Complex rare-earth titanates with the perovskite structure: Rietveld studies and dielectric properties

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Abstract

Several new compositions of the type (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3 and (Ln1/3Ba1/3Ca1/3)(Cd1/3Ti2/3)O3 (Ln = La, Nd, Sm, Gd, Dy) pertaining to the perovskite structure have been investigated. We have also tried to substitute the cadmium site with zinc. The oxides are found to crystallize in the disordered cubic structure (by powder X-ray diffraction studies) with lattice parameters of 4.0360(6) and 3.9996(6) Å for Ln = La and Nd, respectively. Rietveld refinement of powder X-ray data of La-Cd-based oxide gave conclusive evidence in favor of the cubic perovskite structure with refined composition (La0.361(7)Ba0.690(7)Ca0.17(2))(Cd0.114(3)Ti0.886(7))O3.096(24) (a = 4.0411(26) Å, space group Pm3m, Rp = 10.40, Rwp = 13.82) for the oxide with the loaded composition (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3. Note that the composition obtained by Rietveld refinement shows lower cadmium content than the nominal compositions. The refined compositions for the oxide with the nominal composition (Ln1/3Ba1/3Ca1/3)(Cd1/3Ti2/3)O3 was (La0.36(3)Ba0.62(3)Ca0.12(1))(Cd0.146(8)-Ti0.854(8))O2.77(9) (a = 4.0304(12) Å; wRp = 0.0590, Rp = 0.0341). In case of the oxide with nominal composition (La2/5Ba2/5Ca1/5)/(Cd1/5Zn0.5/5Ti3/5)O3 the composition obtained after Rietveld studies was (La0.4Ba0.4Ca0.2)(Cd0.072(5)Zn0.128(5)Ti0.80)(0.9)O2.58(2) (a = 3.9875(18) Å, space group Pm3m; R(F2) = 0.0323, Rp = 0.0823, Rwp = 0.0965). The dielectric constant for the oxides with nominal composition (Ln1/3Ba1/3Ca1/3)(Cd1/3Ti2/3)O3 lie in the range of 35 to 50 with reasonably low loss of 0.0017 to 0.0021. The dielectric constant of the oxides with nominal composition (Ln1/3Ba1/3Ca1/3)(Cd1/3Ti2/3)O3 show higher values in the range of 57 to 80 and slightly higher loss of ~ 0.006-0.007. These oxides also show reasonable stability of the dielectric constant with temperature.

Keywords: Sintering; Rietveld studies; Perovskites; Dielectric properties

1. Introduction

The perovskite structure has been one of the most versatile structures [1,2] for tailoring the properties of materials. Oxides belonging to this structure can show properties ranging from colossal magnetoresistance (CMR), superconductivity and ferroelectricity. The ferroelectric and dielectric properties of metal oxides with the perovskite structure are of utmost importance in the electronic industry. These materials include oxides like BaTiO3, PbTiO3, SrTiO3 and their substituted derivatives. Hence, there is tremendous research activity towards discovering new dielectric materials [3-10] or to explore new properties in known materials [11-13]. Recently, quite a number of layered perovskites exhibiting dielectric [14], ferroelectric [15] and piezoelectric [16] properties have been synthesized. The perovskite structure forms the basis of several complex structures which may be due to intergrowths, oxygen deficiency or due to cation ordering [17-19]. Cation ordering can induce significant alterations in electronic and magnetic properties. Extensive research in the area of high TC superconductors [20-22] has lead to the synthesis of many new copper-based perovskites [23,24] which are nonsuperconducting. The rare earth based copper titanates of the formula Ln2Ba2Ca2Ti5O14 (Ln = La, Nd, Sm, Eu, Gd, etc.) have been synthesized recently [25,26]. The structure of these oxides can be conceived of as the intergrowth of three TiO6 octahedral and two CuO5 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. The ordered structure can be considered to be a five-layered perovskite oxide.

