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Reactivity of NH$_4$H$_2$PO$_4$ toward LaCl$_3$ in LiCl-KCl Melt Flux. Step by Step Formation of Monazite-Like LaPO$_4$.

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The synthesis of lanthanum phosphates in molten LiCl-KCL eutectic was chosen to address the preliminary treatment of chlorinated wastes containing fission products that are already present in a Li/Cl eutectic. The obtained monazite compound shows interesting properties to be considered as a good candidate to trap lanthanum for a long-time. The synthesis route based on LaCl$_3$ reaction with NH$_4$H$_2$PO$_4$ in a stoichiometric amount is a key point to obtain monazite as a pure phase. Hence, the salt composition is not modified during the synthesis reaction. The chemical reactivity of ammonium dihydrogenphosphate (NH$_4$H$_2$PO$_4$, hereafter abbreviated ADP) toward lanthanum chloride (LaCl$_3$) in molten LiCl-KCl eutectic is probed by NMR spectroscopy to follow the formation of LaPO$_4$. Formally, a direct transformation of the two aforementioned precursors into LaPO$_4$, NH$_4$Cl and HCl can be discarded on the basis of the low thermal stability of ADP. To shed some light on the formation of LaPO$_4$, in situ and ex situ NMR experiments were carried out on LiCl-KCl/LaCl$_3$/ADP, as well as LiCl-KCl/ADP, KCl/ADP, and LiCl/ADP mixtures. First, the reactivity of the precursors in contact with the eutectic was studied from room temperature to 600 °C by means of ^{31}P, ^{35}Cl, and ^{139}La high temperature NMR. Second, ex situ room temperature magic angle spinning (MAS) and RadioFrequency driven recoupling (RFDR) ^{31}P solid-state NMR experiments were carried out on solid samples prepared in different conditions (i.e., temperature and atmosphere) and quenched at room temperature to identify frozen intermediate species in their metastable state. On the basis of this approach, we propose a model for the LaPO$_4$ formation based on a multistep mechanism which highlights the strong reactivity of ADP toward the alkaline salts but without final change in the composition of the solvent.

1. Introduction

The precipitation of lanthanum phosphates was investigated in molten LiCl-KCl eutectic to address the conditioning of nuclear wastes . Pyrochemical treatment used for spent fuel reprocessing is based on the use of non-aqueous solvents. After this step, fission products that have to be conditioned for the long-term are present in the salt as chlorides (e.g., LaCl$_3$). The synthesis of monazite directly in the molten bath seems to be an interesting way to trap lanthanum for long-term storage. Before the investigation on the mechanism of a particular reaction of LaCl3 with NH$_4$H$_2$PO$_4$, we present in this paper a review of the different synthesis routes to obtain monazite along with their different fields of application.

REPO$_4$ monazite-type compounds (RE = rare earth), prepared as powders, thin films, or dense ceramics, are widely used in the industry. Because of their high luminescence quantum efficiency, RE doped phosphates are employed in laser technology, compact fluorescent lamps, and plasma display panels.[1,2] Phosphate glasses and ceramics are also well designed for biological implants and glass metal joining.[3] Moreover, monazite-like LaPO$_4$ is well-known as solid-state protonic conductor when a small percentage of La is substituted by Sr or Ca[4−7] and is also a good candidate as a

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novel interphase material for oxide−oxide ceramic matrix composites.[8−10] At the end, monazite is a naturally occurring mineral which has the ability to encapsulate uranium and/or thorium. Similar synthetic phases, which present both a high stability under irradiation and an important leaching resistance, can also be considered as potential host matrixes for long-term storage of radioactive wastes.[11−13]

In materials science, it is well-known that the elaboration process may strongly influence the physical and chemical properties of the ceramics. Namely, the chosen chemical route may be crucial to control the purity of the final product, the grain size and their distribution, the morphology, the crystallinity, and so on. So far, various methods are reported in the literature to prepare REPO$_4$-based materials. We briefly sum up some of them for the particular case of LaPO$_4$ and its derivatives.

Commonly, the solid route involves a direct reaction between RE oxides or salts (e.g., RE$_2$O$_3$, RE(NO$_3$)$_3$, RE-(OH)$_3$) and phosphates (e.g., (NH$_4$)$_2$HPO$_4$, NH$_4$H$_2$PO$_4$). According to Bregiroux et al.,[14] Onada et al.,[15] and Su et al.[16] this ceramic method, applied to the preparation of various REPO$_4$ (RE = La, Ce, Pr, Nd), requires very high temperatures (typically 1200 °C−1300 °C) to form pure monazite.

Alternatively, soft chemistry routes may also be called on. Hence, Lucas et al.[17,18] reported on the precipitation of REPO$_4$ compounds (RE = La, Ce) from RECl$_3$ and H$_3$PO$_4$ or (NH$_4$)$_2$HPO$_4$ in aqueous solutions. Unfortunately, this method systematically ends at the stabilization of the rhabdophane structure like REPO$_4$·nH$_2$O hydrated phase. Others authors suggested the dissolution of La$_2$O$_3$ or La-(OH)$_3$ in H$_3$PO$_4$ to access to LaPO$_4$.[19−21] Here again, the precipitation reaction at room temperature (RT) leads to the rhabdophane structure. Whatever the technique used, soft chemistry routes require an additional annealing treatment in the 700 °C−900 °C temperature range to convert the rhabdophane structure into the monazite one. Nevertheless, if a large crystal size is required, the annealing treatment has to be done at 1000 °C. Moreover, formation of pure monazite can require an annealing step at a temperature as high as 1400 °C[17,18].

