Journal of Solid State Chemistry **148,** 492–498 (1999)
Article ID jssc.1999.8485, available online at http://www.idealibrary.com on IDEAL®

Synthesis and Thermodynamic Stability of Ba$_2B'B''$O$_6$ and Ba$_3B^*B''_2$O$_9$ Perovskites Using the Molten Salt Method

Wei Meng and Anil V. Virkar[1]

Department of Materials Science and Engineering, 122 South Central Campus Drive, Rm. 304, University of Utah, Salt Lake City, Utah 84112
E-mail: anil.virkar@m.cc.utah.edu

Received May 24, 1999; in revised form July 27, 1999; accepted August 11, 1999

A number of mixed perovskites of the types Ba$_2B'B''$O$_6$ (Ba$B'_{1/2}B''_{1/2}$O$_3$) and Ba$_3B^*B''_2$O$_9$ (Ba$B^*_{1/3}B''_{2/3}$O$_3$) where B' = Gd, La, Nd, Sm, or Y; B'' = Nb and B^* = Ca were synthesized by a conventional calcination process, as well as by the molten salt method. The former consists of calcining appropriate mixtures of oxide or carbonate precursors in air at elevated temperatures (~1250°C). The latter method consists of adding appropriate mixtures of oxide or carbonate precursors to a molten salt bath at relatively low temperatures (on the order of 300 to 500°C) so that the requisite compound is formed by dissolution–reprecipitation. *X*-ray diffraction confirmed the formation of a single-phase perovskite in each case with calcination at 1250°C. In a molten salt bath, however, all except Ba$_2$LaNbO$_6$ and Ba$_2$NdNbO$_6$ formed the perovskite structure. On the contrary, powders of Ba$_2$LaNbO$_6$ and Ba$_2$NdNbO$_6$ formed by a high-temperature calcination process readily decomposed when introduced into the molten salt bath. The formation of the requisite perovskite at a temperature as low as 350°C in a molten salt suggests that: (a) The perovskite is stable at 350°C. (b) The molten salt exhibits sufficient precursor solubility for the dissolution–reprecipitation process to occur in a reasonable time. Similarly, the decomposition of Ba$_2$LaNbO$_6$ and Ba$_2$NdNbO$_6$ in a molten salt bath shows that these materials are thermodynamically unstable at the temperature of the molten salt bath.

Key Words: **mixed perovskites; proton conductors; stability; molten salt synthesis.**

INTRODUCTION

High temperature protonic conductors have a number of potential applications, including as electrolytes in fuel cells, in steam electrolysis, and in sensors. Iwahara *et al.* (1) were the first to demonstrate protonic conductivity in BaCeO$_3$ and SrCeO$_3$ doped with a number of rare earth oxide dopants. Many researchers have subsequently investigated proton conduction in a number of ABO$_3$ type perovskites containing aliovalent dopants (2–11). A partial substitution of tetravalent Ce by a trivalent rare earth creates oxygen vacancies. Subsequent heating in a moist environment leads to the dissolution of H$_2$O into the lattice, which occurs by filling up oxygen vacancies by oxygen ions and releasing quasi-free protons into the structure. The presence of quasi-free protons leads to protonic conductivity in these materials. After the original work by Iwahara *et al.* on BaCeO$_3$ and SrCeO$_3$, protonic conduction has been demonstrated in a number of perovskites, although doped BaCeO$_3$ is by far the best known perovskite proton conductor.

Recent work, however, has shown that both BaCeO$_3$ and SrCeO$_3$ are entropy-stabilized phases which are thermodynamically unstable, respectively, below ~630°C and ~366°C with respect to the constituent oxides (12). The instability of these perovskites has been demonstrated by both galvanic cell measurements and the molten salt method. Galvanic cells using BaF$_2$ and SrF$_2$ electrolytes were made for measuring, respectively, the free energies of the reactions $\mathrm{BaCO_3 + CeO_2 \rightarrow BaCeO_3 + CO_2}$ and $\mathrm{SrCO_3 + CeO_2 \rightarrow SrCeO_3 + CO_2}$. Then, using the literature data on free energies for the reactions $\mathrm{BaO + CO_2 \rightarrow BaCO_3}$ and $\mathrm{SrO + CO_2 \rightarrow SrCO_3}$, free energies for the formation of BaCeO$_3$ and SrCeO$_3$ from the respective constituent oxides were determined. In the molten salt method, the stabilities of BaCeO$_3$ and SrCeO$_3$ were examined by heating the respective perovskite powders in a molten salt bath wherein rapid kinetics in a liquid medium facilitated the attainment of the equilibrium state. These studies have shown that BaCeO$_3$ and SrCeO$_3$ are unstable in molten NaOH–KOH at the temperature of the experiments, typically ~350°C. Later work has shown that BaCeO$_3$ also reacts with H$_2$O at low temperatures by the reaction $\mathrm{BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2}$ (13–15). Since BaCeO$_3$ and SrCeO$_3$-based proton conductors are doped with RE$_2$O$_3$ (RE = rare earth), the temperature below which these materials become unstable is expected to depend on the type and the concentration of the dopant. Nevertheless, recent work has shown that all doped

---

[1] To whom correspondence should be addressed.

