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Molten salt synthesis of the lead titanate $PbTiO_3$, investigation of the reactivity of various titanium and lead salts with molten alkali-metal nitrites

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The reactivity of titanium salts (the oxychloride, the oxysulfate and the potassium fluorotitanate) and lead salts (the chloride, the nitrate and the sulfate) is investigated first separately, then simultaneously. A molten salt synthesis procedure of the lead titanate $PbTiO_3$ is deduced from the results.

Introduction

Because of its high Curie point (*ca.* 490 °C), its low relative permittivity and its high spontaneous polarization, tetragonal $PbTiO_3$ is used as a stable piezoelectric material at high temperature and frequency. It can be obtained by the usual firing technique,[1] the sol–gel method,[2] coprecipitation reactions[3] and lastly by hydrothermal synthesis.[4] In the first three methods, calcination at high temperature (>600 °C) is necessary for the crystallization of ferroelectric $PbTiO_3$, involving the formation of hard aggregates which are unfavourable for sintering. The molten salt method allows the preparation of nano-sized oxides, at moderate temperature, with interesting applications (ceramics, catalytic supports).[5,6] This method has never been used to obtain ferroelectric $PbTiO_3$. The literature only reports the preparation of solid solutions $Ba_{1-x}Pb_xTiO_3$ by the reaction of the solid barium titanate ($BaTiO_3$) with molten $PbCl_2$.[7]

The present paper deals with the investigation of the reactivity of lead and titanium salts with a molten alkali metal oxonitrite medium in order to prepare ferroelectric $PbTiO_3$.

Previous results

The reactivity of K_2TiF_6 and $TiCl_4$ with molten $LiNO_3$–KNO_3 eutectic yields TiO_2 anatase as a final product. In the more basic melts, *e.g.* in the presence of NaOH added to nitrates, TiO_2 is slowly transformed into titanates.[8] Nano-sized powders of anatase were prepared, taking advantage of the reaction of $TiOSO_4$ with the molten $NaNO_3$–KNO_3 medium.[6]

The reactions of Pb^{II} salts with the molten nitrate media lead, whatever the anion (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}), to PbO with the intermediate formation of Pb_3O_4 which is reduced into PbO by the nitrite anions.[9] Pb^{2+} is stabilized by NO_3^-, so that the reaction of $Pb(NO_3)_2$ dissolved in molten $LiNO_3$–KNO_3 occurs with a maximum rate at about 500 °C which is higher than the temperature of the decomposition of $Pb(NO_3)_2$ alone (440 °C). When the alkali nitrates are changed into nitrites, PbO is also the final product but its formation temperature is decreased by about 100 °C.[10] The transformation of $Pb(NO_2)_2$ into PbO, with the intermediate formation of a basic nitrite $PbO\cdot 2Pb(NO_2)_2$, is indicated as being the key reaction in the transformation of several Pb^{II} salts, especially chloride and nitrate. The reactivity of $PbSO_4$ with the alkali-metal nitrites was not studied.

On account of the stability of Pb and Ti cations in the molten alkali-metal nitrates and nitrites, it is thought that the formation of PbO and TiO_2 involves Lux–Flood acido–basic reactions in which O^{2-} is the exchanged species. The base is a donor of O^{2-} (*e.g.* NO_3^- or NO_2^-) and the acid an acceptor (*e.g.* Pb^{2+}, Pb^{3+}, Ti^{4+}, TiO^{2+}). Because of their low solubility, the lead and the titanium oxides precipitate. Considering the Lux–Flood principle, the change of the nitrates into nitrites is understood as a strong increase of the basicity of the medium, the dissociation constant of NO_2^- being $10^{10}\times$ higher than that of NO_3^-.

Experimental

Starting materials

TiO_2 appeared as the more stable species in the molten nitrates, whereas increasing the basicity seemed to promote the formation of titanates. Consequently, it could be reasonably thought that, with the aim of precipitating $PbTiO_3$ from a molten medium, *via* a Lux–Flood acido–basic reaction, the alkali-metal nitrites are preferred to the nitrates. The $NaNO_2$–KNO_2 eutectic (65 mol% $NaNO_2$, mp 224 °C) was prepared by quickly grinding $NaNO_2$ (Prolabo >99%) and KNO_2 (Fluka >98%) and maintaining the mixture in a drying oven at 100 °C. KNO_2 (mp 440 °C) was also used alone.