In another context, Lenggoro et al.[1] proposed a one step method to prepare pure Ce and Tb doped monazite-like LaPO$_4$ phosphors on a spray pyrolysis for about 5 s with temperature ranging from 600 to 1550 °C. With such a method, spherical particles were obtained, well-crystallized particles being only observed for temperatures higher than 1000 °C. Recently, Gallini et al.[22] applied the combustion technique to the preparation of strontium doped LaPO$_4$. Such technique leads to a rhadophane/monazite blend, an annealing at 400 °C and 800 °C for 12 h being necessary for access to pure monazite and high crystallinity, respectively.

Very low temperature routes for monazite synthesis were also proposed. Fujishiro et al.[23] prepared LaPO$_4$ particles via an hydrothermal reaction at 150 °C with La[EDTA] complex. Besides, according to Erdei et al.[24,25] LaPO$_4$ nanoparticles have been prepared at $T < 100$ °C at room pressure by the hydrolyzed colloid reaction technique. Nevertheless, only X-ray diffraction (XRD) patterns collected after annealing at 800 and 1500 °C are reported, suggesting again that resorting to high temperature is mandatory to get pure and crystallized materials.

Recently, the molten salt technique (flux method) was applied to the synthesis of REPO$_4$ compounds with the monazite form by Volkovich et al.[26−28] and Hudry et al.[29]. Both studies used the molten LiCl-KCl eutectic as solvent at 500 °C with LaCl$_3$ and A$_3$PO$_4$ (A = Li, K) or LaCl$_3$ and NH$_4$H$_2$PO$_4$ (hereafter abbreviated ADP) as pristine materials, respectively. Volkovich's route allowed the formation of LaPO$_4$ but the complete precipitation of lanthanum required using an excess of A$_3$PO$_4$ (P/La molar ratio ≈ 5) that caused the formation of partially soluble secondary phases (Li$_3$PO$_4$) which cannot be entirely separated from the target compound. At the opposite end, the route presented in ref 29 allowed the direct formation of LaPO$_4$ without impurity, the solvent being dissolved in distilled water or polar solvents afterward.

In fact, if the flux method is well established in solid chemistry for exploratory and target syntheses for oxides and chalcogenides,[30−33] little information is available concerning the nature of the solvated species or the reactivity of the melt toward the precursors.

The goal of the present study is to shed some light on the formation mechanism of LaPO$_4$-monazite in LiCl-KCl eutectic by tracking transitory species by NMR in LiCl-KCl eutectic versus different parameters such as temperature, atmosphere, mixture chemical composition, and reaction duration. In this context, investigations on the reactivity of LiCl-KCl melt toward LaCl$_3$ and ADP were carried out in

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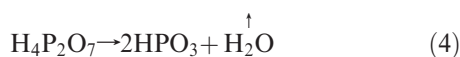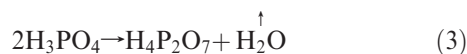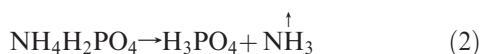
situ by ^{31}P, ^{35}Cl, and ^{139}La high temperature nuclear magnetic resonance spectroscopy (HT-NMR) from RT to melting temperature of the mixture, and ex situ by 1D Magic Angle Spinning (MAS) and 2D RadioFrequency Driven Recoupling (RFDR) ^{31}P solid-state NMR spectroscopy at RT on quenched samples. This leads to the identification of some of the intermediate species, and allows proposing a conversion pathway from $LaCl_3$ and ADP to $LaPO_4$.

2. Outline

So far, no study has been devoted to the understanding of what happens in a LiCl-KCl solvent in contact with $LaCl_3$ and ADP. Because of the low thermal stability of ADP, we may speculate that the formation of $LaPO_4$ in a melt at 500 °C cannot result from the direct interaction between $LaCl_3$ and ADP on the basis of reaction 1.

$$LaCl_3 + NH_4H_2PO_4 \xrightarrow[500°C]{(LiCl-KCl)e} LaPO_4 + NH_4Cl\uparrow + 2HCl\uparrow \quad (1)$$
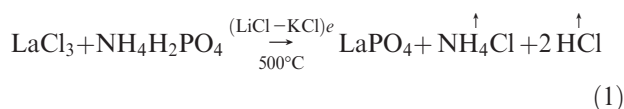
In fact, several authors reported on the thermal decomposition in air or neutral gas of pure solid ADP in the 170 °C–210 °C temperature range.[34–37] So far, the decomposition process is not clearly identified, and some controversies remain. On the basis of Abdel-Kader et al. investigations[34,35], the ADP would decompose under Ar atmosphere according to the three following reactions.

$$NH_4H_2PO_4 \rightarrow H_3PO_4 + NH_3\uparrow \quad (2)$$

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O\uparrow \quad (3)$$

$$H_4P_2O_7 \rightarrow 2HPO_3 + H_2O\uparrow \quad (4)$$

In contrast, Torijano et al.[36] suggested the thermal decomposition of ADP would consist first in a condensation reaction according to reaction 5 followed by a decomposition above 200 °C of the so-formed compound. This model was also supported by Maciejewski et al.[37]

$$2NH_4H_2PO_{4(s)} \rightarrow (NH_4)_2H_2P_2O_{7(s)} + H_2O\uparrow \quad (5)$$
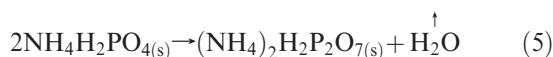
In the present study, ADP is in contact with both the LiCl-KCl eutectic and $LaCl_3$ which makes the reactive system much more complex. Namely, the ADP decomposition pathway may significantly differ from that observed for the pure compound in neutral atmosphere or in air. Basically, ADP can react at low temperature to give rise to the formation of transient phases, as shown below.

