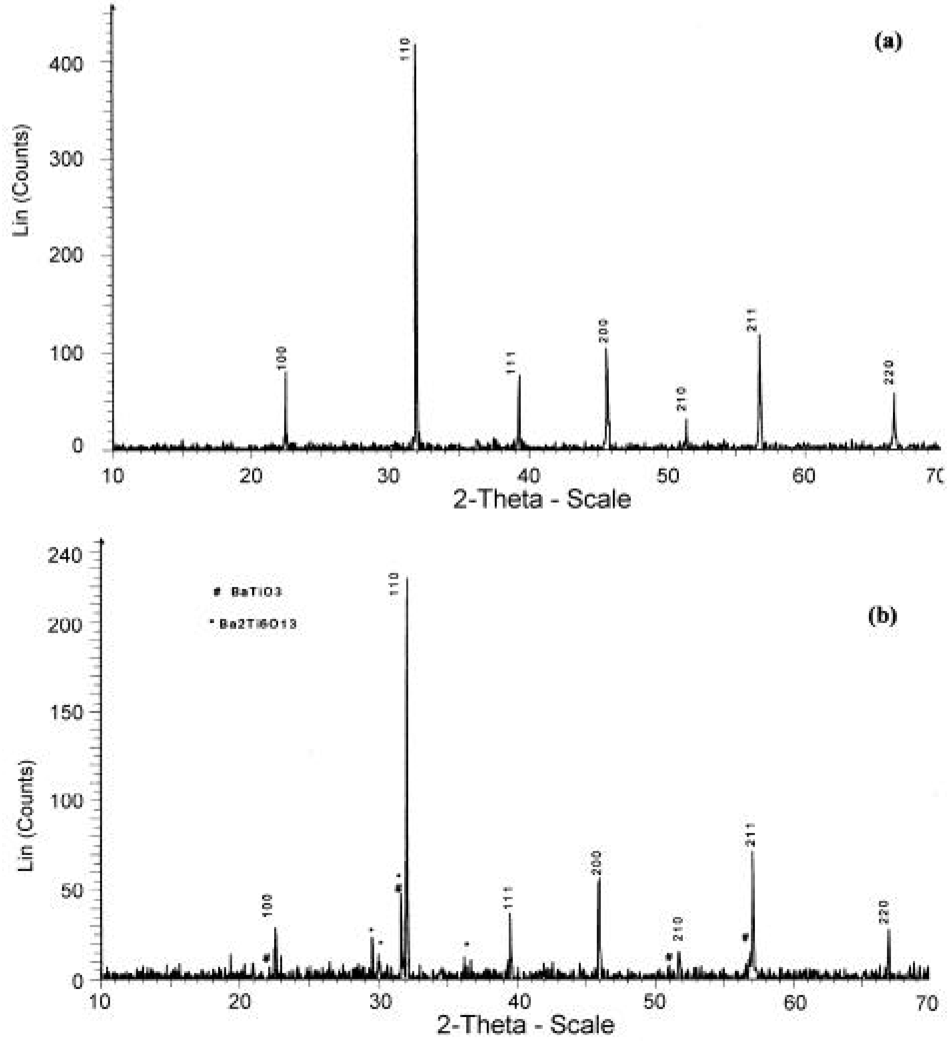

Figure 2. Powder X-ray diffraction pattern for (**a**) $La_2Ba_2CaZn_2Ti_3O_{14}$ and (**b**) $Pr_2Ba_2CaZn_2Ti_3O_{14}$.

the cations. It may be noted that in the reported[8,12] copper-based oxide $Nd_2Ba_2Ca Cu_2Ti_3O_{14}$, the copper layers were made of corner-shared CuO_5 square-pyramidal units. The probability of having zinc in such a coordination would be unusual, since Zn prefers tetrahedral or octahedral coordination. This may be an important factor in the stability of the disordered perovskite structure, as seen in all the Zn based compositions studied by us till now.