For the titanium precursor, the three following salts were used: K_2TiF_6 (Fluka >98%), $TiOSO_4\cdot 2H_2O$ (Riedel de Haën) dehydrated at 300 °C for 2 h, and $TiO_{1.5}Cl\cdot xH_2O$. $TiCl_4$ was not used directly on account of the complexity of its reactions with the nitrates and nitrites. It was replaced by the oxychloride, $TiO_{1.5}Cl$, which is not commercially available, but was prepared in our laboratory by evaporation at 60 °C on a sand bath and under a primary vacuum of an aqueous solution of $TiCl_4$. The evaporation was reproducible and the X-ray diffraction patterns of the powders identified the oxychloride $Ti_{29}O_{42}Cl_{32}\cdot 110H_2O$ (ICDD file no. 21–1237). Chemical analysis (Ti 22.6%, Cl 22.0%, H 4.3%) was in agreement with the formula $TiO_{1.5}Cl\cdot xH_2O$ which is adopted in the following. Two batches were used in the present work, differing in the amount of water present ($x=1.9$ and 3.9). The calcination of the oxychloride in air at 550 °C and its reaction with the molten alkali-metal nitrates at 250 °C led to TiO_2.

The lead(II) precursors were either $PbCl_2$ (Aldrich 98%), $PbSO_4$ (Prolabo 99%) or $Pb(NO_3)_2$ (Acros >99%).

Procedure and characterization

The lead salt and the titanium salt were intimately mixed in a mortar in a suitable ratio (stoichiometric, or slight excess of lead) and then added to a large excess of the nitrite eutectic. For the powder preparation, the reacting mixture was poured into a cylindrical Pyrex reactor placed inside a vertical tubular regulated furnace closed at the bottom. The reaction was carried out following a chosen temperature profile and the exhaust gases were swept away by an air flow. After quenching at room temperature, the insoluble residue of the reaction was extracted by water washing until no anion (chloride, fluorine or sulfate) was detected in the filtrate. The powder was oven-dried at 100 °C for 24 h.

For the reactivity investigation, a small amount of the reacting mixture was poured inside the crucible (2.5 ml) of a Setaram G70 thermobalance and the thermogram was recorded at a rate of 2.5 °C min^{-1} up to 600 °C. The mass losses are given as percentage of the precursor starting mass.

The insoluble formed solids were identified by XRD using a diffractometer for powder samples (Siemens D 500) working with Cu-Kα radiation. The purity of the lead titanate samples was checked by chemical analysis performed in the CNRS Microanalysis Center of Solaize. Data are given in mass%.

Individual reactions of the metal precursors in the molten $NaNO_2$–KNO_2 eutectic

Lead precursors

Whatever the lead(II) precursor, its reaction at 500 °C for 2 h leads to a red–purple powder identified by XRD as a mixture of massicot and litharge and by chemical analysis as more or less hydrated lead(II) monoxide $PbO\cdot xH_2O$ ($0.4 < x < 1.1$). The temperature of the polymorphic transformation of massicot into litharge is close to 500 °C.[11]

The thermogravimetric investigation of the reactive mixtures (Fig. 1) always reveals a multistep transformation, but the profiles of the three curves are quite different. The behaviour of lead nitrate is the easiest to understand [Fig. 1(a)]. The whole experimental mass loss at 450 °C (18.3 %) is in fair agreement with that calculated from eqn. (1) (18.1%). Therefore, the transformation of $Pb(NO_3)_2$ into PbO is complete and the further loss starting above 550 °C is due to the beginning of the decomposition of the excess of nitrites.

$$Pb(NO_3)_2 + 3\ NO_2^- \rightarrow PbO + 3\ NO_3^- + 2\ NO \qquad (1)$$

Two steps are clearly identified in the TG and DTG curves. The first can be attributed to the formation of a basic lead nitrite and the second to its transformation into PbO. The mass loss of each step would suit better the formula $Pb(NO_2)_2\cdot 2PbO$ than that proposed by Kerridge.[9] Moreover, both reactions are shifted by about 50 °C towards high temperatures.

For the lead chloride and sulfate, if it was assumed that the formation of PbO proceeded *via* reaction (2), similar to reaction (1), the calculated mass losses would be respectively 21.6 and 19.8%. For $PbCl_2$ [Fig. 1(b)] the experimental loss is only 17.3% at 500 °C and the calculated value is not reached even at 600 °C. For $PbSO_4$, an experimental loss of 18% is reached in three steps at about 470 °C [Fig. 1(c)]. So, the reactivity of $PbCl_2$ and $PbSO_4$ is more difficult to interpret; nevertheless, we cannot agree with Kerridge's previous results.[10] The difference might be due to the fact that, in the present study, the reactions are performed in air whereas Kerridge's experiments were carried out under nitrogen atmosphere and with a significantly lower molar ratio Pb/NO_2^-.