Table 1. Composition of the different systems (mol) which were studied for the "direct" and the "indirect" approach[a]

	composition (mol)				
system	LiCl	KCl	$LaCl_3$	ADP	remark
I	$(1 - x)$	x	0	0	$0 \leq x \leq 1$[b] (DA)
II_a	$8.40.10^{-2}$	$5.96.10^{-2}$	$8.15.10^{-3}$	$2.04.10^{-2}$	P/La = 2.5 (DA)
II_b	$8.40.10^{-2}$	$5.96.10^{-2}$	$8.15.10^{-3}$	$8.15.10^{-3}$	P/La = 1 (DA, IA)
II_c	$8.40.10^{-2}$	$5.96.10^{-2}$	$8.15.10^{-3}$	$2.72.10^{-3}$	P/La = 0.33 (DA)
III_a	$8.40.10^{-2}$	$5.96.10^{-2}$	0	$8.15.10^{-3}$	(IA)
III_b	0	$5.96.10^{-2}$	0	$8.15.10^{-3}$	(IA)
III_c	$8.40.10^{-2}$	0	0	$8.15.10^{-3}$	(IA)

[a] DA and IA correspond to samples used for the "direct" and "indirect" approaches, respectively. [b] x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.57, 0.60, 0.7, 0.8, 0.9, 1.

3. Experimental Section

3.1. Systems Studied. To tackle the reactivity of $LaCl_3$ and ADP in the flux, two approaches were used: the "direct" and the "indirect" approaches to follow the liquid and the solid-state reactivity, respectively. Compositions of the different systems studied are gathered in Table 1. Chloride salts (LiCl, KCl, and $LaCl_3$, Aldrich, 99.99%) and ADP (Aldrich, 99.9%) were handled in a glovebox under dried argon and used without further purification. The pure eutectic solvent with 58.5 mol % LiCl/41.5 mol % KCl composition had a melting point (mp) of 353 °C. All samples for the "direct" and "indirect" approaches were prepared in the glove box by mixing suitable amounts of the reactants in an agate mortar.

3.2. Direct Approach. First, the LiCl-KCl eutectic, hereafter labeled (LiCl-KCl)$_e$, was progressively loaded with $LaCl_3$ with a substitution rate ranging from 0 to 100% (samples of system I). The dissolution of $LaCl_3$ into (LiCl-KCl)$_e$ was followed by the evolution of ^{35}Cl and ^{139}La NMR signals with temperature and chemical composition of the melt.

Then, ADP was added to a 95 mol % (LiCl-KCl)$_e$/5 mol % $LaCl_3$ mixture in a stoichiometric amount compared to La content (P/La = 1, system II_b), in excess (P/La = 2.5, system II_a), and in default (P/La = 0.33, system II_c) to address the reactivity of ADP toward lanthanum chloride by means of ^{31}P, ^{35}Cl, and ^{139}La HT-NMR.

For these in situ experiments, each sample ($\approx$ 50 mg) was introduced in a high purity boron nitride (BN) crucible, tightly closed by a screwed BN cap, and placed inside the Radio-Frequency coil at the center of the cryomagnet. For the experiments labeled "air atmosphere" the crucibles were opened in air just before the introduction into the NMR probe. As mentioned in section 4.4, air atmosphere is needed to ensure the formation of pure monazite. It was then heated with the laser heating device developed in CEMHTI, Orleans.[38] Samples of system I were heated up to their mp (with a maximum temperature at 900 °C for pure $LaCl_3$) while those of system II were heated up to 600 °C. The total time spent above RT was $\approx$ 15 min for samples of system I and $\approx$ 30 min for samples of system II. After reaching the maximum temperature, the sample was rapidly cooled back to RT. Besides, only samples of system II were recovered after cooling and ground to powder in the glove box. The powder samples were then packed into 4 mm zirconia rotors for ex situ ^{31}P MAS NMR characterization at RT.

3.3. Indirect Approach. First, experiments were carried out on samples of system II_b to try to identify the nature of the intermediate species directing the formation of $LaPO_4$. Samples were heated in air up to six different target temperatures (i.e., 100 °C, 200 °C, 300 °C, 340 °C, 370 °C, 470 °C) during 5 min. Then systems III_a, III_b, and III_c were investigated in a similar

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way to probe and highlight the reactivity of ADP toward LiCl and KCl. Nevertheless, heating was just realized in air at 300 °C during 5 min. Finally, the role of the atmosphere composition on the LaPO$_4$ formation was investigated with system II$_b$ at 500 °C during 5 h under different atmospheres (i.e., air, argon, and oxygen).

All the samples of the indirect approach ($\approx$ 10 g) were prepared in a homemade quartz reactor as discussed in[29], the whole set being quenched under a flux of compressed air to freeze intermediate species in their metastable state. Samples were then introduced in the glove box, reduced to powder, and packed into 4 mm zirconia rotors for ex situ ^{31}P MAS as well as RFDR NMR characterizations at RT.