Materials having ions with closed shell (d') electronic configuration are known to have interesting dielectric properties, e.g., oxides of Ti', Nb' and Ta'. Since our interest was to synthesize new dielectric materials, we chose the closed shell metal ions to replace copper in the rare earth-based cuprates mentioned earlier [25,26]. The successful synthesis of the oxides Ln2Ba2CaZn2Ti3O14 [9,10], and their encouraging dielectric properties have prompted us to explore similar compounds with other closed shell metal ions in the zinc site. In this paper we report the synthesis, detailed structural characterization using Rietveld refinement of X-ray data and compositional analysis using EDX of two new families of oxides with the nominal composition (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3 and (Ln1/2Ba1/2Ca1/2)(Cd1/3Ti2/3)O3. We explored the possibility of formation of solid solutions by substituting zinc in the cadmium sites. We also report their temperature and frequency-dependent dielectric properties, which appear to be promising. Our attempts to synthesize similar phases with Ln = Sm, Gd and Dy were unsuccessful.

2. Experimental

The oxides were prepared by the ceramic method. Stoichiometric amounts of La2O3, Nd2O3, Gd2O3, Sm2O3, and Dy2O3 (CDH, 99.9%), TiO2 (Fluka, 99.99%), CaCO3 (Merek, 98.5%), BaCO3 (Loba Chemie, 99%) and CdCO3 (CDH, 99.5%) were taken. The rare-earth oxides were dried at 90 °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, 1000 °C for 24 h, 1050 °C for 6 h, 1100 °C for 4 h and at 1200 °C for 6 h with intermittent grindings after each stage of heating. The resulting powder was ground, mixed with PVA (polyvinyl alcohol) and compacted into pellets at a pressure of 8 t. The pellets were then sintered at 1200 °C for 15 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 2θ range of 10 to 70°. The raw data was subjected to background correction and to Kα2 stripping.

For Rietveld refinement of powder X-ray data, a step size of 0.02° and a step time of 8 s was used. Data was collected on a Bruker D8 Advance diffractometer. Structure refinement was done using the GSAS software [27] for Rietveld refinement. Standard procedure was followed for the refinement with La, Ba and Ca statistically allocated to the 1a site (m-3m symmetry), and Ti and Cd to the 1b site (m-3m symmetry). The final refinement cycle involved the

3. Results and discussion

Powder X-ray diffraction patterns of 'Nd'- and 'La'-based oxides heated at 900 °C shows impurities like Nd2O3, La2O3, TiO2 and cadmium oxide. For these oxides the product (perovskite phase) started to form only after heating at 1000 °C. The amounts of impurities diminish after each stage of heating and a pure phase of the oxide with the nominal composition (La2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3 was obtained at 1100 °C. At this temperature the Nd-analog was obtained with around 2-3% impurity of cadmium oxide. A pure phase could be obtained after heating further at 1200 °C for 6 h. For the other rare earth-based oxides ('Sm', 'Gd' and 'Dy') there were impurities present along with the product phase even after heating at 1200 °C. Attempts to make pure phases of the oxides based on 'Gd', 'Sm' and 'Dy' by heating to temperatures upto 1200 °C for longer durations have not met with success. The X-ray diffraction pattern of (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3 (Ln = La, Nd) could be indexed satisfactorily in a cubic structure. The lattice parameters for the pure phases were refined using a least squares fit to the observed X-ray pattern and was found to be 3.9996(6) Å for the oxide with Ln = Nd and 4.0360(6) Å for that with Ln = La. The increase in lattice parameter from Nd to La is expected because of the higher ionic radius of La3+ as compared to Nd3+. The lattice parameters for the oxides as calculated from a least squares fit of the observed powder X-ray pattern are given in Table 1.

Rietveld refinement of powder X-ray diffraction data confirmed the cubic structure for the oxide with nominal composition (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3 (a = 4.0411(26) Å, space group Pm3m). The structure refined to reasonable R factors (Table 2). The site occupancy factors for each atom was refined separately and then fixed at
from our experiments, no sign of ordering was observed. Would correspond to the five-layered and six-layered per-phase for the ABO3 structure. Note that the loaded refinement is given in Fig. 1.