$$PbX + 3\ NO_2^- \rightarrow PbO + NO_3^- + 2\ NO + X^{2-} \quad (X = Cl_2, SO_4) \qquad (2)$$

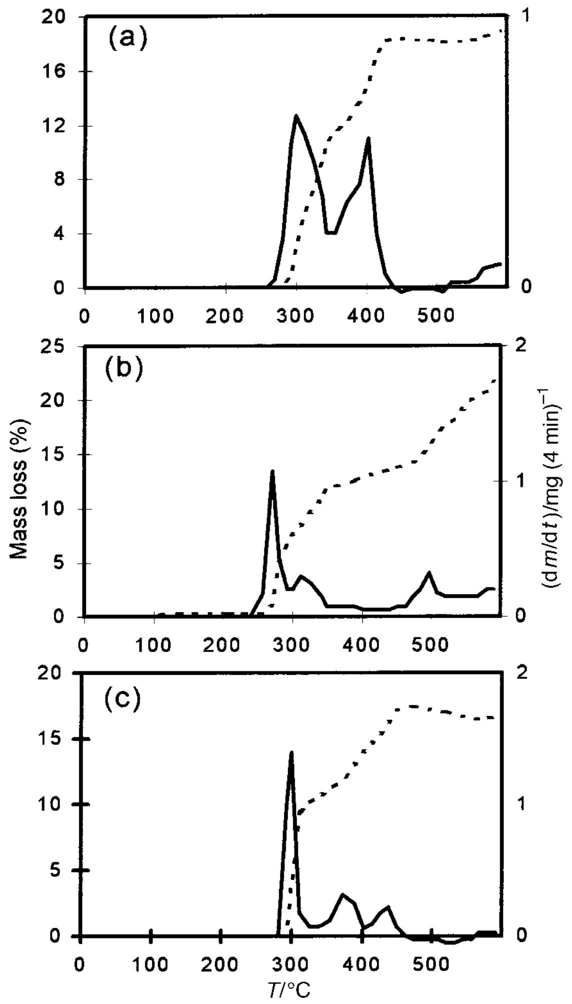

Fig. 1 TG (---) and DTG (——) curves of the reactions of lead precursors in $NaNO_2$–KNO_2: (a) $Pb(NO_3)_2$, (b) $PbCl_2$ and (c) $PbSO_4$

Titanium precursors

Titanium oxychloride $TiO_{1.5}Cl\cdot xH_2O$. Heated alone, titanium oxychoride is fully transformed into TiO_2 anatase as early as 400 °C [Fig. 2(a)]. The experimental mass loss (43.1%) conforms perfectly to the loss calculated from eqn. (3) (43.1%).

$$TiO_{1.5}Cl\cdot 1.9H_2O \rightarrow TiO_2 + 1.4\ H_2O + HCl \qquad (3)$$

Thermogravimetric investigation of the reaction of $TiO_{1.5}Cl\cdot 1.9H_2O$ with the $NaNO_2$–KNO_2 eutectic shows a significant mass loss in the range 100–200 °C, *i.e.* below the melting of the eutectic medium, and then a low and regular loss up to 500 °C [Fig. 2(b)]. A brown–red release of NO_2 is observed during the two losses. The XRD pattern of the residue of a reaction carried out at 150 °C reveals an amorphous powder whose annealing at 900 °C leads to TiO_2 rutile containing a small proportion of sodium titanates. The XRD pattern of the residue of the thermogravimetry up to 550 °C, annealed at 900 °C, shows a significant increase of the proportion of sodium titanates in the mixture. Consequently, the first step is attributed mainly to the formation of TiO_2 and the second one to its partial transformation into sodium titanates $Na_2Ti_nO_{2n+1}$, both steps involving a Lux–Flood acido–basic reaction *via* eqn. (4) and (5). The reaction of NO_2^- anions before melting could be explained by the presence of water brought by the oxychloride in the reaction mixture.

$$TiO_{1.5}Cl\cdot 1.9H_2O + 1.5\ NO_2^- \rightarrow TiO_2 + NO + 0.5\ NO_3^- + Cl^- + 1.9\ H_2O \qquad (4)$$