3.4. NMR Spectroscopy. All the NMR experiments were carried out in Orleans (CEMHTI) on a Bruker ADVANCE 400 spectrometer with a magnetic field of 9.4 T operating at frequencies of 161.99, 39.2, and 56.5 MHz for ^{31}P, ^{35}Cl, and ^{139}La, respectively. In situ HT-NMR spectra were collected with a CO$_2$ laser heating system[38].

The HT-NMR spectra were acquired using a single pulse sequence, with a recycle delay of 0.5 s and between 64 and 256 accumulations. The pulses were $\pi/12$ for ^{35}Cl and $\pi/2$ for ^{139}La. The chemical shifts were referred to 85% H$_3$PO$_4$ for ^{31}P, 1 M NaCl, and LaCl$_3$ solutions, for ^{35}Cl and ^{139}La respectively.

Solid-state ^{31}P NMR data were collected with a 14 kHz spinning rate and single pulse sequence with $\pi/18$ pulses and an optimized delay time of 200 s.

The RadioFrequency Driven Recoupling (RFDR)[39] spectrum was acquired at a MAS speed of 14 kHz, using a mixing time of 20 ms, a recycling delay of 60 s, 24 accumulated Free Induction Decay (FID) per t_1 and 168 t_2, a t_1 increment of 80 μs, acquisition mode in TPPI, 14 kHz in t_2 dimension. Radio-Frequency field: 70 kHz. Chemical shifts are reported relative to 85% H$_3$PO$_4$. All NMR spectra (HT and MAS) were modeled with the Dmfit program[40].

4. Results and Discussion

4.1. "Direct" Approach: In Situ Studies. 4.1.1. System I: $(1 - x)$(LiCl-KCl)$_e$ − xLaCl$_3$. The evolution of ^{35}Cl spectrum with temperature is displayed in Figure 1a for pure (LiCl-KCl)$_e$ solvent. Below its m.p, two broad peaks are observed. They are assigned to the two distinguishable environments of chlorine in LiCl and KCl solid salts. When the temperature is raised above the mp, the ^{35}Cl NMR spectrum becomes well resolved with only one single sharp peak. This originates from the fact that in the liquid phase, a fast exchange regime takes place. Namely, the isotropic chemical shift (δ_{iso}) is the average of the chemical shifts of chlorine anions with distinct first coordination spheres balanced by their relative abundance in the melt:

$$\boldsymbol{\delta}_{iso}(N) = \sum_i X_{A_i}^N \cdot \boldsymbol{\delta}^N(A_i)$$

where N is the nucleus considered, $\delta^N(A_i)$ the chemical shift for N in the species A_i, and $X^N(A_i)$ the abundance of A_i species in the melt. δ_{iso} is not significantly affected by temperature, at least up to the degradation of the flux. For all the samples with the $(1-x)$ (LiCl-KCl)$_e$ + xLaCl$_3$ (with $0 \leq x \leq 1$) chemical composition (i.e., samples of
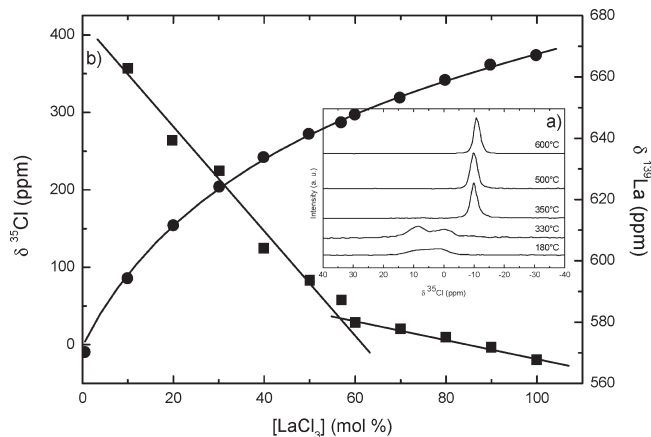

Figure 1. In situ HT-NMR experiments on $\{(1 - x)$(LiCl-KCl) + xLaCl$_3\}$ with $0 \leq x \leq 1$. (a) Example of the evolution of the ^{35}Cl spectrum for pure eutectic as a function of temperature. (b) Evolution of the chemical shifts for ^{35}Cl (black circle, left scale) and ^{139}La (black square, right scale) as a function of LaCl$_3$ concentration in the eutectic solvent (LiCl-KCl)$_e$.

system I), NMR spectra exhibit similar features. The same observations were done for ^{139}La spectra not given here.

The evolution of chemical shifts for ^{35}Cl and ^{139}La with temperature for the whole series are depicted in Figure 1b. The spectra were recorded for temperature ranging in the 350−900 °C interval depending on the composition of the mixture. The evolution of the ^{139}La chemical shifts evidence two domains. Namely, from 0 to 60% LaCl$_3$ and then from 60% to 100% LaCl$_3$, δ decreases linearly with the La content, that is, first from $\approx$660 ppm to $\approx$580 ppm and then from $\approx$580 ppm to $\approx$570 ppm. The occurrence of these two segments suggests the existence of three well-defined chemical environments for La in the liquid (i.e., different coordination polyhedra) with the coexistence of two of them in each domain. In contrast, the ^{35}Cl chemical shift varies monotonically with LaCl$_3$ content from − 10 ppm for (LiCl-KCl)$_e$ to +375 ppm for the pure LaCl$_3$. This suggests that different kinds of Cl$^-$ anions exist over the whole range of compositions.