0022-4596/99 $30.00

$BaCeO_3$-based materials studied are unstable in boiling water and the kinetics are rather rapid (15). This is a significant problem for potential applications of $BaCeO_3$ as a solid electrolyte in fuel cells and steam electrolyzers which would be subjected to numerous thermal cycles between room temperature and the operating temperature. The destabilization and disintegration that can occur at low temperatures in the presence of water cannot be reversed unless the material is heated above about 1500°C, the typical sintering temperature, which is well above the operating temperature of any device. Thus, the damage (by reaction with water) is expected to be cumulative, and it is imperative that the prospective proton conductor be stable between room temperature and the operating temperature for application in a device.

Nowick *et al.* (16–20) have examined protonic conduction in mixed perovskites of the type $A_2B'_{(1+x)}B''_{(1-x)}O_{(6-\delta)}$, with $A = $ Sr, Ba, $B' = $ trivalent ion (Nd, Gd, Sm, La, Y), and $B'' = $ pentavalent ion (Nb), and in $A_3B^*_{(1+x)}B''_{(2-x)}O_{(9-\delta)}$, where $B^* = $ divalent ion (Ca) and $B'' = $ pentavalent ion (Nb). Nowick and Du (18) have reported that off-stoichiometric $Ba_3CaNb_2O_9$ exhibits protonic conductivity close to that for Nd-doped $BaCeO_3$. All of the materials synthesized in their work were perovskites. Samples in their study were first equilibrated in a water-vapor-containing atmosphere at a high temperature. Subsequently, protonic conductivity was measured at low enough temperatures such that proton concentration was essentially fixed and not temperature dependent. Work by Nowick *et al.* shows that many of the mixed perovskites are proton conductors. However, little is known about their thermodynamic stabilities. Any anticipated use of these materials would require a thorough knowledge of their thermodynamic stability in the application environments. Of specific interest is the stability of these mixed perovskites with respect to constituent oxides and in the presence of water.

The objective of the present work was to examine the synthesis and the stability of mixed perovskites of the type $Ba_2B'B''O_6$ ($BaB'_{1/2}B''_{1/2}O_3$) and $Ba_3B^*B''_2O_9$ ($BaB^*_{1/3}B''_{2/3}O_3$) using the molten salt method, as well as by a conventional processing method, and to investigate their stability in boiling water. The molten salt method has been used by several researchers for the synthesis of complex oxides (21–27). The molten salt method has also been recently used to investigate phase stabilities and phase equilibria (28, 29).

EXPERIMENTAL

Synthesis of Mixed Perovskites by Calcination

For synthesis using a conventional calcination process, carbonates and/or oxides of the precursors were mixed in requisite proportions. For example, Ba_2LaNbO_6 was synthesized by calcining an appropriate mixture of $BaCO_3$, La_2O_3, and Nb_2O_5 in air at 1250°C for 2 h. Similarly, $Ba_3CaNb_2O_9$ was synthesized by calcining a mixture of $BaCO_3$, $CaCO_3$, and Nb_2O_5 in air at 1250°C for 2 h. XRD traces of the as-calcined powders were obtained using $CuK\alpha$ radiation.

Experiments in a Molten Salt Bath

The objective of these experiments was to determine if the formation of $Ba_2B'B''O_6$ and $Ba_3B^*B''_2O_9$ can occur in a molten salt mixture and/or to determine the stabilities of these perovskites. In addition, selected experiments on the stability and the formation of compounds of the type $B'B''O_4$ were conducted. Two types of experiments were conducted. In one type of experiment, for example for the synthesis of $Ba_2B'B''O_6$, precursors $BaCO_3$, B'_2O_3, and B''_2O_5 in a molar ratio 4 : 1 : 1 were mixed and added to a molten salt mixture in a refractory crucible (at ~350°C). The objective of this experiment was to determine if the synthesis of $Ba_2B'B''O_6$ can be accomplished in a molten salt bath. In the other type of an experiment, $Ba_2B'B''O_6$ powder formed by solid state synthesis at 1250°C was added to a molten salt mixture to determine if the material remains stable. The prospective salt bath must satisfy the following requirements: (a) The molten salt should not react with the precursors or the final product. (b) The molten salt must exhibit some solubility for the precursors in order for the reaction to occur by dissolution and reprecipitation in a reasonable time.