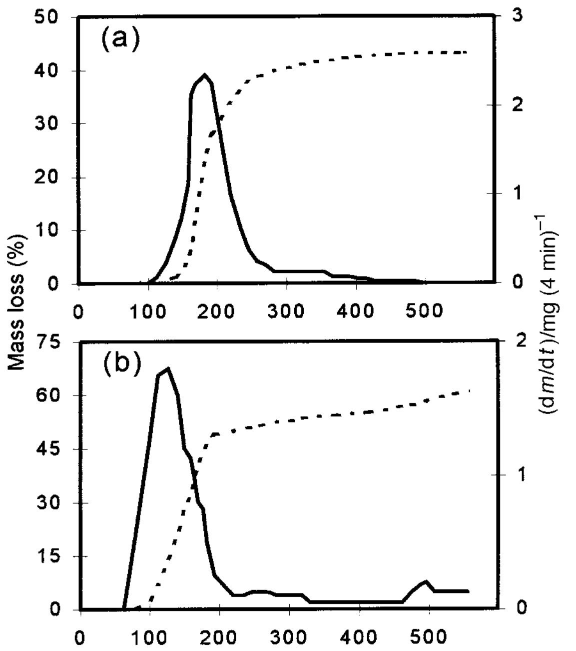

Fig. 2 TG (---) and DTG (——) curves of the reactions of $TiO_{1.5}Cl \cdot 1.9H_2O$: (a) alone, (b) in $NaNO_2$–KNO_2

$$n\,TiO_2 + 3\,NO_2^- + 2\,Na^+ \rightleftarrows Na_2Ti_nO_{2n+1} + NO_3^- + 2\,NO \quad (5)$$

Chemical analysis of a powder prepared at 550 °C (Ti: 40.15%, Na: 11.5%) corroborates the presence of a significant amount of sodium, but gives a Na/Ti molar ratio (0.6) too high to be explained by the formation of the only XRD identified sodium titanate, $Na_2Ti_6O_{13}$. The formation of other titanates richer in sodium has to be admitted. The increase of the slope above 500 °C is attributed to the beginning of the decomposition of the excess of nitrites.

Potassium hexafluorotitanate K_2TiF_6. The thermogravimetric curve of the reaction of anhydrous K_2TiF_6 with the molten $NaNO_2$–KNO_2 eutectic [Fig. 3(a)] is characterized by a significant mass loss above the melting of the nitrite medium, between 300 and 380 °C. A white precipitate is rapidly formed as early as 380 °C. Then, a very small loss is noticed up to 480 °C; above 500 °C, in contrast with the reaction of titanium oxychloride, decomposition of the excess of nitrites does not occur. This difference is interpreted by a stabilization of the nitrite ions by the fluoride ions. The experimental mass loss (48.4% at 500 °C) could be in good agreement with that calculated from eqn. (6) (50%), in which TiO_2 is the reaction product. However, the XRD pattern does not identify TiO_2 and the chemical analysis (Ti: 39.5%, Na: 7.0%, $F < 0.02\%$ and H: 1%) reveals the presence of a significant amount of sodium (molar ratio $Na/Ti = 0.37$), an unusual hydrogen content and the almost complete absence of fluorine. The XRD pattern is different from those of the sodium titanates listed in the ICCD index and from those of the titanates obtained in the reactions of titanium oxychloride.

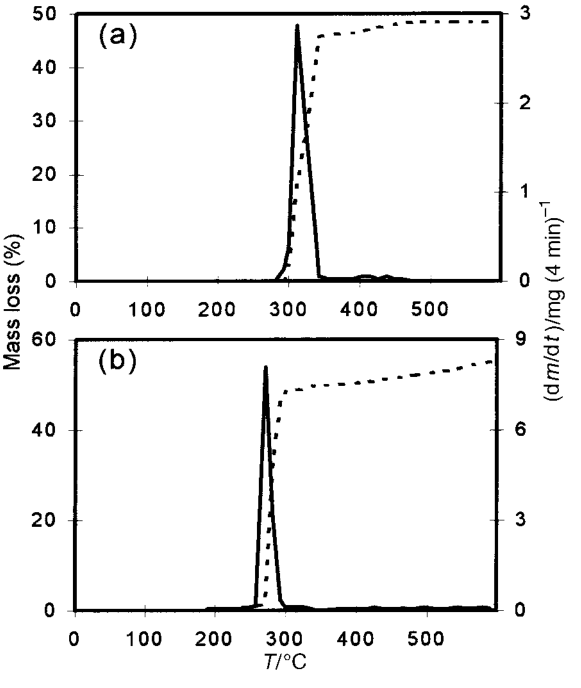

Fig. 3 TG (---) and DTG (——) curves of the reactions in $NaNO_2$–KNO_2 of (a) K_2TiF_6 and (b) $TiOSO_4$

$$K_2TiF_6 + 6\,NO_2^- \rightarrow TiO_2 + 4\,NO + 2\,NO_3^- + 6\,F^- + 2\,K^+ \quad (6)$$

