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Molten alkali metal oxonitrates, a liquid state for nanosized perovskite phase elaboration†

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Alkali metal nitrates or nitrites have rather low melting points and provide a powerful liquid medium for the precipitation of metal oxides from their common salts. Oxonitrate anions are Lux–Flood bases; the basicity can be chosen between nitrate or nitrite depending on the acidity of the metal cation or the kind of oxide desired. Once the experimental conditions are determined, generally by using TGA, one can obtain phases such as $BaTiO_3$, $PbTiO_3$ or $LaMnO_3$ quickly and reproducibly. Elementary particles, single crystals about 100 nm in size, form rather soft aggregates of approximately 2 μm. The purity is suitable for most applications.

Introduction

The use of metal nitrates to prepare the corresponding oxides has been known for a very long time. In the *Traité de Chimie Minérale* (1932 issue), Duval[1] told about the works of Berzelius (1779–1848) who prepared palladium oxide by calcination of the nitrate. The same author mentionned that, as early as 1924, Shriner and Adams[2] obtained the same oxide in a molten mixture of $PdCl_2$ and $NaNO_3$ at 500 °C.

At the same time (1930), Lux[3] formulated the concept of acido–basic properties of molten salts as an exchange of oxide ions:

$$\text{Base} \rightleftharpoons \text{Acid} + O^{2-}$$

A $p(O^{2-})$ scale quantifies the acido–basic behaviour of such pairs. It shows that sulfate ions are less basic than nitrate ions, which are themselves less basic than carbonate ions. This property can be used to precipitate metal oxides from their salts without any aqueous medium.

For this purpose, alkali metal nitrates or nitrites are the most useful. Their melting points are lower than those of sulfates and carbonates and they form mixtures with still lower melting points (Table 1). It is then possible to perform precipitations in liquid media at very low temperatures. During the 1960s Kerrige[4] embarked upon a systematic study of the reactivity of metal salts in molten alkali metal nitrates[5] and nitrites,[6] and thus established molten salt chemistry. Durand *et al.*[7] were the first to recognize the physico-chemical properties of such obtained powders and to develop their uses. The interest is provided by the small sizes of the crystallites grown at low temperature (< 100 nm); they form soft agglomerates and specific surface areas are generally developed ($100\ m^2\ g^{-1}$). These properties make the powders attractive for both catalysis[8,9] and elaboration of ceramics.[10] The ability to form mixed oxides in molten salts was induced by the preparation of zirconia partially stabilized by yttria.[11,12] The powders were shown to be homogeneous at the lowest level of detection and, moreover, such small particles must by very reactive. $BaTiO_3$, $PbTiO_3$ and also $LaMnO_3$ were chosen for their industrial interest and for the commonly known laboratory synthesis of TiO_2.[13] Today, the molten salt route is not extensively used. Hayashi *et al.*[14] synthesized $BaTiO_3$ by reacting $BaCO_3$ with various titanium salts in NaCl–KCl eutectic at 700 °C for 1 h. No reference was found related to $PbTiO_3$. One paper[15] mentioned the partial substitution of Ba^{2+} ions in $BaTiO_3$ by Pb^{2+} ions in molten $PbCl_2$. Lead zirconate titanate (PZT) was prepared by Arendt *et al.*[16] at high temperature (1000 °C) in NaCl–KCl eutectic. Some other attempts, in particular oriented growth, were made by Kimura *et al.*[17] Here too, the compounds reacted at elevated temperature (1250 °C) and a complicated multistep process was involved. With this background we attempted the synthesis of the perovskite phases $BaTiO_3$, $PbTiO_3$ and $LaMnO_3$.