Several molten salt baths have been used for the synthesis of many oxides. The two most frequently used molten salts are the LiCl–KCl eutectic and the NaOH–KOH eutectic. In the present work, the molten NaOH–KOH eutectic salt bath was found to be satisfactory for the synthesis of many materials. Hence, all molten salt experiments were conducted using the NaOH–KOH eutectic. The eutectic composition and temperature for the NaOH–KOH system are as follows: NaOH, 49 mol%; KOH, 51 mol%; and $T_{eu} = 170°C$ (30). Typically, 5 g of the requisite precursor mixture was introduced into 50 g of the molten salt eutectic. The temperature was typically maintained between 350 and 550°C, with most experiments being conducted at 350°C. All experiments were conducted in air. The typical duration of the experiment was between 12 and 24 h, after which the crucible was cooled to room temperature. The resulting mass was washed in water, and the residue was filtered, dried, and examined by X-ray diffraction (XRD).

Stability in Boiling Water

Calcined, single-phase perovskite powders were boiled in water for several days, typically one week, to investigate the stability of mixed perovskites in water. After being boiled in water, the powder samples were dried and examined by XRD.

RESULTS

Experiments on $Ba_3CaNb_2O_9$

Various experiments were conducted on $Ba_3CaNb_2O_9$. These experiments and the corresponding results are described in what follows. (a) A powder mixture of $BaCO_3$, $CaCO_3$, and Nb_2O_5 in a 3 : 1 : 1 molar proportion was calcined at 1250°C for 2 h in air. An XRD pattern of the same confirmed the formation of the perovskite phase, as shown in Fig. 1a. (b) In another experiment, 5 g of powder mixture of $BaCO_3$, $CaCO_3$ and Nb_2O_5 in 3:1:1 proportion was added to 50 g of a molten NaOH–KOH salt bath at 350°C and maintained for 16 h. The salt bath was cooled and dissolved in water. The residue was filtered, washed, dried, and examined by XRD. Figure 1b gives the corresponding XRD pattern which shows that the perovskite phase readily formed at 350°C. This suggests that the process of dissolution–reprecipitation occurs readily and that the NaOH–KOH salt bath is suitable for investigating the formation as well as the stability of the material. (c) A single-phase $Ba_3CaNb_2O_9$ powder formed by calcination at 1250°C in air for 2 h was introduced into the molten NaOH–KOH salt bath at 350°C and maintained for 16 h. Subsequently, the salt bath was cooled to room temperature and dissolved in water. The powder residue was filtered, washed, dried, and examined by XRD. Figure 1c shows the corresponding XRD trace. It is seen that the perovskite phase formed at elevated temperatures remains unaltered in the salt bath, suggesting further that the material is stable at 350°C. (d) A single-phase $Ba_3CaNb_2O_9$ powder formed by calcination in air at 1250°C was boiled in water for 1 week. The corresponding XRD trace given in Fig. 1d shows that the powder is indeed stable, unlike $BaCeO_3$ (15). Similar experiments were conducted on several other mixed perovskites, namely, Ba_2SmNbO_6, Ba_2GdNbO_6, and Ba_2YNbO_6. All of them exhibited similar behaviour.