The positions occupancies and the thermal parameters of X-ray diffraction data obtained for analogous ‘Zn’-based oxides [9,10]. However, till now, the six-layered titanate has not been reported. Annealing in oxygen at a temperature of 950 °C for several days followed by slow cooling was carried out to check for any possible ordering of the cations. However, there was no sign of ordering in either of the two compounds. This may be due to the preference of Cd2+ for octahedral coordination than the square pyramidal coordination, which is required in the ordered structures as has been reported [25,26] in the case of the copper-based oxide Nd2Ba2CaCu2Ti3O14.

In case of the oxides belonging to the family with the nominal composition (Ln/Ba/Ca) and two (Cd/Ti) for the B-site may lead to the presence of three different cations for the A-site (Ln/Ba/Ca) and two (Cd/Ti) for the B-site may lead to the A-site occupancy was not reported.

The results obtained by us were in accordance with those obtained for analogous ‘Zn’-based oxides [9,10]. However, from our experiments, no sign of ordering was observed. Annealing in oxygen at a temperature of 950 °C for several days followed by slow cooling was carried out to check for

the refined value. In the final refinement, the isotropic thermal parameters and the oxygen occupancy factor were refined. The positions occupancies and the thermal parameters are listed in Table 2. The final refined composition comes out to be (La0.361(7)Ba0.690(7)Ca0.17(2))(Cd0.114(3)Ti0.886(7))O3.096(24) obtained by Rietveld refinement of X-ray diffraction data.

Table 2
Positional, thermal and occupancy factors of (La0.361(7)Ba0.690(7)Ca0.17(2))(Cd0.114(3)Ti0.886(7))O3.096(24) obtained by Rietveld refinement of X-ray diffraction data.

<table>
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<tr>
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<th>Wyckoff symbol</th>
<th>Occupancy x</th>
<th>y</th>
<th>z</th>
<th>Uiso x 100</th>
<th>Atoms</th>
<th>Wyckoff symbol</th>
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<td>0.0</td>
<td>0.1239(20)</td>
<td>La</td>
<td>1a</td>
</tr>
<tr>
<td>Ba</td>
<td>1a</td>
<td>0.690(7)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1239(20)</td>
<td>Ba</td>
<td>1a</td>
</tr>
<tr>
<td>Ca</td>
<td>1a</td>
<td>0.166(20)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.239(2)</td>
<td>Ca</td>
<td>1a</td>
</tr>
<tr>
<td>Cd</td>
<td>1b</td>
<td>0.114(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.674(77)</td>
<td>Cd</td>
<td>1b</td>
</tr>
<tr>
<td>Ti</td>
<td>1c</td>
<td>0.886(7)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.674(77)</td>
<td>Ti</td>
<td>1b</td>
</tr>
<tr>
<td>O</td>
<td>1c</td>
<td>1.032(24)</td>
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<td>0.5</td>
<td>4.084(528)</td>
<td>O</td>
<td>3c</td>
</tr>
</tbody>
</table>

The structure obtained by us was in accordance with those obtained for analogous ‘Zn’-based oxides [9,10]. However, from our experiments, no sign of ordering was observed. Annealing in oxygen at a temperature of 950 °C for several days followed by slow cooling was carried out to check for

any possible ordering of the cations. However, there was no sign of ordering in either of the two compounds. This may be due to the preference of Cd2+ for octahedral coordination than the square pyramidal coordination, which is required in the ordered structures as has been reported [25,26] in the case of the copper-based oxide Nd2Ba2CaCu2Ti3O14.

In case of the oxides belonging to the family with the nominal composition (Ln1/3Ba1/3Ca1/3)(Cd1/3Ti2/3)O3 nearly pure phases (with ~ 3% impurities) were obtained at 1100°C for Ln = La and Nd. For the other rare-earth oxides (Ln = Sm, Gd and Dy) pure phases were not obtained. These oxides crystallize in the cubic perovskite structure. The lattice parameters a obtained by a least-squares fit to the observed d values are 4.0055(5) and 3.9894(6) for the oxides based on La and Nd, respectively. It is observed that the lattice parameters obtained for the above oxides is lower than those with the nominal composition (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3. This is because the average size of the A- and B-cations are much less for the above oxides than those of (Ln2/5Ba2/5Ca1/5)(Cd2/5Ti3/5)O3. As in the case of the oxides with the nominal composition (La/Ba/Ca) and two (Cd/Ti) for the B-site may lead to the presence of three different cations for the A-site (La/Ba/Ca) and two (Cd/Ti) for the B-site may lead to the A-site occupancy was not reported.