Table 1 Melting points of some akali metals oxosalts

	Melting points/°C		
	Nitrate	Sulfate	Carbonate
Lithium	225	857	723
Sodium	307	884	858
Potassium	334	1076	893
'Eutectic' Li–Na	132	535	
'Eutectic' Na–K	225	830	704

Experimental

Commercially available reactants were used with the best purity supplied. Alkali metal nitrates and nitrites (Prolabo products with 99 and 98% purity respectively) were dehydrated and kept in an oven at 100 °C. The titanium salt was prepared in the laboratory by dehydration, at 60 °C under reduced pressure, of an aqueous solution of $TiCl_4$ kindly provided by Thann and Mulhouse. The XRD pattern of the solid phase corresponded to $Ti_{29}O_{49}Cl_{32}\cdot110H_2O$ (ICDD-21 137) and after chemical analysis the formula $Ti_2O_3Cl_2\cdot xH_2O$ was adopted, with x varying between the preparations.

The operating process is linear, typical reaction conditions are summarized in Table 2. The mixing of metal precursors with nitrates or nitrites was done roughly. Increasing the temperature caused fusion and further, most frequently, reaction. After the temperature was held at a set value dependent on the oxide being prepared, the reactor was cooled. The resulting cake was extracted into water; any excess salts, and

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Table 2 Typical conditions of the syntheses of perovskite phases

Oxide	M1 salt	M2 salt	Medium	Container	Exp. conditions
$BaTiO_3$	$Ba(NO_3)_2$	$Ti_2O_3Cl_2$	$NaNO_2$ KNO_2	Glass	500 °C, 2 h
$PbTiO_3$	$Pb(NO_3)_2$	$Ti_2O_3Cl_2$	$NaNO_2$ KNO_2	Al_2O_3	1 g of oxide
$LaMnO_3$	$La(NO_3)_3$	$Mn(NO_3)_2$	KNO_3	Glass	ANO_x (stoichiometry = 6)

any alkali metal salts generated by the reaction, are solubilized, and any possible excess metal precursor is also dissolved in this step. The insoluble oxide, after filtration and washing, was oven dried at 100 °C for 24 h.

Results

Individual metal precursors

In the typical ABO_3 formula of the perovskites, A are generally large cations and B are much smaller, strongly polarizing ones. Thus their acido–basic properties are different.

A cations. A cations have relatively low basicity in molten salts and they frequently react at the highest temperatures.

The barium precursor is the nitrate salt and the molten bath consists of alkali metal nitrites. TGA curves [Fig. 1(a)] show that the loss of mass corresponds to the thermal decomposition of nitrites. BaO cannot precipitate in this medium because of the very low acidity of Ba^{2+} which is comparable with that of alkali metals.

We used the hydrated nitrate of lanthanum as precursor. TGA gives no useful information because the dehydration of the salt is complex; on heating, $La(OH)_3$ is formed at relatively low temperature and is still present at 800 °C. The contact for 2 h at 500 °C of $La(NO_3)_3$ and molten nitrates leads, after washing, to a powder identified by XRD as $La(OH)_2NO_3$ (ICDD 26-1146). It is not yet possible to determine whether hydroxide ions are created in the melt or appear on washing. Nevertheless, this result corresponds to the trend of trivalent lanthanides to form LnO^+ ions. It seems that the pair Ln^{3+}/LnO^+ [or $Ln(OH)_2{}^+$] is sufficiently acid in molten nitrate to react whereas the pair LnO^+/Ln_2O_3 is not [when molten nitrites are used instead of nitrates, we obtain $La(OH)_3$].

Like $Ba(NO_3)_2$, $Pb(NO_3)_2$ does not react with molten nitrates. Nevertheless it reacts in molten nitrites at 450 °C [Fig. 1(b)] just before their thermal decomposition. The resulting powder is a mixture of both polymorphs of PbO, litharge and massicot.

B cations. B cations are strong acids in molten nitrates and even more so in nitrites.