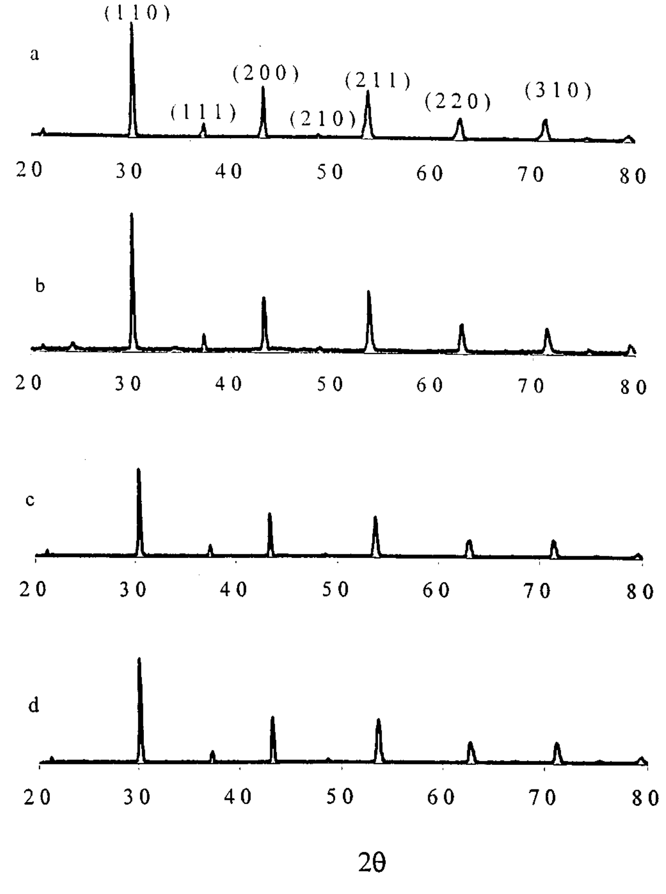

FIG. 1. (a) An XRD trace of a sample of $Ba_3CaNb_2O_9$ synthesized by calcining a mixture of $BaCO_3$, $CaCO_3$, and Nb_2O_5 at 1250°C for 2 h in air, showing the formation of a single-phase perovskite structure. (b) An XRD trace of a sample of $Ba_3CaNb_2O_9$ synthesized by placing a mixture of $BaCO_3$, $CaCO_3$, and Nb_2O_5 in molten NaOH–KOH eutectic at 350°C for 16 h in air, showing the formation of a single-phase perovskite structure. (c) An XRD trace of a sample of $Ba_3CaNb_2O_9$ synthesized in step (a) after treatment in molten NaOH–KOH salt eutectic at 350°C for 16 h. The XRD trace shows that the perovskite structure remains unaffected. (d) An XRD trace of a sample of $Ba_3CaNb_2O_9$ synthesized in step (a) after being boiled in water for 1 week showing that the structure is stable in water.

Experiments on Ba_2LaNbO_6

The following experiments were conducted on Ba_2LaNbO_6. (a) A powder mixture of $BaCO_3$, La_2O_3, and Nb_2O_5 in a 4 : 1 : 1 proportion was calcined at 1250°C for 2 h in air. The corresponding XRD trace given in Fig. 2a shows that the perovskite phase did form. (b) In another experiment, 5 g of a powder mixture of $BaCO_3$, La_2O_3, and Nb_2O_5 in a 4 : 1 : 1 proportion was introduced into 50 g of a molten NaOH–KOH salt bath and maintained at temperature for 16 h. The salt bath was cooled and dissolved in water. The residue was filtered, washed, dried, and examined by XRD. The corresponding XRD pattern is given in Fig. 2b, which shows that the perovskite phase did not form in the molten salt bath. This suggests that the perovskite phase is not stable at 350°C. An analysis of the XRD trace shows the presence of BaO and tetragonal $LaNbO_4$. (c) A few grams of a powder of single-phase Ba_2LaNbO_6 synthesized by calcining at 1250°C in step (a) was introduced into a molten salt bath and maintained at 350°C for 16 h. An XRD trace obtained on washed and dried residue is shown in Fig. 2c. It is seen that the perovskite structure is unstable and readily decomposes. An analysis of the XRD trace shows the presence of BaO and $LaNbO_4$. This suggests that Ba_2LaNbO_6 is thermodynamically unstable at 350°C with respect to BaO and $LaNbO_4$. (d) A single-phase Ba_2LaNbO_6 powder formed in step (a) was boiled in water for 1 week. The corresponding XRD pattern given in Fig. 2d