The chemical data, as well as the XRD pattern, could be interpreted assuming the formation of a sodium titanium oxyfluoride $Na_nTiO_2F_n$ and its hydrolysis into sodium titanium oxyhydroxide during the aqueous extraction according to reactions (7) and (8)

$$K_2TiF_6 + 6\,NO_2^- + n\,Na^+ \rightarrow Na_nTiO_2F_n + 4\,NO + 2\,NO_3^- + (6-n)\,F^- + 2\,K^+ \quad (7)$$

$$Na_nTiO_2F_n + n\,H_2O \rightarrow Na_nTiO_2(OH)_n + n\,HF \quad (8)$$

Titanium oxysulfate $TiOSO_4$. As for K_2TiF_6, the reactivity of $TiOSO_4$ [Fig. 3(b)] is revealed by a significant mass loss between 270 and 300 °C related to the formation of TiO_2, followed by a low and regular loss up to 600 °C attributed to the progressive transformation of TiO_2 into sodium titanates. The XRD pattern of a powder prepared at 500 °C for 2 h, then annealed at 900 °C, identifies a mixture of TiO_2 and sodium titanates. Chemical analysis (Ti: 44.5%, Na: 11% and $S < 0.03\%$) corroborates the presence of sodium.

Simultaneous reactions of titanium and lead precursors in the molten $NaNO_2$–KNO_2 eutectic

Reaction of the titanium oxychloride with either lead nitrate or lead chloride

By comparison of the thermogram of reaction of a mixture of the titanium oxychloride and the lead salt (Fig. 4) with the curves of the individual reactions of each precursor (Fig. 1 and 2), it is unambiguously concluded that, whatever the lead salt, the two precursors react independently, as the temperature is raised to 450 °C. $TiO_{1.5}Cl \cdot 3.9H_2O$ reacts first mainly below melting; then the lead salt reacts above melting.

Taking into account the amounts of both precursors in the reaction involving $Pb(NO_3)_2$, it is noteworthy that the whole mass loss at 450 °C agrees with the sum of the losses that should be observed in the separate reactions of the precursors. Consequently it can be reasonably thought that, in the reaction, sodium titanates and lead oxide are formed as intermediates and then react together to precipitate lead titanate, the molten medium playing the role of a flux. In the reaction involving $PbCl_2$ it is not possible to locate the end of the reaction.

The yellow powder prepared from $Pb(NO_3)_2$, at 500 °C for 2 h, is identified as $PbTiO_3$ macedonite whereas, in the one elaborated from $PbCl_2$, a small proportion of $PbTiO_3$ is detected beside PbO (Fig. 5). The difference is corroborated by the chemical analysis which leads for the powder ex-$Pb(NO_3)_2$ (Pb: 63.20%, Ti: 14.60%, Na: 0.65%, K: 0.10%, $N < 0.02\%$) and for the powder ex-$PbCl_2$ (Pb: 55.35%, Ti:

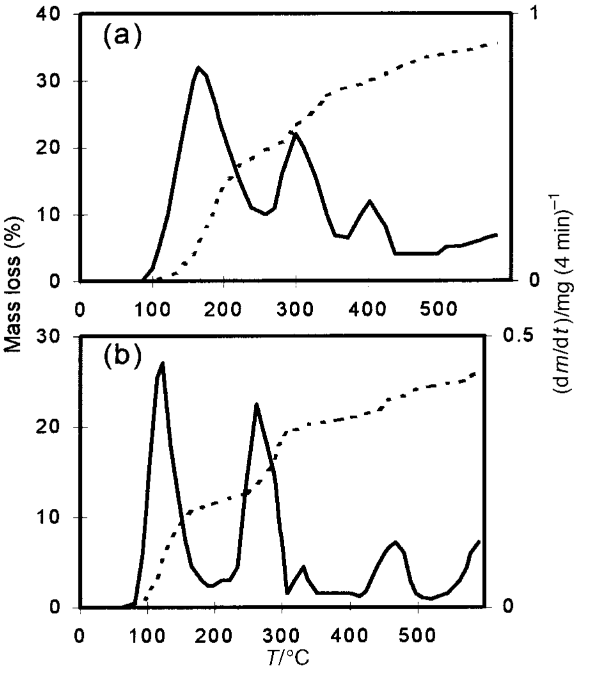

Fig. 4 TG (---) and DTG (——) curves of the reactions in $NaNO_2$–KNO_2 of mixtures: (a) $Pb(NO_3)_2 + TiO_{1.5}Cl \cdot 3.9H_2O$ and (b) $PbCl_2 + TiO_{1.5}Cl \cdot 3.9H_2O$