By analogy with molten fluoride mixtures, we can draw a parallel in the monotonic evolution observed for ^{19}F chemical shifts in REF$_3$-AF (RE = La or Y, A = alkaline) binary systems, by Rollet et al.[41] and Bessada et al.[42,43] and the ^{35}Cl data obtained in the present work. The evolution of ^{19}F chemical shifts versus the RE content was explained with the existence of at least three different fluoride anions: (i)"free" fluoride anions weakly interacting with alkali metals, (ii) fluorine anions strongly solvate to RE because of the ability of lanthanides for bonding with halogens, as soon as REF$_3$ salt is introduced to form "REF$_x$" polyhedra, and (iii) bridging fluorides for higher RE concentrations when the REF$_x$ polyhedra start condensing, the higher the ReF$_3$ concentration, the higher the degree of polymerization. This description agrees with the ^{35}Cl chemical shift evolution observed in ternary molten

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$(LiCl-KCl)_e$-$LaCl_3$ system and goes along with the occurrence of three types of chemical environments for La.

Unfortunately, if NMR is capable of detecting the presence of new species, this technique cannot alone provide insight on the chemical environment of the probed element. This is why the proposed explanations will have to be corroborated by other techniques (X-ray diffraction coupled with a pair distribution function analysis, HT-Raman spectroscopy, dynamic calculations on the flux in its liquid state, EXAFS versus temperature). In the literature, different studies using spectroscopy or molecular dynamic calculations have been reported on molten $LaCl_3$ and show some controversial conclusions. Okamoto and Madden[44] studied the structure of pure molten $LaCl_3$ by XRD and found a coordination number of 6, suggesting the existence of $[LaCl_6]^{3-}$ complexes. However, a coordination number of 8.2 was found by Wasse et al.[45,46] in their neutron scattering studies on molten $LaCl_3$ supported by numerical simulations with a coordination number between 7 and 8.[47,48] On the other hand, structural data on molten $RECl_3$-ACl binary systems seem to converge. The group of Papatheodorou[49−52] studied the local structure by means of HT Raman spectroscopy. They found that the RE is surrounded by six Cl^- over the whole range of compositions and independently of the alkali. Glover et al.[53] deduced the same coordination number for $LaCl_3$−NaCl and $LaCl_3$−CsCl systems at infinite dilution in lanthanum. These observations are also supported by Ikawada et al.[54].

In their NMR study of solid lanthanum halides, Ooms et al.[55] found a ^{139}La chemical shift of 305 ± 5 ppm. Such a value strongly differs from the value we have obtained in the liquid state: 567 ppm for pure $LaCl_3$. Thus, we assume that the coordination of lanthanum in pure molten $LaCl_3$ cannot be the same as in the solid. To get more detailed interpretation on the nature and the coordination number in the molten state, additional solid state ^{139}La NMR experiments at high magnetic field are in progress.

4.1.2. System II: $(LiCl-KCl)_e - LaCl_3 - ADP$. Recently, Hudry et al.[29] evidenced the possibility to fully convert $LaCl_3$ into $LaPO_4$ in molten $(LiCl-KCl)_e$ with ADP in stoichiometric amount. As mentioned before, a direct interaction between the two precursors seems
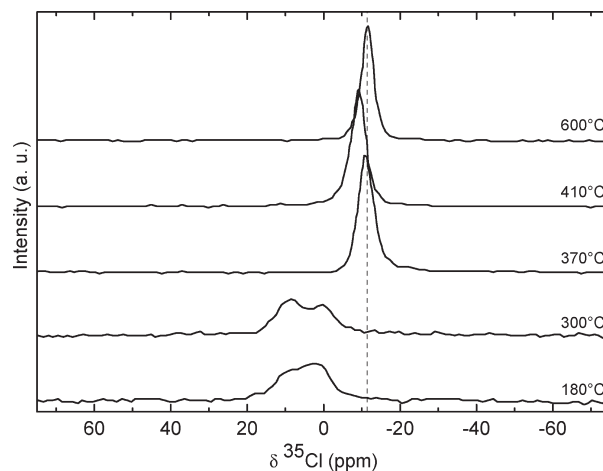

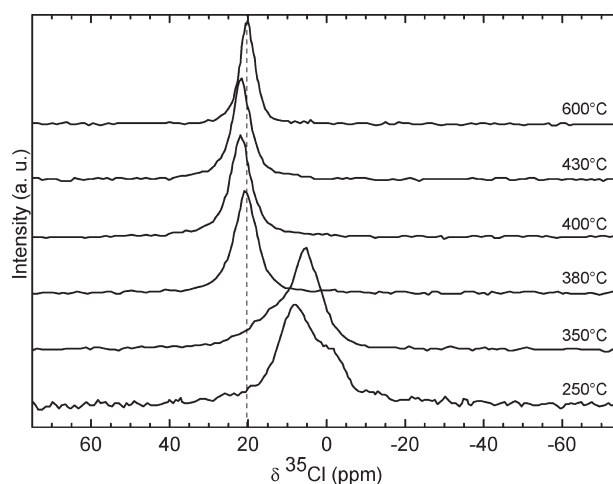**Figure 2.** Evolution of the ^{35}Cl spectrum, as a function of temperature, for the II_b system {$(LiCl-KCl)+LaCl_3+NH_4H_2PO_4$, $P/La = 1$}.