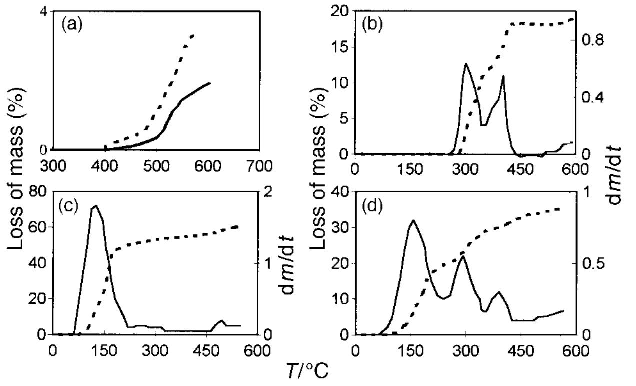

Fig. 1 TGA curves [except for (a), plain line relates to dm/dt and dashed line to dm/m_0]: (a) alkali metal nitrites alone (—), $Ba(NO_3)_2$ plus nitrites (---), (b) $Pb(NO_3)_2$ plus nitrites, (c) $Ti_2O_3Cl_2$ plus nitrites, (d) $Pb(NO_3)_2$ plus $Ti_2O_3Cl_2$ plus nitrites.

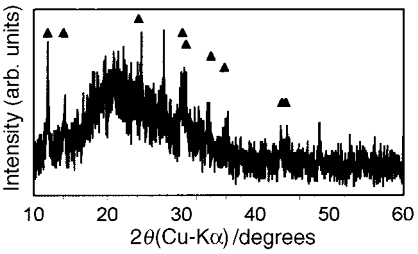

Fig. 2 XRD, after annealing at 900 °C, of the powder obtained by reaction between $Ti_2O_3Cl_2$ and nitrites. Triangles identify $Na_2Ti_6O_{13}$ (ICDD 37 0951).

$Ti_2O_3Cl_2$ reacts with nitrites at low temperature [Fig. 1(c)] before the fusion of the mixture. The loss of mass shown on the TGA curves corresponds to the formation of TiO_2 by reaction with nitrites [reaction (1)] and not by thermal decomposition [reaction (2)]:

$$Ti_2O_3Cl_2{\cdot}3.8H_2O + 2(Na,K)NO_2 \rightarrow 2TiO_2 + NO_2 + NO + 2(Na,K)Cl + 3.8H_2O \qquad (1)$$

(relative loss of mass 51%)

$$Ti_2O_3Cl_2{\cdot}3.8H_2O \rightarrow 2TiO_2 + 2HCl + 2.8H_2O \qquad (2)$$

(relative loss of mass 43%)

The weak slope of the following loss indicates the formation of sodium titanates (Fig. 2), identified by XRD after crystallization at 900 °C. In nitrite medium, titanium exhibits two acido–basic couples; the first is a strong acid one Ti^{4+}/TiO_2 (or $TiO_{1.5}{}^+/TiO_2$), the second is weaker, $TiO_2/Ti_nO_{2n+1}{}^{2-}$. It seems that metatitanate ions $TiO_3{}^{2-}$ could not be formed.

Manganese differs markedly from titanium in its oxido-reduction behaviour. The starting material is a nitrate of manganese(II), which is readily oxidizable into Mn^{III} and Mn^{IV} salts. The reaction of this salt in molten potassium nitrate leads within 2 h at 500 °C to poorly crystallized oxides (Fig. 3), among which MnO_2 is clearly evidenced by XRD. No alkali metal manganite seems to be synthesized in this medium.

Simultaneous reactions

$BaTiO_3$. The TGA curve of the reaction of the (1 : 1) mixture of Ba and Ti precursors in molten nitrites is similar to that of the reaction of $Ti_2O_3Cl_2$ alone. Nevertheless, XRD indicates the presence of $BaTiO_3$ in the resulting solid. Patterns of powders obtained at various reaction temperatures and calcined at 900 °C to crystallize the amorphous solids, show that the proportion of sodium titanate is decreased at the expense

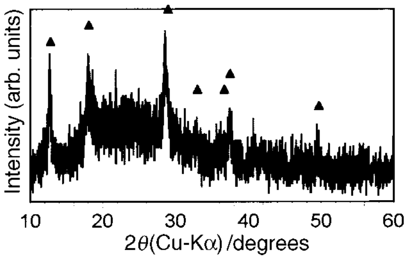

Fig. 3 XRD of the powder obtained by reaction between $Mn(NO_3)_2$ and KNO_3. Triangles identify MnO_2 (ICDD 44 0141).