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The La, Ba and Ca ions were statistically allocated to the 1a site in the fixed ratio of 0.4:0.4:0.2. The Cd, Ti/Cd0.75/Zn0.25)(x = 0.2).

The refined composition obtained was (La0.35Ba0.35Ca0.3)(Cd0.025(7) Ti0.810(7))O2.775(27). Table 3 lists the positions Wyckoff symbols, the occupancy factors and the thermal parameters of all the atoms. The observed, calculated and the difference plot after Rietveld refinement is given in Fig. 2.

We have also substituted the cadmium site in order to obtain solid solution with zinc and cadmium in the B-sites. Thus we have tried to synthesize oxides belonging to the family with nominal composition (La2/5 Ba2/5 Ca1/5)-(Cd2/5-xZn x Ti3/5)O3 (0 < x < 0.4) by the ceramic route. It is seen from the powder X-ray diffraction patterns that solid solutions are formed for the entire range of composition and all the oxides crystallize in the cubic structure. Thus, the amount of cadmium is much less than the loaded composition and is consistent with the results obtained in the two Rietveld refinement studies discussed earlier. The positional, thermal and occupancy factors are given in Table 4.

Table 3
Positional, thermal and occupancy factors of (La0.35 Ba0.35 Ca0.31)-(Cd0.025(7) Ti0.810(7))O2.775(27) as obtained by refinement of X-ray diffraction data

<table>
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<th>Atom</th>
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<th>y</th>
<th>z</th>
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<th>( U_{iso} \times 100 )</th>
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</thead>
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<td>0.75(21)</td>
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<tr>
<td>Cd</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.025(7)</td>
<td>1.264(89)</td>
</tr>
<tr>
<td>Ti</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.810(7)</td>
<td>1.264(89)</td>
</tr>
<tr>
<td>Zn</td>
<td>3c</td>
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<td>0.935(27)</td>
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Space group \( Pn\bar{3}m \), \( a = 4.0119(12) \text{ Å}, wRp = 0.0866, Rp = 0.0737.\)

Fig. 2. Observed, calculated and difference plot of (La0.35 Ba0.37 Ca0.31)-(Cd0.025(7) Ti0.810(7))O2.775(27) obtained by Rietveld refinement of powder X-ray data.

Fig. 3. (a) Variation of lattice parameter \( a \) for (La2/5 Ba2/5 Ca1/5)-(Cd2/5-xZn x Ti3/5)O3 as a function of x. (b) Observed, calculated and difference pattern of the oxide with refined composition (La0.4 Ba0.4 Ca0.2)-(Cd0.072 Zn0.128 Ti0.872) O2.58 obtained by Rietveld refinement of powder X-ray data.

Table 4
Positional, thermal and occupancy factors of (La0.4 Ba0.4 Ca0.2)(Cd0.072-Zn0.128 Ti0.872) O2.58 \( ^{+1+} \) refinement of powder X-ray data

<table>
<thead>
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<th>Atoms</th>
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<th>y</th>
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<th>( U_{iso} \times 100 )</th>
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<td>0.062(9)</td>
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<td>0.155(20)</td>
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<td>0.5</td>
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<td>0.155(20)</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.31(7)</td>
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</table>

\( a = 3.9875(18) \text{ Å}, \) space group \( Pn\bar{3}m \), \( R(F^2) = 0.0323, \) \( Rp = 0.0823, Rwp = 0.0965. \)

tors the 1b and 3c sites. The refinement yielded satisfactory \( R \) values of 0.0823, using the cubic perovskite as the structural model. The refined composition obtained was (La0.4 Ba0.4 Ca0.2)(Cd0.072-Zn0.128(5) Ti0.872(5))O2.58(2). Thus, the amount of cadmium is much less than the loaded composition and is consistent with the results obtained in the two Rietveld refinement studies discussed earlier. The positional, thermal and occupancy factors are given in Table 4. The observed, calculated and the difference plots obtained after the refinement is shown in Fig. 3(b).
Fig. 4. Scanning electron micrographs of oxides with nominal compositions \((\text{Ln}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_{3/5})\text{O}_{14}\). (a) \(\text{Ln} = \text{Nd}\), (b) \(\text{Ln} = \text{La}\) and \((\text{Ln}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_{3}\). (c) \(\text{Ln} = \text{La}\), (d) \(\text{Ln} = \text{Nd}\), (e) \((\text{La}_{2/5}\text{B}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{1/5}\text{Z}_{1/5}\text{Ti}_{3/5})\text{O}_{3}\).

