

## **Stability of Mixed Perovskite Proton Conductors**

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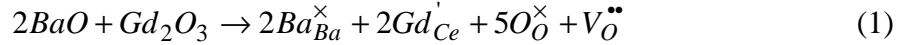
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## ABSTRACT

Rare earth oxide doped  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$  are known to be proton conductors at elevated temperatures. Rare earth oxide doping creates oxygen vacancies. Heating in water vapor leads to the absorption of water and the introduction of protons into the structure. However, both  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$  are unstable at low temperatures with respect to constituent oxides, as well as in the presence of water. Many mixed perovskites of the general formula  $\text{AB}'_{1/2}\text{B}''_{1/2}\text{O}_3$  where the valences of A, B', and B'' are respectively +2, +3, and +5; and of the type  $\text{AB}_{1/3}\text{B}''_{2/3}\text{O}_3$  where the valence of B is +2 are also known to be proton conductors. Oxygen vacancies can be introduced with an appropriate deviation in stoichiometry on the B-sublattice. It has been observed that mixed perovskites are in general more stable. Their stability is investigated using the molten salt method and by exposure to water. Their enhanced stability is rationalized on the basis of their Madelung energies.

## I. INTRODUCTION

Many rare earth oxide-doped perovskites such as BaZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaCeO<sub>3</sub> and SrCeO<sub>3</sub> exhibit protonic conduction in a moist environment over a wide range of temperatures [1-15]. These protonic conductors are potential candidates as solid electrolytes in fuel cells since fuel dilution can be prevented due to water formation at the cathode instead of at the anode. Doping with rare earth oxides creates oxygen vacancies by a reaction of the following type:

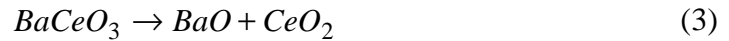


When an oxygen deficient perovskite is heated in a water-containing environment, protons are formed by the absorption of water, as given by:

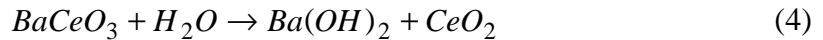


Proton conduction occurs by hopping between two adjacent oxygen ions; that is by the Grotthus mechanism. Widespread application of these proton conductors requires that they exhibit adequate protonic conductivity, and stability in the application environment.

Some of the highest protonic conductivity is exhibited 20 mole % Gd-doped BaCeO<sub>3</sub>, a material which has been extensively investigated [4, 7-9]. Many researchers have examined protonic conductivity of BaCeO<sub>3</sub> containing several dopants at various concentrations. But relatively few studies on the stability have been reported. Thermodynamic measurements have shown that below ~630°C, the  $\Delta G^\circ$  for the reaction



is negative indicating instability of BaCeO<sub>3</sub> [16]. In the presence of water, the reaction



is favored at low temperatures [17]. For example, BaCeO<sub>3</sub> doped with 20 mole % Gd rapidly decomposes when boiled in water [18-20]. Recent work has shown that 20 mole % Gd-doped BaCeO<sub>3</sub> is also unstable in water vapor ( $p_{H_2O} = 0.0964$  atm) at 200°C [19,20]. Devices such as fuel cells are expected to undergo several heating and cooling cycles during their entire useful life. Thus, despite its stability at elevated temperature (600°C), degradation is expected at lower temperatures. The damage caused by the decomposition of BaCeO<sub>3</sub> at lower temperatures is cumulative since the reverse reaction (the formation of dense BaCeO<sub>3</sub>) would require resintering; a process that cannot be accomplished at temperatures typically lower than ~1500°C, which is well above the operating temperature range of all the devices of interest.