Table 3 Evolution with temperature of the phases obtained by reaction of $Ba(NO_3)_2$, $Ti_2O_3Cl_2$ and $Ti_2O_3Cl_2$ in nitrite medium

Temperature/ °C	XRD of obtained powder	XRD after annealing at 900 °C
350	TiO_2 anatase + extra phases	$BaTi_5O_{11} + Na_2Ti_6O_{13}$
450	TiO_2 anatase + extra phases	$BaTi_5O_{11}$ + some $Na_2Ti_6O_{13}$
500	$BaTiO_3$	$BaTiO_3 + BaTi_4O_9 + BaTi_2O_5$

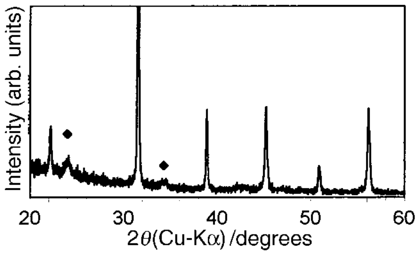

Fig. 4 XRD of the powder obtained by reaction for 60 h with Ba/Ti = 5 between $Ba(NO_3)_2$ and nitrites. Diamonds identify $BaCO_3$ arising from air-flow through the medium (ICDD 44 1487).

of barium titanates when the temperature is raised (Table 3). At the lowest temperature, the phases are $Na_2Ti_6O_{13}$ and $BaTi_5O_{11}$, and at the highest, the solid no longer contains the sodium salt but only $BaTi_2O_5$, $BaTi_4O_9$ and $BaTiO_3$. Assuming that the sodium ions of the titanate are slowly exchanged for the barium ions, we modified the experimental parameters. The Ba/Ti ratio was increased from 1 to 5 and the reaction duration from 2 or 5 h to 60 h at the same temperature 500 °C. Under these conditions we obtained cubic $BaTiO_3$ (Fig. 4). Moreover, the powder calcined at 1300 °C does not evolve; the phase remains pure $BaTiO_3$ as its tetragonal polymorph. In the solid, before annealing (Table 4), the sodium and potassium contents are quite low (5 and 1 mol% respectively).

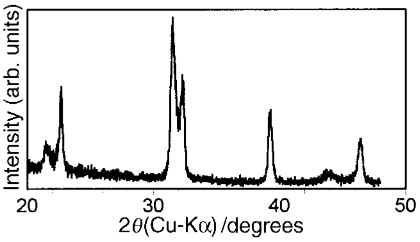

Fig. 5 XRD of the powder obtained by reaction between $Pb(NO_3)_2$, $Ti_2O_3Cl_2$ and nitrites corresponding to $PbTiO_3$ (ICDD 6 0452).

Table 5 Chemical analysis of $PbTiO_3$. H content corresponds to the water remaining in the solids

Pb (wt.%)[a]	Ti (wt.%)[a]	Pb/Ti	H/Pb	Na/Pb	K/Pb
63.2	14.6	1.00	1	0.1	<0.01

[a] Calc. for $PbTiO_3$: Pb, 68.3; Ti, 15.8%.

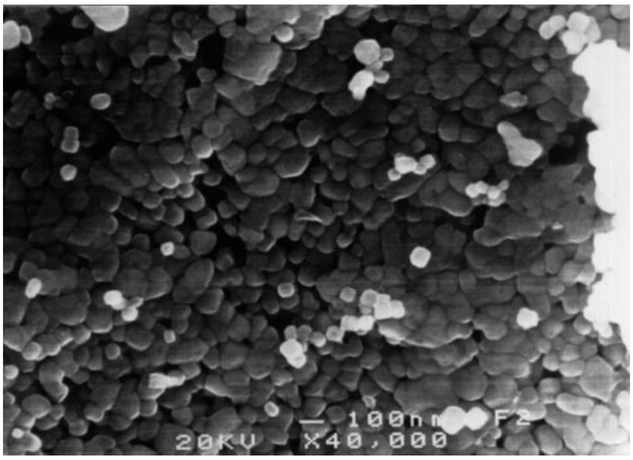

Fig. 6 SEM of $PbTiO_3$ powder.