Scanning electron microscopy of the oxides with the nominal composition \((\text{Ln}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_{3/5})\text{O}_{3}\) has been obtained from pellets sintered at 8t pressure (Fig. 4(a) and 4(b)). It is observed that the materials are highly dense and do not have well-defined shape and grain boundaries. This is probably because of partial melting of the grains at the high temperature of around 1200 °C. The Nd-based oxide shows bigger grains (2-4 um) while the grain size of the La-based is smaller (1-2 um). The scanning electron micrographs of the oxides with the nominal composition \((\text{Ln}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_{3}\) are shown in Fig. 4(c) and 4(d) for the oxides with \(\text{Ln} = \text{La}\) and \(\text{Nd}\), respectively. There is partial melting of grains for the La-based oxide and the grain size obtained is 1-2 um. The melting of the grains become more pronounced and made it difficult to calculate the grain size for the analogous Nd-based oxide. The SEM of the oxide \((\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{1/5}\text{Z}_{1/5}\text{Ti}_{3/5})\text{O}_{3}\) shows nearly spherical grains of sizes 0.5 to 2 um (Fig. 4(e)). Note that for the oxide with \(x = 0.4\) \((\text{Nd}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Zn}_{2/5}\text{Ti}_{3/5})\text{O}_{3}\) the grain size was much larger (4 um) [20].

Energy dispersive analysis of X-rays (EDX) has been carried out on the above compositions. The quantitative analysis was carried out by using the ZAF procedure (3 iterations). All the elements were analysed and the results normalized. The calculated compositions were \((\text{La}_{0.52(1)}\text{Ba}_{0.48(1)}\text{Cd}_{0.25(1)})(\text{Ti}_{0.65(1)}\text{O}_{2.85(1)})\) and \((\text{Nd}_{0.48(1)}\text{Ba}_{0.45(1)}\text{Ca}_{0.18(1)})(\text{Zn}_{0.62(1)}\text{Ti}_{0.25(1)})\). The larger concentration of \(\text{Ln/ Ba/ Ca}\) ions in the above oxides and low cadmium content suggests that part of the A-site ions \((\text{Ln/ Ba/ Ca})\) may be occupying the B-sites of the above oxides. However, the composi-
tion of the La-based oxide as obtained from Rietveld refinement was \((\text{La}_{0.36(3)}\text{Ba}_{0.62(3)}\text{Ca}_{0.12(1)})(\text{Cd}_{0.146(8)}\text{Ti}_{0.854(8)})\text{O}_{2.77(9)}\) suggesting higher cadmium content as compared to the EDX data.

The EDX analyses of the oxides with nominal composition \((\text{Ln}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_3\) show that these oxides have practically very little 'Cd' as is the case with the oxides of the composition \((\text{Ln}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_3/5)\text{O}_3\). The calculated composition from the EDX analysis for the La-based oxide is \((\text{La}_{0.41(1)}\text{Ba}_{0.43(1)}\text{Ca}_{0.38(1)})(\text{Cd}_{0.004(1)}\text{Ti}_{0.7(1)})\text{O}_{2.84(1)}\). Thus, the cadmium present is less than 1%, which is the accuracy limit of EDX data. From Rietveld refinement of X-ray data of the La-based composition a composition of \((\text{La}_{0.35}\text{Ba}_{0.37}\text{Ca}_{0.31})(\text{Cd}_{0.025(7)}\text{Ti}_{0.810(7)})\text{O}_{2.775(27)}\) was obtained. So there is some difference in the two compositions especially with respect to titanium occupancy. However, both EDX and Rietveld studies show that cadmium content is much lower than that expected in the nominal composition. EDX analysis of the oxide with the nominal composition \((\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{1/3}\text{Zn}_{1/3}\text{Ti}_{3/5})\text{O}_3\) yielded the composition \((\text{La}_{0.41(1)}\text{Ba}_{0.40(1)}\text{Ca}_{0.32(1)})(\text{Cd}_{0.06(1)}\text{Zn}_{0.11(1)}\text{Ti}_{0.58(1)})\text{O}_{2.67(1)}\). The composition obtained from Rietveld refinement was \((\text{La}_{0.36(3)}\text{Ba}_{0.62(3)}\text{Ca}_{0.12(1)})(\text{Cd}_{0.146(8)}\text{Ti}_{0.854(8)})\text{O}_{2.77(9)}\). Thus, there is a close agreement between the composition obtained by Rietveld refinement and EDX analysis.