Several compounds of the type AB'<sub>1/2</sub>B''<sub>1/2</sub>O<sub>3</sub> or AB<sub>1/3</sub>B''<sub>2/3</sub>O<sub>3</sub> where B' = trivalent ion, B'' = pentavalent ion, B = divalent ion and A = divalent ion are known to form the perovskite

structure. Oxygen vacancies may be introduced by an appropriate deviation in stoichiometry on the B-sublattice. Nowick and coworkers [21-25] have examined proton conduction in mixed perovskites of type  $A_2B'_{(1+x)}B''_{(1-x)}O_{(6-\delta)}$  with  $A = \text{Ba}$  or  $\text{Sr}$ ,  $B' =$  trivalent ion, and  $B'' =$  pentavalent ion; and in compounds of the type  $A_3B_{(1+x)}B''_{(2-x)}O_{(9-\delta)}$  where  $B =$  divalent ion and  $B'' =$  pentavalent ion with off-stoichiometric  $\text{Ba}_3\text{CaNb}_2\text{O}_9$  [ $\text{BaCa}_{1/3}\text{Nb}_{2/3}\text{O}_3$ ] exhibiting higher protonic conductivity than Nd-doped  $\text{BaCeO}_3$ . No information has been reported on the stability of these materials. The objective of the present work was to investigate the stability of mixed perovskites.

## II. THERMODYNAMIC STABILITY

The stability of the perovskite structure has often been rationalized in terms of a parameter, termed Goldschmidt tolerance factor,  $t$ , which is based on the ionic radii of the ions comprising the unit cell defined as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (5)$$

where,  $r_A$ ,  $r_B$ , and  $r_O$  are the ionic radii of A, B and O ions, respectively [26-29]. The tolerance factor is 1.0 for the ideal perovskite structure. The closer the  $t$  is to unity, the greater is the stability of the perovskite structure. For example,  $\text{BaTiO}_3$  has a tolerance factor over 0.97 and it is stable over a wide temperature range.  $\text{BaCeO}_3$ , on the other hand, has a tolerance factor of  $\sim 0.89$ , and is unstable at low temperatures [16].

The cohesive energy is an important parameter which determines the stability of a structure. Madelung energy is the dominant part of the cohesive energy of compounds with predominantly ionic bonding. The repulsive contribution is typically  $\sim 10\%$  of the Madelung energy (in magnitude). As a result, the cohesive energy is  $\sim 90\%$  of the Madelung energy. For the  $A^{+2}B^{+4}O^{2-}_3$  perovskite, the Madelung energy (a negative quantity) is inversely proportional to the lattice parameter. Thus, the smaller the lattice parameter, the greater should be the stability.  $\text{BaTiO}_3$  with a lattice parameter of  $4.031 \text{ \AA}$  is expected to be more stable than  $\text{BaCeO}_3$  with a lattice parameter of  $4.377 \text{ \AA}$ . Nakamura [30] and Kimizuka et. al. [31] have examined the stability of a number of perovskites on the basis of their Madelung energies.

In mixed perovskites, the B-site is occupied by two different ions. A tolerance factor may be defined in terms of the average radius of ions occupying the B-site. In the mixed perovskites with the B-site is occupied by ions of different valences, there should be an additional

contribution to the Madelung energy [32-34]. The rationale can be described using a simple, one-dimensional lattice.

For a linear crystal, which consists of ions with charge  $q_1$  and  $q_2$  ( $n$  is a positive integer) placed on alternate sites at an interionic distance of  $a$ , the Madelung energy per ion is readily shown to be given by [35]

(6)

where

(7)

$M$  is the Madelung constant. For a linear crystal wherein there are two cations of valence  $+n$  and  $+m$  (with  $n > m$ ) on alternate cation sites, and there are two anions of valence  $-n$  and  $-m$  (with  $n > m$ ) on alternate anion sites, it can be easily shown that the Madelung energy, defined per ion, is given by [34]

(8)

where

(9)

$M$  is the Madelung constant, which is clearly greater than  $M_0$  for a linear crystal with cations of valence  $+n$  and anions of valence  $-n$ . A larger Madelung constant where cations and/or anions of two different valences occupy the respective sites indicates a greater stability of such a structure. Clearly, the larger the difference in valences of the ions occupying a given site, the greater should be the stability.