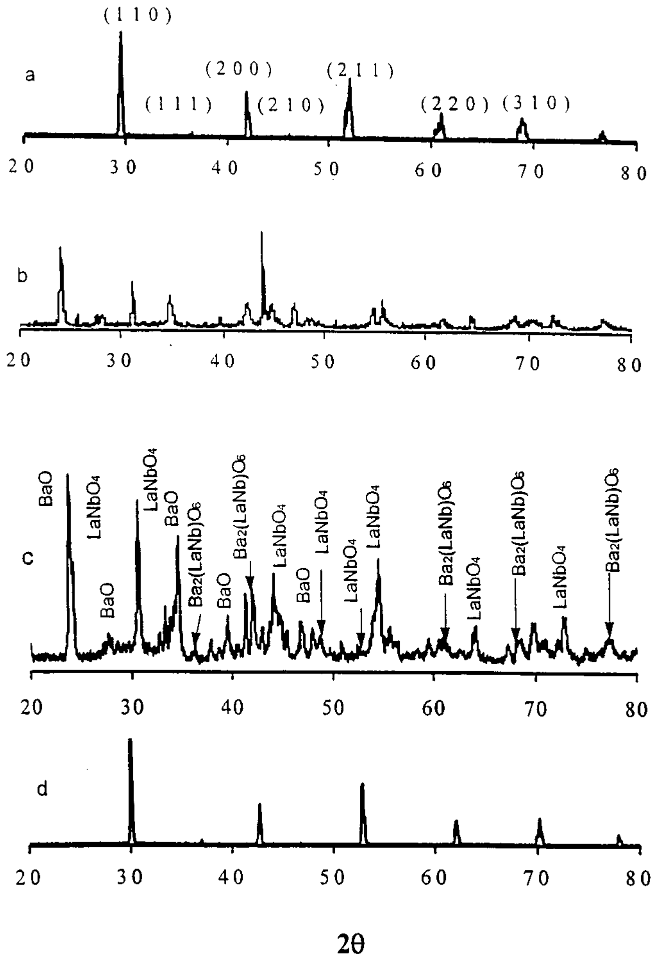

FIG. 2. (a) An XRD trace of a sample of Ba_2LaNbO_6 synthesized by calcining a mixture of $BaCO_3$, La_2O_3, and Nb_2O_5 at 1250°C for 2 h in air, showing the formation of a single-phase perovskite structure. (b) An XRD trace of a mixture of $BaCO_3$, La_2O_3, and Nb_2O_5 after 16 h in molten NaOH–KOH eutectic at 350°C in air. Note that the perovskite phase did not form. The XRD peaks can be identified with BaO and $LaNbO_4$. (c) An XRD trace of a sample of Ba_2LaNbO_6 synthesized in step (a) after treatment in a molten NaOH–KOH salt eutectic at 350°C for 16 h. The XRD trace shows that the perovskite structure is unstable at 350°C and decomposes into a mixture of BaO and $LaNbO_4$. (d) An XRD trace of a sample of Ba_2LaNbO_6 synthesized in step (a) after being boiled in water for 1 week, showing that the structure is stable in water.

shows that the perovskite structure remains unaffected. Similar experiments were also performed on Ba_2NdNbO_6, and it exhibits behavior similar to Ba_2LaNbO_6. Table 1 summarizes the results of the experiments conducted on the various mixed perovskites in the present work.

Synthesis of LaNbO4

The following experiments were conducted on the synthesis of $LaNbO_4$. (a) A powder mixture of La_2O_3 and Nb_2O_5 in a 1 : 1 molar ratio was introduced into molten NaOH–KOH eutectic and maintained at 350°C for 16 h. The salt bath was cooled and dissolved in water. The residue was filtered, washed, dried, and examined by XRD. The corresponding XRD trace is shown in Fig. 3a. The original peaks of the constituent oxides are absent from the trace, suggesting that some reaction must have occurred. The trace shows two very broad peaks, probably representative of a very fine (nanosize) structure. (b) A powder mixture of La_2O_3 and Nb_2O_5 in a 1 : 1 molar ratio was calcined at 1300°C in air for 6 h. The corresponding XRD trace is shown in Fig. 3b. The trace corresponds to a single phase, monoclinic $LaNbO_4$ (31). (c) The $LaNbO_4$ powder from step (b) was introduced into a molten NaOH–KOH bath and maintained at 350°C for 16 h. The salt bath was cooled and dissolved in water. The residue was filtered, washed, dried, and examined by XRD. The corresponding XRD trace given in Fig. 3c is identified with tetragonal $LaNbO_4$ (31). Figure 3d is the same trace as that given in Fig. 2c, which corresponds to the decomposition of Ba_2LaNbO_6, synthesized by high temperature calcination, in molten NaOH–KOH.

DISCUSSION

The formation of the mixed perovskite $Ba_3CaNb_2O_9$ and of the type $Ba_2B'B''O_6$, where $B' =$ Gd, La, Sm, Nd or Y, and $B'' =$ Nb after calcination at 1250°C of mixtures of requisite precursors, shows that these perovskites are stable at the temperature of synthesis. The formation in a molten NaOH–KOH eutectic at 350°C of all perovskites examined here, with the exception of Ba_2LaNbO_6 and Ba_2NdNbO_6, shows that these perovskites are also stable at 350°C and that the precursors exhibit sufficient solubilities in the salt bath to effect the reactions. The fact that the mixed perovskites Ba_2LaNbO_6 and Ba_2NdNbO_6 did not form from their precursors in the molten salt bath, and readily decomposed when single-phase materials synthesized by a high temperature calcination were introduced in the salt bath, clearly shows that they are unstable at 350°C. Thus, it is clear that Ba_2LaNbO_6 and Ba_2NdNbO_6 are unstable relative, respectively, to BaO, La_2O_3, and Nb_2O_5 and Bao, Nd_2O_3, and Nb_2O_5 at low temperatures (~350°C). Prior work has shown that $BaCeO_3$ is also unstable with respect to constituent oxides at low temperatures (<630°C) (12). The stability of simple perovskites of the type ABO_3 is often interpreted in terms of the Goldschmidt tolerance factor, t, defined by

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \qquad [1]$$

where r_A, r_B, and r_O are the ionic radii of A, B and O ions, respectively. For example, Navrotsky (32), Gramsch *et al.*

TABLE 1

Material	Pseudo-cubic lattice parameter (Å)	High temperature calcination (1250° C/2 h in air)	Molten salt synthesis (NaOH–KOH eutectic 350°C/16 h)	High temperature calcination followed by molten salt treatment
$Ba_3CaNb_2O_9$	8.35	formed	formed	stable
Ba_2YNbO_6	8.436	formed	formed	stable
Ba_2GdNbO_6	8.45	formed	formed	stable
Ba_2SmNbO_6	8.528	formed	formed	stable
Ba_2NdNbO_6	8.54	formed	did not form	decomposes
Ba_2LaNbO_6	8.6	formed	did not form	decomposes