The dielectric properties of the above oxides have been measured on sintered disks in the frequency range of 50 Hz to 500 kHz. Dielectric measurements have also been carried out as a function of temperature in the range of 35 (room temperature) to 300 °C. All these compounds have shown encouraging dielectric properties. The oxide \((\text{Nd}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/3}\text{Ti}_{3/5})\text{O}_3\) was found to have a dielectric constant \((\varepsilon)\) of around 50 at 100 kHz. It also showed a reasonably low dielectric loss of 0.0021 (Fig. 5(a)). The dielectric constant \((\varepsilon)\) was found to be highly stable with frequency in the entire frequency range studied. It shows a marginal rise beyond 400 kHz and has a value of 52 at 500 kHz \((d\varepsilon/dF = 5.335 \times 10^{-6})\). The dielectric loss \((D)\) showed a rise and has a value of 0.05 at 500 kHz (Fig. 5(a)). The dielectric constant \((\varepsilon)\) is highly temperature stable and varies between 49 and 50 in the temperature range of 35 to 300 °C. The dielectric loss \((D)\) decreases till a frequency of 3 kHz, beyond which it remains high and shows a rise (inset of Fig. 5(a)). The oxide with the composition \((\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_{3/5})\text{O}_3\), shows a dielectric constant \((\varepsilon)\) of 35 at 100 kHz and a dielectric loss \((D)\) of 0.0017 at 100 kHz at room temperature \((35 °C)\) (Fig. 5(b)). The dielectric constant is stable in a frequency range from 3 to 500 kHz. The dielectric loss shows a sharp increase and rises to 0.06 at 500 kHz. The dielectric properties have also been studied with respect to temperature in the range of 35 to 300 °C. It is seen that the dielectric constant \((\varepsilon)\) is highly stable with temperature and varies from 32 to 35 at 100 kHz in the range of temperature studied (inset of Fig. 5(b)). The dielectric loss is reasonably stable till 200 °C, beyond which it shows an increase and has a value of 0.0027 at 100 kHz. Similar increase in the dielectric loss was observed in the Nd composition, too (inset of Fig. 5(a)).

![Fig. 5. Variation of dielectric constant (a) and dielectric loss (b) with frequency for the oxide having nominal composition of (La2/5Ba2/5Ca1/5)(Cd1/3Ti3/5)O3. (a) Ln = Nd, (b) Ln = La. Inset shows variation of dielectric properties with temperature at 100 kHz for both these oxides.](image1)

![Fig. 6. Variation of dielectric constant (a) and dielectric loss (b) for the oxide having the nominal composition (La2/5Ba2/5Ca1/5)(Cd1/3Ti3/5)O3 with frequency at room temperature.](image2)
0.007. The behavior of the dielectric properties of the oxide \((\text{La}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_3\) with temperature is interesting. The variation of dielectric properties with temperature at different frequencies is shown in Fig. 7. It is found that the dielectric constant shows a maximum and the dielectric loss a minimum at the same temperature of 50 °C. This behavior is observed at all frequencies till 300 kHz (see Fig. 7(a) and 7(b)). The minimum in the dielectric loss becomes less pronounced at 300 kHz (Fig. 7(b)). From 400 kHz onwards, the maximum in the dielectric constant is still observed at 50 °C. However, the minimum in the dielectric loss is no more observed and the loss steadily increases with increasing temperature (Fig. 7(c)).