This logic was extended to the three dimensional perovskite lattice. In order to estimate the Madelung energies of mixed perovskites, a program in C was written. The following steps were used in calculating the Madelung energy.

- (1) The crystal was simulated using an equivalent cubic lattice parameter.
- (2) The two B site elements were dispersed randomly or in an ordered manner, as desired, for the mixed perovskites.
- (3) In the case of doped perovskites with an average B-site valence less than four, the dopant  $X$  was randomly dispersed in appropriate proportions and oxygen vacancies were added to maintain charge neutrality and site balance.

- (4) Finally, the electrostatic interactions were calculated by summing up over a crystal large enough so that convergence of the Madelung energy to the second decimal (in electron volts) was obtained.

Table I shows the calculated values of the Madelung energy for  $\text{BaEr}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (B-site ordered) with a lattice parameter of 4.304 Å, and for  $\text{BaCa}_{1/2}\text{Mo}_{1/2}\text{O}_3$  (B-site ordered) with a lattice parameter of 4.162 Å [36]. The table also gives the corresponding values of Madelung energies for (hypothetical)  $\text{ABO}_3$  compounds of the corresponding lattice parameters. As expected, it is seen that the Madelung energy for the mixed perovskite structure ( $\text{BaEr}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ) (-166.94 eV) is lower than that for the simple perovskite structure (-165.64 eV) having the same lattice parameter of 4.304 Å. The difference in the energies is on the order of -124 kJ/mole which is large enough to influence the stability.

### III. EXPERIMENTAL PROCEDURE

Sample Preparation: RE-doped  $\text{BaCeO}_3$  powders were made of stoichiometry:  $\text{BaCe}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ , where RE is a rare earth, and x is the site fraction occupied by the dopant. Gd and La were used as the RE with x varying between 0.05 and 0.3. Mixtures of  $\text{BaCO}_3$ ,  $\text{CeO}_2$  and the dopants in their respective oxide forms were calcined in air at 1450°C for 6 hrs. Gd-doped  $\text{BaPrO}_3$  powder was made in a similar manner by calcining at 1350°C.

For mixed perovskites of the type  $\text{AB}'_{1/2}\text{B}''_{1/2}\text{O}_3$ , Ba was the divalent element A, with Er, Gd, Yb or La as the trivalent element (B'), and Ta or Nb as the pentavalent element (B''). The materials from this group were made by mixing  $\text{BaCO}_3$  and the respective oxides ( $\text{Gd}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  in the case of  $\text{BaGd}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ) in proper proportions and calcining them at 1450°C for 6 hrs.

Stability in a Water-containing Atmosphere: All calcined powders were boiled in water for few hours to a few days in order to study their stability in water.

Materials Characterization: All powders in the as-calcined state as well as after boiling in water were examined by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation.

#### IV. RESULTS AND DISCUSSION

All doped  $\text{BaCeO}_3$  powders used in the present study decomposed into  $\text{Ba(OH)}_2$  and  $\text{CeO}_2$  (doped  $\text{CeO}_2$  in the case of doped  $\text{BaCeO}_3$ ), after boiling in water for a few hours, in accord with prior work [19]. Similarly, 15 mole % Gd-doped  $\text{BaPrO}_3$  was also found to be unstable in boiling water. However, none of the mixed perovskites synthesized decomposed even after boiling in water for 5 days. This demonstrates that the mixed perovskites are stable in water, unlike  $\text{BaCeO}_3$ .