(33), Morss *et al.* (34), and Kreuer (35) have explained the stability of many perovskites in terms of the tolerance factor. The tolerance factor for the ideal perovskite is 1.0. In general, the lower the tolerance factor, the lower is the stability. In this context, $BaTiO_3$, which has a tolerance factor of ~ 0.97, is stable over a wide temperature range. $BaCeO_3$ by contrast has a tolerance factor of ~ 0.89 and is unstable below 630°C. The tolerance factor for both Ba_2LaNbO_6 and Ba_2NdNbO_6 is ~ 0.87, in which the *B*-site ionic radius is assumed to be an arithmetic average of the two ions occupying the site, i.e., La and Nb or Nd and Nb. As seen readily, the tolerance factors for these two mixed oxides are even lower than those for $BaCeO_3$. Thus, their instability at 350°C may be attributed to their low tolerance factors. By comparison, the tolerance factor for $Ba_3CaNb_2O_9$ is ~ 0.90, which is greater than that for Ba_2LaNbO_6 and Ba_2NdNbO_6, and slightly larger than that for $BaCeO_3$. As mentioned above, $Ba_3CaNb_2O_9$ was found to be stable with respect to constituent oxides, and also in boiling water.

Molten salt synthesis of $LaNbO_4$ was inconclusive (Fig. 3a). However, the observation that peaks corresponding to La_2O_3 and Nb_2O_5 disappeared suggests that $LaNbO_4$ probably formed. Very large peak widths in Fig. 3a suggest that the $LaNbO_4$ formed is of a very fine particle size. It was observed that monoclinic $LaNbO_4$ synthesized by a high temperature calcination process converts into tetragonal $LaNbO_4$ at 350°C in molten NaOH–KOH bath. The role the salt bath plays in this transformation is not known. Perhaps the monoclinic to tetragonal transformation occurs by dissolution–reprecipitation. However, the observation that Ba_2LaNbO_6 synthesized by calcination at 1250°C decomposes into BaO and tetragonal $LaNbO_4$ suggests that: (1) Ba_2LaNbO_6 is unstable with respect to BaO and $LaNbO_4$ at 350°C. (2) The stable form of $LaNbO_4$ at 350°C is the tetragonal polymorph.

Recent work (36) has shown that in general mixed perovskites may be more stable than simple perovskites of the same lattice parameters due to their lower Madelung energy (their higher |Madelung energy| since Madelung energy < 0). That is, the Madelung energy for a perovskite of the type $AB'_{1/2}B''_{1/2}O_3$ (that is $A_2B'B''O_6$) is lower than that for ABO_3 of the same lattice parameter and should thus exhibit greater stability. The Madelung energy of Ba_2LaNbO_6 (*B*-site ordered) was estimated to be -163.48 eV while that for $BaPrO_3$ was estimated to be -163.52 eV (36). It is known that $BaPrO_3$ is unstable at low temperatures ($\sim$350°C) with respect to constituent oxides, BaO and "PrO_2" (which is actually Pr_6O_{11}), as evidenced by the observation that it cannot be synthesized in a molten salt bath. Based on the fact that the Madelung energies of the two compounds are comparable, and that Ba_2LaNbO_6 has a lower tolerance factor than $BaPrO_3$, it may be expected that Ba_2LaNbO_6 may also be unstable at low temperatures with respect to BaO and $LaNbO_4$, consistent with observations. By contrast, Ba_2GdNbO_6 could be readily synthesized in a molten salt bath. It was also observed that $GdNbO_4$ could be synthesized in molten NaOH–KOH starting with Gd_2O_3 and Nb_2O_5. These observations suggest that Ba_2GdNbO_6 is stable with respect to BaO and $GdNbO_4$. The tolerance factor for Ba_2GdNbO_6 is ~ 0.89, the same as for $BaPrO_3$. However, its Madelung energy is lower by about 2 eV than that of $BaPrO_3$. Thus, the stability of Ba_2GdNbO_6 may be attributed to its lower Madelung energy (36).

$BaCeO_3$ is also known to be unstable when boiled in water. The reaction

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2 \qquad [2]$$

readily occurs. The $Ba(OH)_2$ formed is soluble in water. As a result, the decomposition process proceeds rapidly in boiling water. By contrast, Ba_2LaNbO_6 was observed to be stable in boiling water. Based on the argument presented here, it would be expected that the reaction

$$Ba_2LaNbO_6 + 2H_2O \rightarrow 2Ba(OH)_2 + LaNbO_4 \qquad [3]$$

be favored at the boiling temperature of water. Presumably, the observed stability of Ba_2LaNbO_6 in boiling water is kinetic, and its origin is unknown at the present time.