Scanning electron micrographs (SEM) for the compounds have been obtained from the pellets compacted at 8 ton pressure. It is seen that the material is highly dense (figure 3a and b). The grains of the La-based oxide are smaller with an average grain size of 3–4 *m*m and are round in shape and we could see the presence of well-faceted grain boundaries. The Pr based oxide has large grains that are large with sizes in the range of 6–7 *m*m and do not possess any well-defined shape. This is probably due to the partial melting of these grains of zinc-containing compounds at the high temperature of around 1100°C. It is also observed from the SEM pictures that the materials are highly dense which corroborates values of density obtained experimentally.

We have carried out dielectric measurements of the oxides in the frequency range of 50 Hz to 500 kHz. The dielectric constant and the dielectric loss have also been measured as a function of temperature from 35 to 300°C. For both the oxides, the dielectric properties have been found to be quite interesting. For the La based compound, the value of the dielectric constant is found to be quite high ($e = 70$) and the dielectric loss is very

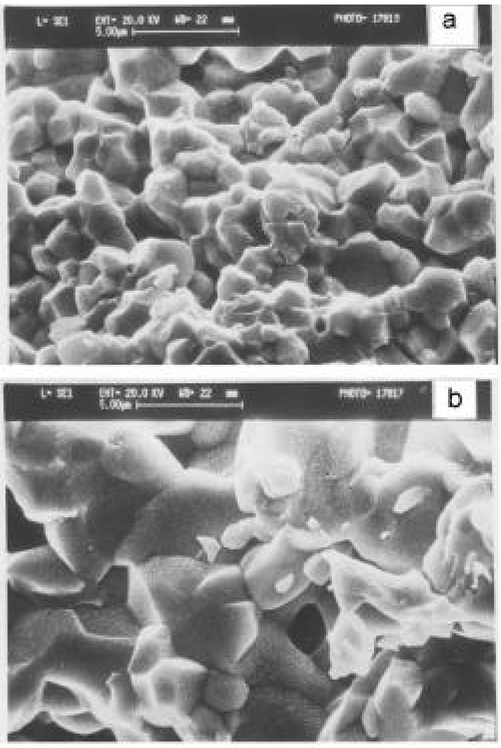

Figure 3. Scanning electron micrographs for (**a**) $La_2Ba_2CaZn_2Ti_3O_{14}$ and (**b**) $Pr_2Ba_2CaZn_2Ti_3O_{14}$.

low ($D \sim 0{\cdot}0034$) at 100 kHz at room temperature. It is also observed from the plot of dielectric constant and dielectric loss against log frequency (figure 4) that at room temperature the ‘*e*’ value is constant over a large range of frequencies (from 750 Hz to 500 kHz) and the coefficient of the dielectric constant de/dF is found to be $1{\cdot}1 \times 10^{-6}$ Hz^{-1}. The dielectric loss shows a decrease with frequency upto 150 kHz (0·003) beyond which it rises sharply and has a value of 0·04 at 500 kHz. This behaviour of dielectric constant and dielectric loss persists at all temperatures for which measurements were carried out. The dielectric constant remains stable at 70 for all temperatures from 35 to 300°C ($de/dT = 1{\cdot}05 \times 10^{-3}$ T^{-1}) and the dielectric loss increases marginally from 0·003 at 35°C to 0.007 at 300°C at 100 kHz (figure 5). The sharp rise in the value of dielectric loss at high frequencies is observed for all the temperatures studied, and this suggests the presence of a loss peak at a frequency close to 500 kHz. For $Pr_2Ba_2CaZn_2Ti_3O_{14}$ the dielectric constant has a value of 57 and a loss value of 0·013 at a frequency of 100 kHz at room temperature (figure 5). The dielectric constant is reasonably stable and there is a marginal increase with temperature and rises from 57 at 35°C to 66 at 300°C at 100 kHz (figure 7). From the plot of dielectric loss against temperature (figure 7), it is seen that the value of dielectric loss (D) remains stable till 150°C, and then shows a rise till 300°C.

Both these compounds have shown to possess a high dielectric constant, which is stable with frequency and temperature, and have reasonably low loss. Very few materials have been reported to have low loss and *e* values more than 30. An important family of oxides of the formula $Ba_{6-3x}(Nd, Bi_y)8_{+2x}Ti_{18}O_{54}$ ($x = 2/3$, $0 \le y \le 0{\cdot}2$) having high dielectric constant (80–90) has been reported.[20] These do not show any ferroelectricity.