Figure 3. Evolution of the ^{35}Cl spectrum, as a function of temperature, for the initial mixture composition II_c {$(LiCl-KCl) + LaCl_3 + NH_4H_2PO_4$, $P/La = 0.33$}.

unlikely. To better delimit the role of ADP, three mixtures with different P/La molar ratio (i.e., $P/La = 2.5$, 1, and 0.33) were investigated; the $LaCl_3$ concentration remaining settled at approximately 5 mol %. For system II_b (i.e., $P/La = 1$), the evolution of ^{35}Cl NMR spectrum with temperature is given in Figure 2.

As expected, below the mp ($T \approx 370$ °C), ^{35}Cl signals are broad. Above the mp, the ^{35}Cl signal is characterized by a single sharp peak with an isotropic chemical shift of -9 ppm. This value is just slightly changed up to 600 °C, within the experimental error (± 1 ppm), and turns out to be very close to that of pure $(LiCl-KCl)_e$. This suggests that the chemical reaction between $LaCl_3$ and ADP is complete, involving the formation of insoluble phase(s) in molten $(LiCl-KCl)_e$. In contrast, the evolution of the ^{35}Cl spectrum with temperature is displayed in Figure 3 for a mixture with $LaCl_3$ in excess ($P/La = 0.33$, system II_c). From 380 °C up to 600 °C, the ^{35}Cl spectrum is sharp with a chemical shift of $+21$ ppm. This value turns out to be intermediate between those of pure $(LiCl-KCl)_e$ (-9 ppm) and of the mixture with 5 mol % $LaCl_3$ ($+49$ ppm, see Figure 1b). Since the initial molar ratio P/La was close to 0.33, such a value for the ^{35}Cl chemical shift indicates the

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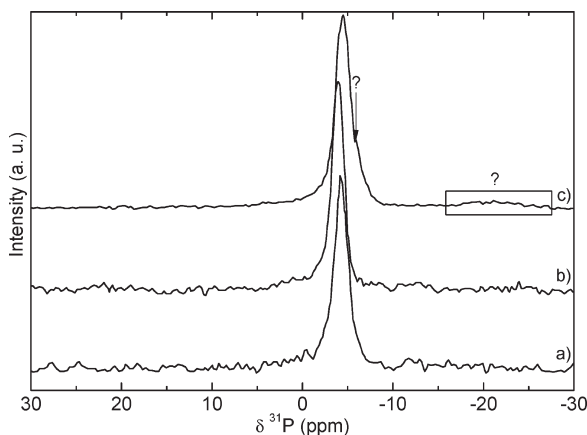
Figure 4. RT ^{31}P MAS NMR spectra for samples of systems (a) II$_b$ (P/La=1), (b) II$_c$ (P/La=0.33), and (c) II$_a$ (P/La=2.5). All mixtures were heated during the HT-NMR experiments up to 600 °C and then quenched under a flux of compressed air.

presence of unreacted LaCl$_3$ dissolved in the liquid. Experimentally, ADP was initially introduced to convert only 33% of the LaCl$_3$ content. The remaining 67% correspond to a eutectic loaded with 3.6 mol % of LaCl$_3$ leading to an expected chemical shift of ≈ +25 ppm (see Figure 1b). Consequently, this value is in good agreement with the expected one. This experiment shows again that ADP and LaCl$_3$ have reacted but that the residual LaCl$_3$ is dissolved in the eutectic solvent and influences the ^{35}Cl chemical shift. The evolution of ^{35}Cl spectrum for the mixture with LaCl$_3$ in default (P/La = 2.5, system II$_a$) displays similar features as that of mixture II$_b$ (spectra are not given here).

^{139}La and ^{31}P HT-NMR have also been carried out on systems II. However, related signals have never been detected except that of ^{139}La in experiment with mixture II$_c$ (P/La = 0.33). This might be probably due to the low amount of P and La in the mixture (< 3 mol %). Moreover, the static conditions in HT-NMR experiments makes difficult the observation of signals associated with solid phases. Since the reactivity between LaCl$_3$ and ADP involves the formation of insoluble compound(s) (i.e., the solid state) in molten (LiCl-KCl)$_e$, we assume that the related ^{31}P and ^{139}La signals cannot be detected in the experimental conditions used.

To characterize the solidified phases after cooling, the three previous samples were analyzed by ^{31}P MAS NMR spectroscopy at RT. The corresponding spectra are depicted in Figure 4. The reaction products of II$_b$ (Figure 4a) and II$_c$ (Figure 4b) are characterized by a single sharp Lorentzian peak with isotropic chemical shifts of −4.4 ppm and −4.3 ppm, respectively. These values are in good agreement with those previously published[14,29] and correspond unambiguously to the formation of LaPO$_4$ with a monazite structure. No additional signals are detected. At the opposite end, for the excess of phosphorus introduced in mixture II$_a$, beside a main peak at −4.4 ppm, both the signal at −5.8 ppm and the broad peak around −20 ppm (Figure 4c) reveal the formation of secondary compounds whose nature is discussed in section 4.3.