The tolerance factors for simple and mixed perovskites are listed in Table II. For the calculation of tolerance factors for mixed perovskites, the radius for the B-site ion was taken as the arithmetic average of radii of B' and B'' ions.  $\text{BaZrO}_3$  and  $\text{BaTiO}_3$  with tolerance factors of 0.92 and 0.97, respectively, are stable with respect to the constituent oxides over a wide temperature range, and are also stable in boiling water. By contrast,  $\text{BaCeO}_3$  and  $\text{BaPrO}_3$ , both with a tolerance factor of about 0.89, are unstable with respect to constituent oxides (as evidenced by their decomposition in a molten salt bath in prior work) and in boiling water. It is to be noted that  $\text{BaCeO}_3$  and  $\text{BaPrO}_3$  also have substantially higher Madelung energies (lower  $|\text{Madelung energy}|$  since  $\text{Madelung energy} < 0$ ) compared to  $\text{BaTiO}_3$  and  $\text{BaZrO}_3$ . An examination of Table II shows that all mixed perovskites are stable in boiling water. Several of the mixed perovskites have tolerance factors about the same as  $\text{BaCeO}_3$  and  $\text{BaPrO}_3$ . For example,  $\text{BaGd}_{1/2}\text{Nb}_{1/2}\text{O}_3$  has about the same tolerance factor as  $\text{BaPrO}_3$ ; the former is stable in water while the latter is not. In addition, recent work has shown that  $\text{BaGd}_{1/2}\text{Nb}_{1/2}\text{O}_3$  can be synthesized in a molten salt at  $350^\circ\text{C}$  from precursors but  $\text{BaPrO}_3$  can not [37]. Table II shows that the Madelung energy of  $\text{BaGd}_{1/2}\text{Nb}_{1/2}\text{O}_3$  is lower than that of  $\text{BaPrO}_3$  by 1.48 eV (if disordered) or by 1.95 eV (if ordered). Thus, the enhanced stability of  $\text{BaGd}_{1/2}\text{Nb}_{1/2}\text{O}_3$  compared to  $\text{BaPrO}_3$  despite the same tolerance factor can be attributed in part to its lower Madelung energy (higher  $|\text{Madelung energy}|$  or a higher Madelung constant).

As mentioned earlier, off-stoichiometric  $\text{Ba}_3\text{CaNb}_2\text{O}_9$  [ $\text{Ba}_3\text{Ca}_{(1+x)}\text{Nb}_{(2-x)}\text{O}_{(9-\delta)}$ ] exhibits excellent proton conductivity [22]. The present calculations show that its Madelung energy is lower than a simple  $\text{ABO}_3$  perovskite of the same lattice parameter. Recent work has also shown that it can be readily synthesized using the molten salt method, thus confirming its low temperature stability [37]. This suggests that  $\text{Ba}_3\text{Ca}_{(1+x)}\text{Nb}_{(2-x)}\text{O}_{(9-\delta)}$  may be a potential candidate as a proton conducting solid electrolyte for solid oxide fuel cells.

## V. SUMMARY

Several simple perovskites such as  $\text{BaCeO}_3$ ,  $\text{BaPrO}_3$ , and mixed perovskites of the type  $\text{BaB}'_{1/2}\text{B}''_{1/2}\text{O}_3$  where  $\text{B}' = \text{Er, Gd, La, or Yb}$ , and  $\text{B}'' = \text{Nb or Ta}$ , were synthesized by calcining mixtures of precursors in air. All synthesized materials exhibited the perovskite structure. When boiled in water for a couple of hours, both  $\text{BaCeO}_3$  and  $\text{BaPrO}_3$  decomposed to form  $\text{Ba(OH)}_2$  and the respective oxide. However, none of the mixed perovskites decomposed even after boiling for several days. Madelung energies for the simple perovskites as well as for the mixed perovskites were computed. The Madelung energy of mixed perovskites was lower ( $|\text{Madelung energy}|$  was higher since  $\text{Madelung energy} < 0$ ) than of  $\text{ABO}_3$  of the same lattice parameter. Lower Madelung energy of mixed perovskites is attributed to lower repulsive electrostatic interaction between ions of different valence, that is  $+2$  and  $+5$ , as compared to ions of valence  $+4$ . The higher stability of mixed perovskites, including that of  $\text{Ba}_3\text{Ca}_{(1+x)}\text{Nb}_{(2-x)}\text{O}_{(9-\delta)}$ , was attributed in part to their lower Madelung energies. Based on the published report of excellent proton conductivity [22] and the observed stability in the present work, off-stoichiometric  $\text{Ba}_3\text{Ca}_{(1+x)}\text{Nb}_{(2-x)}\text{O}_{(9-\delta)}$  appears to be a good candidate as a proton conductor for applications in SOFC.