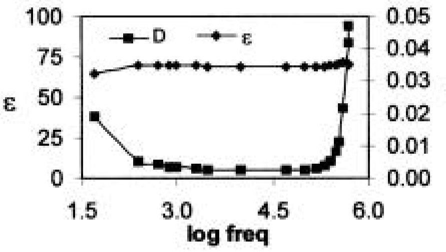

Figure 4. Plot of variation of dielectric constant and dielectric loss with log frequency at room temperature for $La_2Ba_2CaZn_2Ti_3O_{14}$.

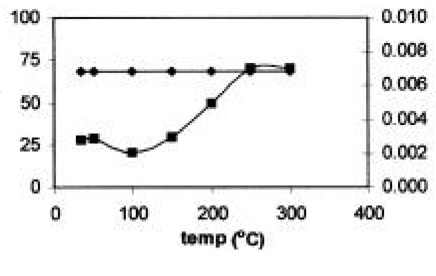

Figure 5. Plot of variation of dielectric constant and dielectric loss with temperature for $La_2Ba_2CaZn_2Ti_3O_{14}$ at a frequency of 100 kHz.

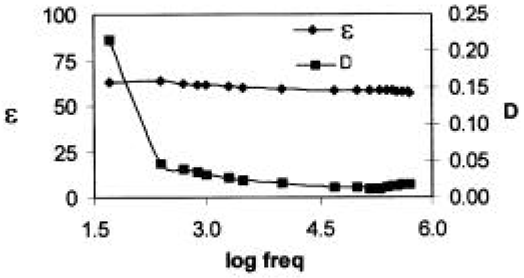

Figure 6. Plot of variation of dielectric constant and dielectric loss with log frequency at room temperature for $Pr_2Ba_2CaZn_2Ti_3O_{14}$.

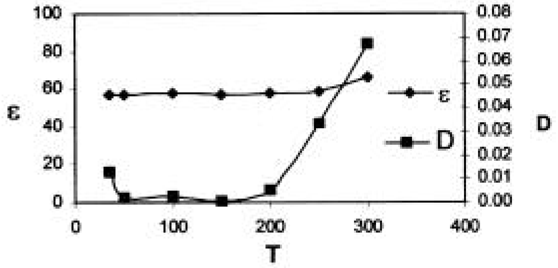

Figure 7. Plot of variation of dielectric constant and dielectric loss with temperature for $Pr_2Ba_2CaZn_2Ti_3O_{14}$ at a frequency of 100 kHz.

The $Ln_2Ba_2CaZn_2Ti_3O_{14}$ (Ln = La, Nd, Pr) obtained by us is a new family of oxides showing high dielectric constant. The compound $La_2Ba_2CaZn_2Ti_3O_{14}$ has loss values around 0·003 and could be a potential candidate for use in the microwave region. However the dielectric loss function for the oxide $Pr_2Ba_2CaZn_2Ti_3O_{14}$ shows sharp rise at high temperatures (> 200). It may be noted that the $Nd_2Ba_2CaZn_2Ti_3O_{14}$ shows a dielectric constant of 59 at 100 kHz. It appears that the dielectric constant is related to the ionic radii of the rare earth (ionic radii: $r_{\mathrm{La}}^{3+} > r_{\mathrm{Nd}}^{3+} > r_{\mathrm{Pr}}^{3+}$). Further studies are currently being carried out on other rare-earth based compounds.

4. Conclusion

We have prepared two new oxides $La_2Ba_2CaZn_2Ti_3O_{14}$ and $Pr_2Ba_2CaZn_2Ti_3O_{14}$, both of which have cubic structure. The Pr-based oxide contains some minor impurity phase. The dielectric constant for the La-based oxide was found to be 70 and is highly stable with temperature and frequency, and the dielectric loss was around 0·003 at 100 kHz at room temperature. The dielectric constant for the Pr based oxide was also high, around 57 at 100 kHz, but was more susceptible to frequency and temperature variation. For this oxide, the dielectric loss was higher (0·013 at room temperature) and highly temperature dependant at higher temperatures (> 200). Both these oxides merit attention for their observed dielectric properties, and need to be studied further.

Acknowledgements

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