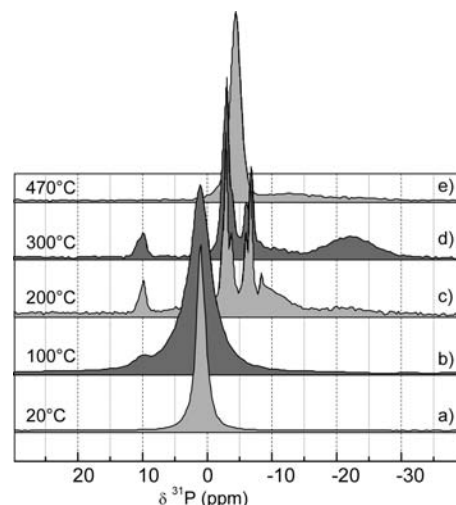To sum up, the ^{35}Cl HT-NMR appears as the appropriate probe to quantify the dissolution of chlorinated

Figure 5. RT ^{31}P MAS NMR spectra for samples of system II$_b$ {(LiCl-KCl)+LaCl$_3$+NH$_4$H$_2$PO$_4$, P/La = 1}. After heating, all samples were quenched under a flux of compressed air.

compounds in molten (LiCl-KCl)$_e$ solvent and to follow the degree of completeness of the LaCl$_3$/ADP reaction. With the observation of the ^{35}Cl HT-NMR spectra, it appears that the formation of monazite-like LaPO$_4$ material occurs in (LiCl-KCl)$_e$ at the mp (or just above) almost instantaneously and that the dissolution of LaPO$_4$ does not take place during the cooling. Moreover, the investigation of the structure/reactivity relationship would be very interesting to understand which phenomenon regulates the reactivity.

4.2. "Indirect" Approach: Toward the Identification of Intermediate Products. The identification of the crystallized compounds is generally achieved through X-ray diffraction (XRD). However, the efficiency of XRD is often tempered with the formation of a large number of phases with low crystallinity, a possible remaining amorphous part, and a very low concentration. On the other hand, NMR that probes the local environment of a nucleus is not limited by the presence of amorphous parts and also by the low crystallinity of the compounds. Moreover, recent developments in solid-state NMR have provided a large set of pulse sequences that have proven to be successful in obtaining structural information on solids.

4.2.1. Evolution of the Reactivity As a Function of the Temperature. To identify the potential transitory products formed before the formation of LaPO$_4$, four samples with the 90 mol % (LiCl-KCl)$_e$ + 5 mol % LaCl$_3$ + 5 mol % ADP composition (i.e., system II$_b$) were heated at 100, 200, 300, and 470 °C in air for 5 min, and afterward air-quenched to RT under a flux of compressed air. The ^{31}P MAS spectra collected at RT are given in Figure 5 for each sample and compared with the spectrum of pure ADP as reference. The latter (Figure 5a) is characterized by a single peak at +1.1 ppm, as reported in the literature,[56,57] what is coherent with only one phosphorus site in the crystal structure. As soon as the sample is heated the ^{31}P NMR spectrum is modified. Hence, for the sample

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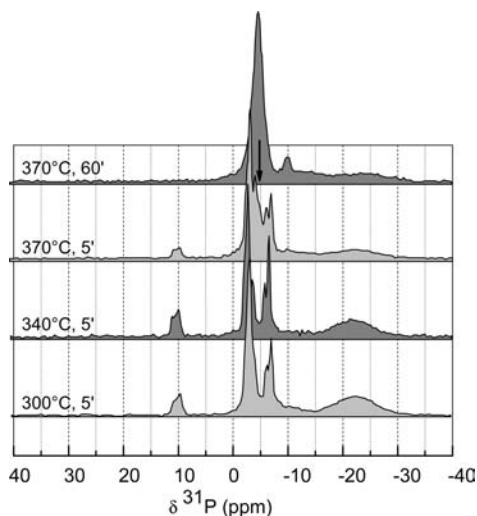(57) Turner, G. L.; Smith, K. A.; Kirkpatrick, R. J.; Oldfield, E. *J. Magn. Reson.* **1986**, *70*, 408–415.

Figure 6. RT ^{31}P MAS NMR spectra for samples of system II$_b$ {(LiCl-KCl) + LaCl$_3$ + NH$_4$H$_2$PO$_4$, P/La = 1} after heating during 5 min under air. After heating, all samples were quenched under a flux of compressed air.

Figure 7. RT ^{31}P RFDR spectrum after heating during 5 min under air at 300 °C of system II$_b$ {(LiCl-KCl)+LaCl$_3$+NH$_4$H$_2$PO$_4$, P/La = 1}.

heated at 100 °C (Figure 5b), if the main peak at 1.1 pm still exists, it appears much broader. It means that the phosphorus environment is not well-defined and that several environments may exist. Besides, new signals appear at +9 ppm and +12 ppm. This indicates that the decomposition of ADP in (LiCl-KCl)$_e$ is already initiated at 100 °C, though temperatures indicated in the literature for pure ADP decomposition lie between 170 and 200 °C[34−37]. At 200 °C, the ^{31}P NMR spectrum does not coincide anymore with pure ADP (Figure 5c): the peak related to the presence of ADP has completely disappeared, unidentified signals observed at 100 °C (+9 ppm and +12 ppm) gain in intensity and are much better defined, while two bundles of peaks, badly resolved, appeared between 0 and −15 ppm and −15 and −28 ppm, respectively. The spectrum obtained after reaction at 300 °C (Figure 5d) is similar to that obtained at 200 °C but the relative intensities are modified. Let us notice that up to 300 °C the samples once cooled kept their powdered form, suggesting that the mp of the mixture was not reached. Consequently, this suggests that the system is reactive in its solid state. On the other hand, the sample heated at 470 °C has been molten. Its spectrum (Figure 5e) evidenced only a single peak with an isotropic chemical shift of −4.4 ppm corresponding, as mentioned before, to LaPO$_4$ with a monazite structure type.