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Table I: Madelung Energies for a Simple and an Ordered Mixed Perovskite

Perovskite	Equivalent Cubic Lattice Parameter (Å)	Madelung energy (eV)		Difference in	
		for AB <sub>1/2</sub> B <sub>1/2</sub> O <sub>3</sub> structures	ABO <sub>3</sub>	AB <sub>1/2</sub> B <sub>1/2</sub> O <sub>3</sub> & ABO <sub>3</sub> structures (eV)	(kJ/mole)
BaEr <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	4.304	-166.94	-165.64	-1.3	-124.9
BaCa <sub>1/2</sub> Mo <sub>1/2</sub> O <sub>3</sub>	4.162	-176.63	-171.29	-5.34	-516.5

Table II: Madelung Energies and Tolerance Factors for Simple and Mixed Perovskites

Perovskite	B Site Ionic Radius (Å)	Reported Structures (from JCPDS)	Equivalent Cubic Lattice Parameter (Å)	Tolerance Factor	Madelung Energy (eV)			Stability in boiling water
					ordered	disordered		
<b>BaCeO<sub>3</sub></b>	0.94	Tetragonal Orthorhombic	4.377	0.887	-162.88		49.506	Unstable
BaPrO <sub>3</sub>	0.92	Orthorhombic	4.360	0.895	-163.52		"	Unstable
BaZrO <sub>3</sub>	0.86	Cubic	4.193	0.921	-170.03		"	Stable
BaTiO <sub>3</sub>	0.745	Cubic Tetragonal Rhombohedral Hexagonal	4.031	0.973	-176.86		"	"
BaEr <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	0.905	Cubic	4.304	0.901	-166.94	-166.31	49.885	"
BaEr <sub>1/2</sub> Ta <sub>1/2</sub> O <sub>3</sub>	0.905	Cubic	4.302	0.901	-166.99	-166.36	"	"
BaGd <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	0.929	Tetragonal	4.342	0.892	-165.47	-164.83	"	"
BaGd <sub>1/2</sub> Ta <sub>1/2</sub> O <sub>3</sub>	0.929	Tetragonal	4.339	0.892	-165.59	-164.99	"	"
BaLa <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	0.983	Monoclinic	4.395	0.87	-163.48	-162.87	"	"
BaLa <sub>1/2</sub> Ta <sub>1/2</sub> O <sub>3</sub>	0.983	Cubic Orthorhombic	4.340	0.87	-165.53	-164.92	"	"
BaYb <sub>1/2</sub> Nb <sub>1/2</sub> O <sub>3</sub>	0.894	Cubic	4.286	0.906	-167.64	-167.03	"	"
BaYb <sub>1/2</sub> Ta <sub>1/2</sub> O <sub>3</sub>	0.894	Cubic	4.337	0.906	-165.67	-165.05	"	"
BaCa <sub>1/2</sub> Mo <sub>1/2</sub> O <sub>3</sub>	0.94	Cubic	4.162	0.887	-176.63	-174.9	51.054	Not tested
BaCa <sub>1/2</sub> Te <sub>1/2</sub> O <sub>3</sub>	0.91	Cubic	4.186	0.899	-175.62	-173.8	"	Not tested
BaCa <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	0.9		4.21			-171.31	50.073	Stable