$PbTiO_3$. As the precursors react at very different temperatures, the TGA curve of the reaction of their 1:1 mixture is the sum of the individual curves [Fig. 1(d)]. The loss of mass below 250 °C corresponds to the formation of TiO_2, and that above 250 °C to the formation of PbO. When the synthesis is carried out in the mixture of alkali metal nitrites at 500 °C for 2 h, the resulting powder is $PbTiO_3$ as proved by XRD (Fig. 5). However chemical analysis (Table 5) shows a significant amount of sodium (10 mol%). Most probably, the presence of this element is due to the two step reaction. While PbO is forming, TiO_2 reacts to some extent to give sodium titanate in which the further replacement of Na^+ by Pb^{2+} will be partially achieved. The SEM micrograph (Fig. 6) shows monodisperse crystallites of small size, below 100 nm. This size agrees well with that calculated from the Scherrer formula. The phase is tetragonal, with parameters $a = 3.902$ Å, $c = 4.086$ Å and $c/a = 1.047$ for powders calcined at 1050 °C under PbO atmosphere (Si used as internal standard). It is possible to lower the sodium content by using other precursors or media.

$LaMnO_3$. The reaction is run in potassium nitrate. The mixture of all the constituents is dehydrated partially at 100 °C for 1 h and then maintained at 500 °C for 2 h. In spite of the result obtained with manganese alone, the obtained compound does not contain Mn^{IV} but this is the non-stoichiometric perovskite phase $La_{1-x}MnO_3$ as its cubic (or rhombohedral) polymorph[18] (Fig. 7). It transforms at high temperature to the rhombohedral polymorph, the orthorhombic form not being observed. The SEM micrograph (Fig. 8) of a rough powder shows agglomerates of about 1 μm and crystallites of *ca.* 100 nm, which coincides well with that calculated from diffraction patterns.

Table 4 Chemical analysis of powders obtained under various reaction conditions. H content corresponds to the water remaining in the solids

Reaction conditions (T = 500 °C)							
Ba/Ti	time/h	Ba (wt.%)[a]	Ti (wt.%)[a]	Ba/Ti	H/Ba	Na/Ba	K/Ba
1	24	48.7	23.7	0.72			
2	60	54.3	20.5	0.92			
5	60	53.4	18.1	1.00	2	0.05	<0.01

[a] Calc. for $BaTiO_3$: C, 58.9; H, 20.5%.

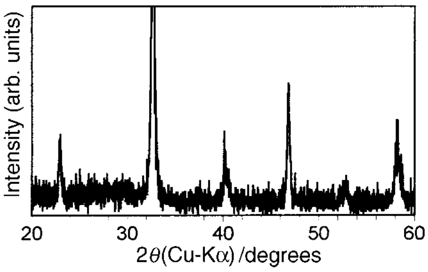

Fig. 7 XRD of the powder obtained by reaction between $Mn(NO_3)_2$, $La(NO_3)_3$ and KNO_3 corresponding to $La_{1-x}MnO_3$ as either the cubic or rhombohedral polymorph.