For the compound with the loaded composition \((\text{Nd}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_3\), the dielectric constant at room temperature and at 100 kHz is found to be 85, while the dielectric loss is 0.006. The dielectric constant remains fairly stable with frequency. The dielectric loss steadily decreases till 3 kHz and then remains almost constant around 0.006 till 200 kHz (Fig. 8). For the entire temperature range the dielectric loss was reasonably low ~ 0.005-0.008 (Fig. 8(b)). Thus it is seen that the dielectric constant of the oxides with the nominal composition \((\text{Ln}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_3\) is higher than that of \((\text{Ln}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_{3/5})\text{O}_3\). Table 5 gives the details of the dielectric properties for comparison. Since there is very little cadmium in the B-sites, as is evident from our EDX data, the B-sites are partially vacant. The partial occupancy of the B-sites by Ti\(^{4+}\) ions is more for the oxides with composition \((\text{Ln}_{1/3}\text{Ba}_{1/3}\text{Ca}_{1/3})(\text{Cd}_{1/3}\text{Ti}_{2/3})\text{O}_3\). Thus, the higher amount vacancies in the \((\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{2/5}\text{Ti}_{3/5})\text{O}_3\) oxides may probably be responsible for the lower dielectric constant in these oxides.

The dielectric measurement of the compounds (with zinc substitution), \((\text{La}_{2/5}\text{Ba}_{2/5}\text{Ca}_{1/5})(\text{Cd}_{(2-x)}\text{Zn}_x\text{Ti}_{3/5})\text{O}_3\) has been carried out in detail. It is seen that there is a regular increase in the dielectric constant with increase in the amount of zinc. However, the dielectric loss increases and attains the maximum value of 0.007 at \(x = 1.5\), and then falls off sharply to 0.003 for the oxide with \(x = 2\). The varia-
tion of dielectric constant and dielectric loss with $x$ is shown in Fig. 9. It is seen that all the oxides possess a reasonably low dielectric loss in the range of 0.002-0.007. The oxide (La$_{2/5}$Ba$_{2/5}$Ca$_{1/5}$)(Cd$_{2/5}$Ti$_{3/5}$)O$_3$ ($x = 1$) has a dielectric constant of 52 and a dielectric loss of 0.004 at 35 °C and 100 kHz. The dielectric constant is highly stable with frequency from 250 Hz to 500 kHz (Fig. 10). The dielectric constant is found to be exceptionally stable with temperature in the entire range of 35 to 300 °C, and remains around 52 (Fig. 10(b)). However, the dielectric loss shows a regular increase with increase of temperature.

Thus all the oxides discussed above have been found to have high dielectric constant > 30 and a very low loss ~ 0.002. Thus they add to the limited number of dielectric oxides which have dielectric constant above 30 and are nonferroelectric. These compounds include Ba$_6$-3x(Nd, Bi)$_8$+2xTi$_{18}$O$_{54}$ ($x = 2/3, 0 < y < 0.2$) [6] and CaCu$_3$Ti$_4$O$_{12}$ [11-13]. Recently, oxides related to those discussed here like Ln$_2$Ba$_2$CaZnTiO$_{14}$ [9,10] have also shown high dielectric constant coupled with low loss. None of these oxides show any ferroelectric behavior. The temperature and frequency stability of the dielectric constant in these oxides make them potential candidates for use in the microwave region provided other aspects like low thermal expansion, high mechanical strength and ease of thin film fabrication are found suitable for use in the electronic industry.

### 4. Conclusion

Synthesis of several new compositions in which the B-site of the perovskite structure is substituted by cadmium and zinc has been attempted. All the oxides crystallize in the cubic structure with lattice parameter ~ 4.00 Å. The lattice parameter $a$ for these oxides was found to be close to 4.00 Å. The lattice parameters obtained for the oxides with nominal composition (Ln$_{1/3}$Ba$_{1/3}$Ca$_{1/3}$)(Cd$_{1/3}$Ti$_{2/3}$)O$_3$ are smaller than those of (Ln$_{2/5}$Ba$_{2/5}$Ca$_{1/5}$)(Cd$_{2/5}$Ti$_{3/5}$)O$_3$ [7].