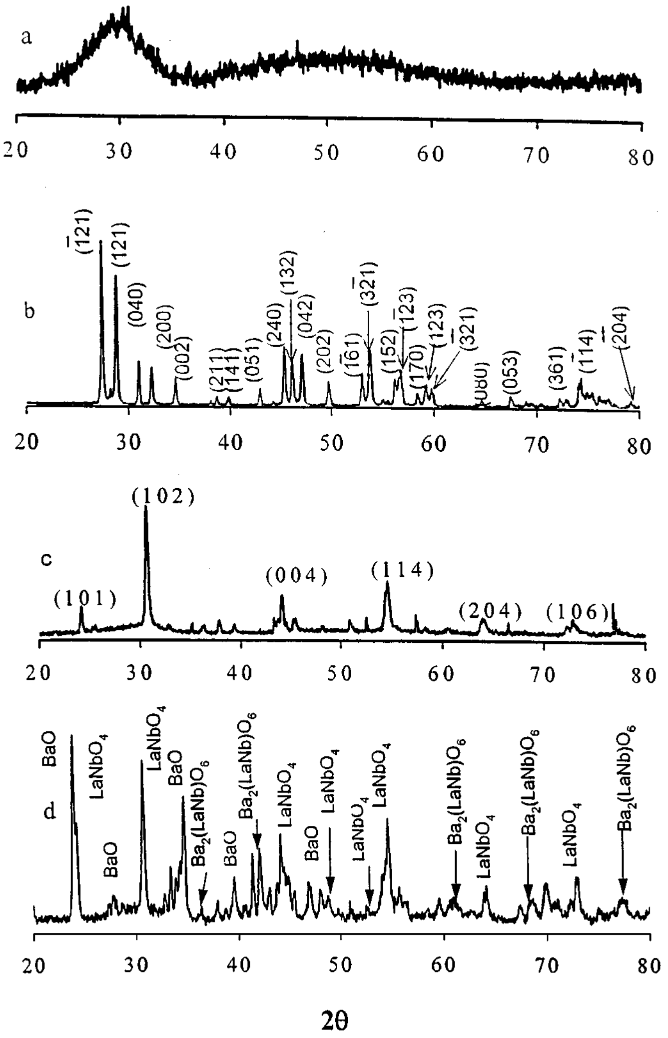

FIG. 3. (a) An XRD trace of the powder residue when La_2O_3 and Nb_2O_5 in a 1 : 1 molar ratio were treated in a molten NaOH–KOH bath at 350°C for 16 h. There is no clear evidence of the formation of the $LaNbO_4$ phase. However, peaks corresponding to the constituent oxides. La_2O_3 and Nb_2O_5, have disappeared. (b) An XRD trace of a sample of $LaNbO_4$ synthesized by calcining a mixture of La_2O_3 and Nb_2O_5 at 1250°C for 2 h. The XRD trace corresponds to a single-phase, monoclinic $LaNbO_4$. (c) An XRD trace of a sample of $LaNbO_4$ from (b) that was treated in molten NaOH–KOH at 350°C for 16 h. The XRD trace corresponds to tetragonal $LaNbO_4$. (d) The same XRD trace as in Fig. 2c.

CONCLUSIONS

Mixed perovskites of the type $Ba_2B'B''O_6$ ($BaB'_{1/2}B''_{1/2}O_3$) and $Ba_3B^*B''_2O_9$ ($BaB^*_{1/3}B''_{2/3}O_3$) where B' = La, Nd, Gd, Sm, or Y, B'' = Nb, and B^* = Ca were synthesized by calcining requisite mixtures of precursors at 1250°C in air for 2 h. All of the compounds formed the perovskite structure. With the exception of Ba_2LaNbO_6 and Ba_2NdNbO_6, all other mixed perovskite compounds were also synthesized at 350°C in a molten NaOH–KOH eutectic salt bath starting with the requisite precursors. By contrast, Ba_2LaNbO_6 and Ba_2NdNbO_6 compounds synthesized by a high temperature calcination process when introduced into a molten NaOH–KOH bath at 350°C readily decomposed. This indicates that both Ba_2LaNbO_6 and Ba_2NdNbO_6 are unstable with respect to constituent oxides, as well as with respect to BaO and $LaNbO_4$ and to BaO and $NdNbO_4$, at low temperatures, similar to $BaCeO_3$ and $BaPrO_3$. The present work shows that the molten salt technique can be successfully used to investigate thermodynamic stabilities of many refractory oxides at low temperatures. All of the compounds synthesized were stable in boiling water, unlike $BaCeO_3$ and $BaPrO_3$. This suggests that the search for perovskite-based proton conductors should be directed toward the mixed perovskites.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under grant DEFG0397ER45661.