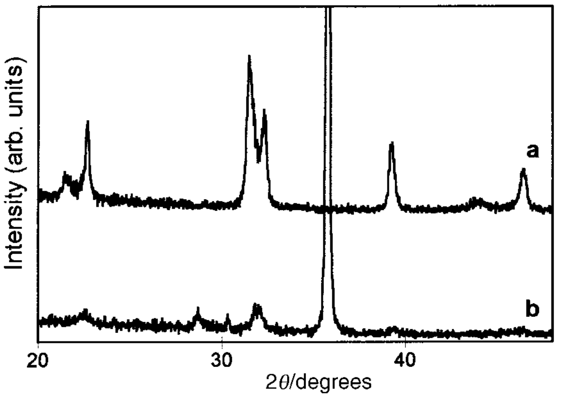

Fig. 5 XRD patterns of $PbTiO_3$ obtained from: (a) $Pb(NO_3)_2 + TiO_{1.5}Cl \cdot 3.9H_2O$ and (b) $PbCl_2 + TiO_{1.5}Cl \cdot 3.9H_2O$

19.00%, Na: 0.70%, Cl: 3.40%) to the respective molar ratios Pb/Ti = 1.01 and 0.65. In both powders, a significant amount of sodium is noticed. For the latter, it has to be concluded from the data that the reaction is incomplete (abnormally high content of Cl), that a part of the lead has been washed away during the extraction and that a significant amount of Ti is present in an amorphous phase, probably TiO_2 or sodium titanates rich in Ti.

Other reactions

The reactivity of four equimolar mixtures was investigated: $K_2TiF_6 + Pb(NO_3)_2$, $K_2TiF_6 + PbSO_4$, $TiOSO_4 + Pb(NO_3)_2$ and $TiOSO_4 + PbSO_4$. The four thermograms (Fig. 6) are characterized by the presence of only one sharp significant mass loss above the melting point in the range 250–300 °C. Then, for the mixtures containing $PbSO_4$, a tenfold smaller loss is noticed about 100 °C above the first loss, after which mass remains quite constant, whereas for the mixtures containing $Pb(NO_3)_2$, a regular small mass loss is observed between 300 and 500 °C. The decomposition of the excess of the alkali-metal nitrites above 500 °C is clearly revealed only for the mixture $Pb(NO_3)_2 + K_2TiF_6$.

For the reaction of the mixture $K_2TiF_6 + Pb(NO_3)_2$, the experimental mass loss at 450 °C (33.6%) is slightly higher than that calculated (31.5%) from eqn. (9). Moreover, the XRD pattern of a sample prepared at 450 °C for 2 h [Fig. 7(a)] reveals only the formation of $PbTiO_3$ macedonite and its chemical analysis (Pb 65.00%, Ti 15.20%, Na 0.25%, K 1.5×10^{-3}%, F <0.02% and N <0.02%) leads to a molar ratio Pb/Ti of 0.998. The XRD pattern of a sample prepared at 350 °C for 2 h indicates that $PbTiO_3$ is already formed as well as an amorphous phase; the presence of lead oxide is not detected [Fig. 7(b)].