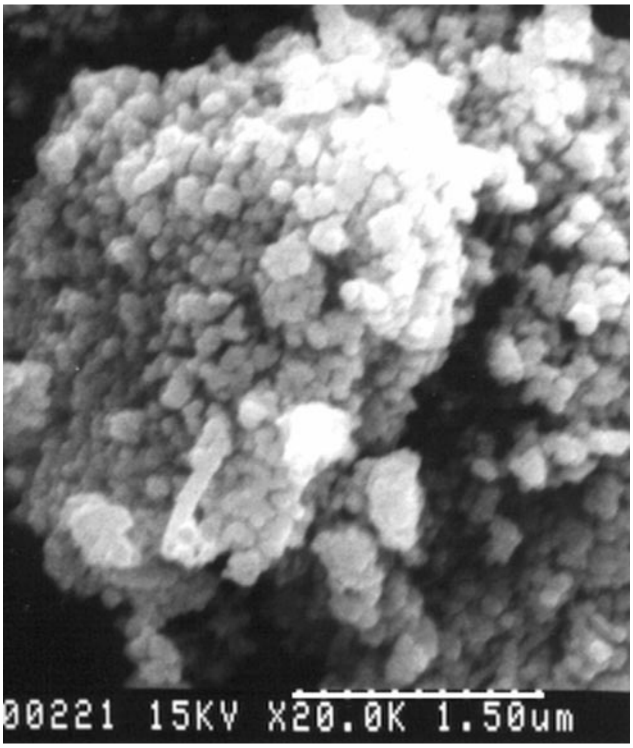

Fig. 8 SEM of $La_{1-x}MnO_3$ powder.

Discussion

It is actually possible to realize syntheses of perovskite phases in molten salts. It is worth noting the very low reaction temperature. Direct reactions between oxides need temperatures higher than 1000 °C and some soft chemistry routes such as electrodeposition[19] are also performed at about 900 °C.

Therefore some chemical elements are easier to react than others, and this is related to their acido–basic power. Moreover, the results depend also on the precursor and the molten medium. Nevertheless, A cations represent the main difficulty as we have seen for $BaTiO_3$. In order for a substitution reaction to run to completion,

$$Na_2Ti_nO_{2n+1} + Ba^{2+} \xrightarrow{\text{slow}} BaTi_nO_{2n+1} + 2Na^+$$

followed by

$$BaTi_nO_{2n+1} + 2NO_2^- \rightarrow BaTiO_3 + Ti_{n-1}O_{2n-1}{}^{2-} + NO_2 + NO$$

we must use a large Ba^{2+}/Ti ratio and a very long reaction time. These conditions are not the best ones for a clean process even if reproducibility is good.

For $PbTiO_3$, kinetic difficulties do not exist and the reaction evolves quantitatively with respect to the precursors. However, examination of the TGA curves raises questions about the mechanism of the reaction. If the hypothesis of a pure solid state reaction between crystallites of PbO and TiO_2 is, *a priori*, dismissed (this point must therefore be checked) the mechanism based on the generally accepted solubility[20] of PbO is an acido–basic one, *i.e.*

$$PbO \rightleftharpoons Pb^{2+} + O^{2-}$$

$$TiO_2 + O^{2-} \xrightarrow{Pb^{2+}} PbTiO_3$$

Total transformation into PbO is necessary to obtain $p(O^{2-})$ values lower than in the alkali metal nitrites alone and in the presence of Ba^{2+}. This kind of reaction avoids, to a great extend but not totally, the formation of $Na_2Ti_nO_{2n+1}$.

For $LaMnO_3$, the question arises from an other chemical point. In the molten potassium nitrate, lanthanum seems to exist in LaO^+ [or $La(OH)_2{}^+$] ion form, intermediate between Ba^{2+} and PbO. The manganese, when processed alone, oxidizes fully into MnO_2. When the reaction is performed with both elements together, the oxidization of manganese ions stops at a level slightly higher than +3 while $La_{1-x}MnO_3$ is precipitated. This could correspond to the difference of acido-basicity between Mn^{III} and Mn^{IV}. In molten nitrate Mn_2O_3 is not a strong acid and forms no oxo anion. As soon as a convenient ratio is oxidized into Mn^{IV}, the acidity of the metal oxide reaches a level where anions appear and precipitate with LaO^+ ions. For example:

$$8\ Mn_2O_3 \xrightarrow[+2O^{2-}]{-4e^-} Mn_{16}O_{26} \qquad (1/4\ Mn^{IV}), \text{ and}$$

$$Mn_{16}O_{26} \xrightarrow[+xO^{2-}\ (x>1)]{-e^-} Mn_{16}O_{26+x}{}^{(2x-1)-} \qquad (5/16\ Mn^{IV})$$

In any case the powders resulting from reactions in molten salts are formed of soft agglomerates of nanosized crystallites. First attempts to sinter $BaTiO_3$ and $PbTiO_3$ gave interesting results.

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