Table 5

<table>
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<tr>
<th>Composition</th>
<th>$\varepsilon$</th>
<th>$D$</th>
<th>$d\varepsilon/dF$ (Hz$^{-1}$)</th>
<th>$d\varepsilon/dT$ ($^\circ$C$^{-1}$)</th>
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<tr>
<td>(La$<em>{2/5}$Ba$</em>{2/5}$Ca$<em>{1/5}$)(Cd$</em>{2/5}$Ti$_{3/5}$)O$_3$</td>
<td>35</td>
<td>0.0017</td>
<td>1.13 $\times 10^{-6}$</td>
<td>5.1 $\times 10^{-6}$</td>
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<tr>
<td>(Nd$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{2/5}$Ti$_{3/5}$)O$_3$</td>
<td>50</td>
<td>0.002</td>
<td>5.33 $\times 10^{-6}$</td>
<td>3.77 $\times 10^{-6}$</td>
</tr>
<tr>
<td>(La$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{1/3}$Ti$_{2/3}$)O$_3$</td>
<td>57</td>
<td>0.007</td>
<td>0.9 $\times 10^{-6}$</td>
<td>2.2 $\times 10^{-6}$</td>
</tr>
<tr>
<td>(Nd$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{1/3}$Ti$_{3/5}$)O$_3$</td>
<td>85</td>
<td>0.006</td>
<td>0.3 $\times 10^{-5}$</td>
<td>1.24 $\times 10^{-5}$</td>
</tr>
<tr>
<td>(La$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{1/3}$Zn$<em>{1/3}$Ti$</em>{3/5}$)O$_3$</td>
<td>52</td>
<td>0.005</td>
<td>1.23 $\times 10^{-5}$</td>
<td>9.7 $\times 10^{-5}$</td>
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<tr>
<td>(La$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{1/3}$Zn$<em>{1/3}$Ti$</em>{3/5}$)O$_3$</td>
<td>58</td>
<td>0.004</td>
<td>1.41 $\times 10^{-5}$</td>
<td>1.6 $\times 10^{-5}$</td>
</tr>
<tr>
<td>(La$<em>{1/3}$Ba$</em>{1/3}$Ca$<em>{1/3}$)(Cd$</em>{1/3}$Zn$<em>{1/3}$Ti$</em>{3/5}$)O$_3$</td>
<td>50</td>
<td>0.007</td>
<td>3.23 $\times 10^{-5}$</td>
<td>1.41 $\times 10^{-5}$</td>
</tr>
</tbody>
</table>

Table 5: A comparison of the dielectric properties of the various oxides obtained as single phases with nominal composition (La$_{2/5}$Ba$_{2/5}$Ca$_{1/5}$)(Cd$_{2/5}$Ti$_{3/5}$)O$_3$, (Nd$_{1/3}$Ba$_{1/3}$Ca$_{1/3}$)(Cd$_{2/5}$Ti$_{3/5}$)O$_3$, (La$_{1/3}$Ba$_{1/3}$Ca$_{1/3}$)(Cd$_{1/3}$Ti$_{2/3}$)O$_3$ and (La$_{2/5}$Ba$_{2/5}$Ca$_{1/5}$)(Cd$_{1/3}$Zn$_{1/3}$Ti$_{3/5}$)O$_3$.

e—dielectric constant, $D$—dielectric loss.
with frequency and temperature. The dielectric constant of the oxides are in the range of 35-85 and the loss values are low (0.002 to 0.006). The oxides with the nominal composition \((\text{Ln1/3Ba1/3Ca1/3})(\text{Cd1/3Ti2/3})\text{O3}\) show a higher value of dielectric constant as compared to the oxides with nominal composition of \((\text{Ln2/5Ba2/5Ca1/5})(\text{Cd2/5Ti3/5})\text{O3}\). The dielectric loss was also marginally higher for the oxides with the nominal composition \((\text{Ln1/3Ba1/3Ca1/3})(\text{Cd1/3Ti2/3})\text{O3}\). In case of the solid solutions, there is an increase in dielectric constant with increase in zinc content.

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**References**