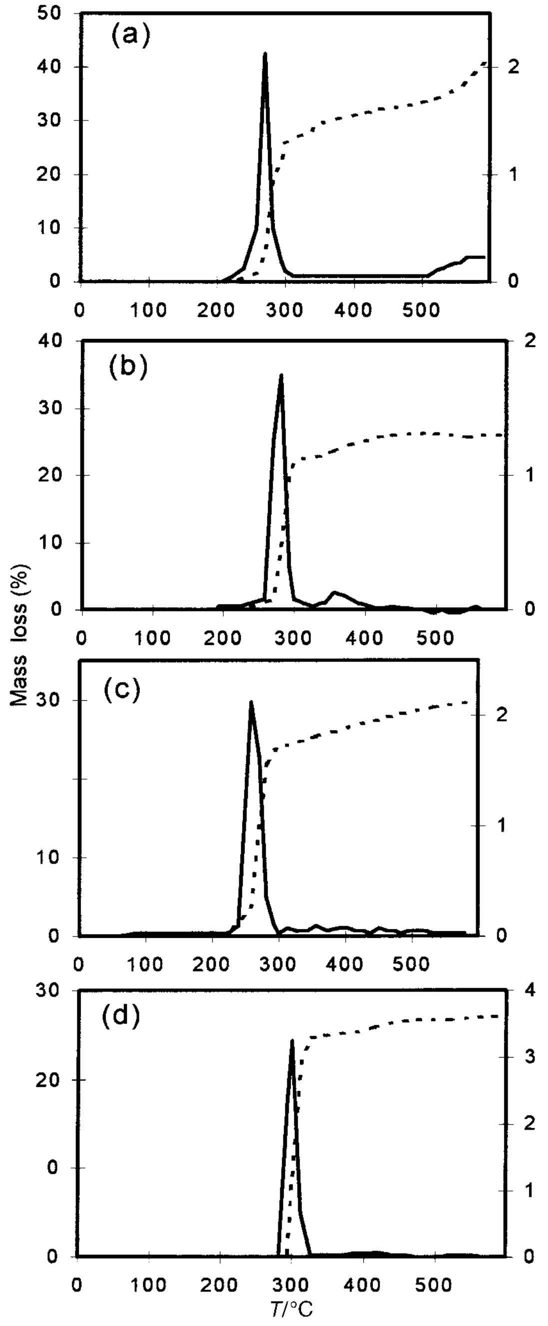

Fig. 6 TG (---) and DTG (——) curves of the reactions in $NaNO_2$–KNO_2 of mixtures: (a) $Pb(NO_3)_2 + K_2TiF_6$, (b) $PbSO_4 + K_2TiF_6$, (c) $TiOSO_4 + Pb(NO_3)_2$ and (d) $TiOSO_4 + PbSO_4$

$$Pb(NO_3)_2 + K_2TiF_6 + 9NO_2^- \rightarrow PbTiO_3 + 6NO + 5NO_3^- + 6F^- + 2K^+ \qquad (9)$$

For the three other mixtures, the experimental losses are significantly lower than those calculated from equations similar to eqn. (9). The XRD patterns of the samples prepared at 500 °C for 2 h (Fig. 8) reveal the formation of a mixture of

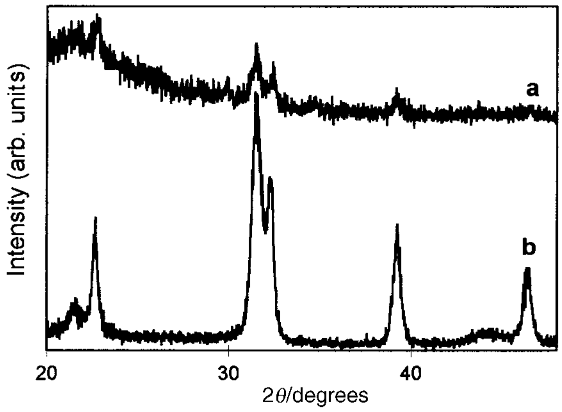

Fig. 7 XRD patterns of $PbTiO_3$ prepared in $NaNO_2$–KNO_2 from reaction of K_2TiF_6 and $Pb(NO_3)_2$ at (a) 350 °C, (b) 450 °C

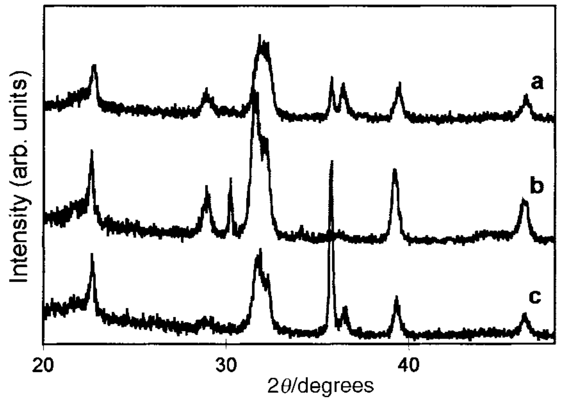

Fig. 8 XRD patterns of $PbTiO_3$ prepared in $NaNO_2$–KNO_2 from reactions: (a) $PbSO_4+K_2TiF_6$, (b) $Pb(NO_3)_2+TiOSO_4$ and (c) $PbSO_4+TiOSO_4$

PbO and $PbTiO_3$ and the chemical analysis (Table 1) leads to Pb/Ti molar ratios different from 1.