REFERENCES

1. H. Iwahara, T. Esaka, H. Uchida, and N. Maeda, *Solid State Ionics* **3/4,** 359–363 (1981).
2. H. Iwahara, H. Uchida, K. Ono, and K. Ogaki, *J. Electrochem. Soc. Solid State Sci. Technol.* **135,** 529–533 (1988).
3. H. Iwahara, *Solid State Ionics* **28–30,** 573–578 (1988).
4. H. Iwahara, T. Yajima, and H. Ushida, *Solid State Ionics* **70/71,** 267–271 (1994).
5. H. Iwahara, T. Yajima, H. Uchida, and K. Morimoto, *in* "2nd International Symposium on Solid Oxide Fuel Cells, Athens," pp. 229–235, 1991.
6. H. Iwahara, H. Ushida, and K. Morimoto, *J. Electrochem. Soc.* **137,** 462–465 (1990).
7. N. Bonanos, *Solid State Ionics* **53–56,** 967–974 (1992).
8. K. D. Kreuer, E. Schönherr, and J. Maier, *Solid State Ionics* **70/71,** 278–284 (1994).
9. N. Taniguchi, K. Hatoh, J. Niikura, T. Gamo, and H. Iwahara, *Solid State Ionics* **53–56,** 998–1003 (1992).
10. H. Iwahara, T. Yajima, T. Hibino, K. Ozaki, and H. Suzuki, *Solid State Ionics* **61,** 65–69 (1993).
11. T. Yajima, H. Iwaharau, and H. Uchida, *Solid State Ionics* **47,** 117–124 (1994).
12. S. Gopalan and A. V. Virkar, *J. Electrochem. Soc.* **140**, 1060–1065 (1993).
13. C. W. Tanner and A. V. Virkar, *J. Electrochem. Soc.* **143**(4), 1386–1389 (1996).
14. Z. Wu and M. Liu, *J. Electrochem. Soc.* **144,** 2170–2175 (1997).
15. S. V. Bhide and A. V. Virkar, *J. Electrochem. Soc.* **146**(6), 2038–2044 (1999).
16. J. F. Liu and A. S. Nowick, *Solid State Ionics* **50,** 131–138 (1992).
17. K. C. Liang and A. S. Nowick, *Solid State Ionics* **61,** 77–81 (1993).
18. A. S. Nowick and Y. Du, *Solid State Ionics* **77,** 137–146 (1995).
19. K. C. Liang, I. Y. Lee, and A. S. Nowick, *Mater. Res. Soc. Symp. Proc.* **293,** 355–360 (1993).
20. K. C. Liang, Y. Du, and A. S. Nowick, *Solid State Ionics* **69,** 117 (1994).

21. R. H. Arendt, *J. Solid State Chem.* **8,** 339 (1973).
22. R. H. Arendt, H. H. Rosolowski, and J. W. Szymaszek, *Mater. Res. Bull.* **14,** 703 (1979).
23. M. Graham, M. Holmes, W. Schultze, and R. E. Newnham, *J. Am. Ceram. Soc.* **64,** C68 (1981).
24. S. S. Lopatin, T. G. Lupeiko, and T. I. Ivleva, *Zh. Neorg. Khim.* **32,** 865 (1987).
25. C. C. Chiu, C. C. Li, and S. B. Desu, *J. Am. Ceram. Soc.* **74,** 38 (1991).
26. Y. Hayashi, T. Kimura, and T. Yamaguchi, *J. Mater. Sci.* **21,** 2876 (1986).
27. S. Gopalan, K. Mehta, and A. V. Virkar, *J. Mater. Res.* **11**(8), 1 (1996).
28. T. Kimura, T. Kanazawa, and T. Yamaguchi, *J. Am. Ceram. Soc.* **66,** 597 (1983).
29. H. P. Naidu and A. V. Virkar, *J. Am. Ceram. Soc.* **81**(8), 2176–2180 (1998).
30. "Phase Diagrams for Ceramists." Am. Ceram. Soc., Westerville, OH, 1975.
31. JCPDS, International Center for Diffraction Data, No. 32-0496 and No. 22-1155, 1996.
32. A. Navrotsky, *in* "Perovskite: A Structure of Great Interest to Geophysics and Materials Science", (A. Navrotsky and D. J. Weinder, Eds.), Geophysics Monograph 45, p. 67. Geophysical Union, Washington, DC, 1989.
33. S. A. Gramsch and L. R. Morss, *J. Chem. Thermodyn.* **27,** 551–560 (1995).
34. L. R. Morss and N. Mensi, *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy, H. B. Silber, and J. J. Rhyne, Eds.), pp. 279–282. Plenum, New York, 1982.
35. K. D. Kreuer, *Solid State Ionics* **97,** 1–15 (1997).
36. S. V. Bhide and A. V. Virkar, submitted.