Discussion

Among the three titanium precursors, the behaviour of the oxychloride is peculiar. When it reacts alone with the $NaNO_2$–KNO_2 medium, it is the only salt for which the reaction exhibits a first step, below melting, leading mainly to TiO_2 and then goes on above melting with a partial transformation of TiO_2 into sodium titanates. When it reacts in the presence of a lead precursor, the step below melting is still observed; consequently both precursors react successively so that two intermediates, lead monoxide and sodium titanates, are formed and finally react together to give the final product $PbTiO_3$, the molten medium playing the role of a flux. Among the lead precursors, the nitrate seems the most reactive and the formation of $PbTiO_3$, by the reaction of mixtures $Pb(NO_3)_2$–$TiO_{1.5}Cl$ in molten $NaNO_2$–KNO_2 at 500 °C for 2 h, can be outlined as follows: (1) formation of TiO_2 below melting *via* reaction (4); (2) melting [eqn. (10)] and formation of the intermediates *via* the Lux–Flood acido–basic reactions (11), (12) and (13):

$$(Na,K)NO_2 \rightarrow (Na,K)^+ + NO_2^- \qquad (10)$$

$$3\ NO_2^- \rightleftarrows 2\ NO + NO_3^- + O^{2-} \qquad (11)$$

$$n\ TiO_2 + O^{2-} \rightleftarrows [Ti_nO_{2n+1}]^{2-} \rightarrow Na_2Ti_nO_{2n+1} \qquad (12)$$

$$Pb^{2+} + O^{2-} \rightarrow PbO \qquad (13)$$

(3) partial dissolution of the intermediates shifted until the complete transformation by the precipitation of $PbTiO_3$ and involving an equilibrium between mono and polytitanate anions *via* reactions (14) and (15):

$$[Ti_nO_{2n+1}]^{2-} + (n-1)O^{2-} \rightleftarrows n\ TiO_3^{2-} \qquad (14)$$

$$Pb^{2+} + TiO_3^{2-} \rightarrow PbTiO_3 \qquad (15)$$

With the other titanium precursors, the reaction with molten $NaNO_2$–KNO_2 in the presence of a lead precursor occurs apparently in one step above melting. For the most reactive mixture, K_2TiF_6–$Pb(NO_3)_2$, $PbTiO_3$ is obtained as early as 350 °C, without identification of the formation of any intermediate. Then, two hypotheses may be assumed: (1) $PbTiO_3$ is directly precipitated from dissolved species, involving reactions (16) and (15):

$$TiF_6^{2-} + 9\ NO_2^- \rightleftarrows TiO_3^{2-} + 6\ NO + 3\ NO_3^- + 6\ F^- \qquad (16)$$

(2) the mechanism is identical to that outlined for the mixture $TiO_{1.5}Cl$–$Pb(NO_3)_2$, but the appearance of intermediates has not been detected because they are formed in the same narrow temperature range.

Table 1 Chemical analysis (mass%) of constitutive elements of samples obtained from: (a) $PbSO_4+K_2TiF_6$; (b) $Pb(NO_3)_2+TiOSO_4$; (c) $PbSO_4+TiOSO_4$

	element						
sample	Pb	Ti	Na	K	F	S	molar ratio Pb/Ti
a	65.30	16.10	1.00	0.03	<0.02	0.6×10^{-2}	0.94
b	67.90	14.00	0.20	0.05			1.12
c	64.95	14.05	0.25	0.06		0.12	1.07

Nevertheless, tetragonal $PbTiO_3$ can be prepared in molten $NaNO_2$–KNO_2, at a moderate temperature and for a relatively short duration, by reaction of lead nitrate and either titanium oxychloride or potassium hexafluorotitanate. In both cases, the powder is characterized by a molar Pb/Ti ratio close to unity, but also by the presence of sodium, in the range 0.2–0.6 mass%, which is liable to influence the electrical properties. Its presence can be avoided by performing the reactions in molten KNO_2. Thus, the reactivity of titanium oxychloride with potassium nitrite, alone and in the presence of lead nitrate, is very similar to that occurring in $NaNO_2$–KNO_2. The only difference is that the formation of alkali-metal titanates as final or intermediary products is never observed; it is replaced by the formation of titanium dioxide.

Conclusion

As foreseen from the literature information, in the sodium containing nitrite molten media, the basicity of the nitrite anions is high enough to promote the transformation of amorphous TiO_2 into sodium polytitanates, when the reactions are performed with a titanium precursor alone. When a lead precursor is involved together with the titanium precursor, the formation of $PbTiO_3$ is always observed, in a more or less significant proportion, as well as PbO. The kinetics of the $PbTiO_3$ formation appear to be strongly dependent on the nature of both precursors, the most reactive ones being the nitrate for lead, the oxychloride and the hexafluoro-potassium salt for titanium.

Using these latter materials, tetragonal lead titanate, exhibiting a molar Pb/Ti ratio close to unity, is able to be synthesized by a thermal treatment at 500 °C for 2 h. When prepared in $NaNO_2$–KNO_2, it contains a small amount of sodium which has an effect on the physical properties.[12] Its presence can be avoided by carrying out the reaction in molten KNO_2.

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