At this stage, let us mention that for 300 °C ≤ T < mp (mp is estimated at 370 °C ± 10 °C), no drastic evolution of the ^{31}P NMR spectra was observed, suggesting that no extra chemical reaction takes place in this temperature range. This conclusion is supported by the comparison of ^{31}P MAS NMR of samples heated at 300 and 340 °C during 5 min and then quenched in air (Figure 6, panels a and b, respectively). In contrast, for a reaction temperature of 370 °C, even if the overall spectrum is very similar to those acquired at 300 and 340 °C, a new peak appears at −4.4 ppm (Figure 6c), which corresponds to LaPO$_4$. At this temperature, an increase of the reaction duration from 5 to 60 min allows the quasi pure formation of LaPO$_4$ (Figure 6d). Thus, we can suppose that
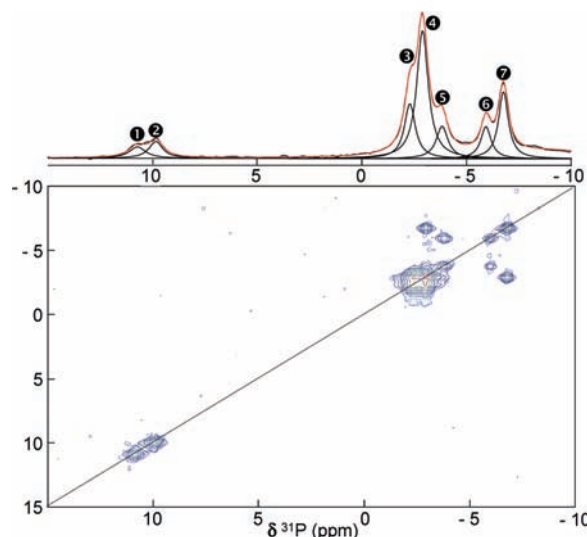
pure LaPO$_4$ could be prepared for a longer plateau at 370 °C.

On the basis of these experiments, we may conclude that (i) below 370 °C (i.e., below the mp), solid state reactions occur in the system II$_b$ leading to the formation of intermediate phosphated compounds associated with the thermal reactivity of ADP with (LiCl-KCl)$_e$; (ii) the LaPO$_4$ formation is triggered at the mp, i.e., at about 370 °C; and (iii) the complete disappearance of ADP below 200 °C confirms that the direct reaction of ADP and LaCl$_3$ cannot explain the formation of monazite.

4.2.2. Identification of the Transient Phases. To shed light on the nature and the number of transient phases leading to the stabilization of LaPO$_4$ in (LiCl-LCl)$_e$ from LaCl$_3$ and ADP as precursors, experiments were carried out using the two-dimensional (2D) ^{31}P MAS technique on a sample of system II$_b$ heated in air at 300 °C for 5 min. Peaks were assigned on the basis of anisotropic and isotropic spin−spin interactions recovered via 2D RFDR. Formally, this technique is well designed to show cross-peaks between phosphorus sites that are spatially close, thus belonging to the same crystallographic phase. Results are displayed in Figure 7. To gain in clarity, the one-dimensional (1D) spectrum is represented between −10 and +15 ppm. In this domain, the 1D spectrum can be deconvoluted into seven peaks. All of them give rise to a signal located on the diagonal of the 2D spectrum. On the basis of the analysis of the cross peaks, i.e., peaks out of the diagonal, the number of coupled P atoms belonging to the same phase may be determined. Namely, peaks 1 and 2 at +10.7 ppm and +9.9 ppm can be associated with two different compounds. Peaks 5 and 6 at −3.9 ppm and −6 ppm, respectively, are coupled and are supposed to be generated by the same phase. Such an interpretation may be extended also to peaks 4 and 7 at −2.9 ppm and −6.8 ppm, respectively. With regard to peak 3 at −2.3 ppm, its coupling to peaks 4 and 7 may be questionable. Nevertheless, since there is no cross peak between peaks 3 and 7, peak 3 may be assigned to an extra phase. Consequently, the system II$_b$ at 300 °C is characterized by the coexistence of at least five different phosphate compounds. They are
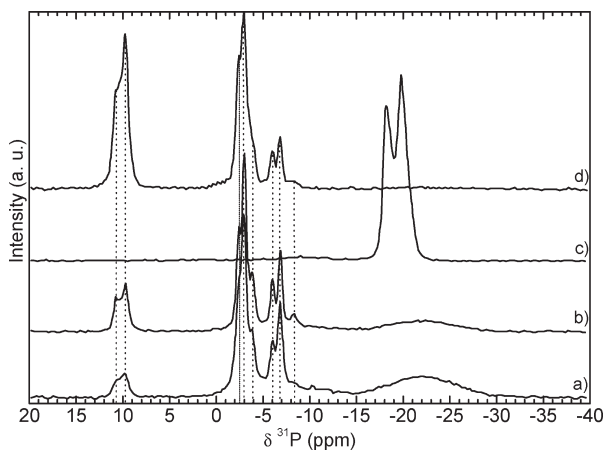
Figure 8. RT ^{31}P MAS NMR spectra for samples of different systems heated during 5 min under air at 300 °C. (a) System II$_b$ {(LiCl-KCl) + LaCl$_3$+NH$_4$H$_2$PO$_4$, P/La=1}, (b) system III {(LiCl-KCl)+NH$_4$H$_2$PO$_4$}, (c) system IV {KCl+NH$_4$H$_2$PO$_4$}, and (d) system V {LiCl+NH$_4$H$_2$PO$_4$}. After heating, all samples were quenched under a flux of compressed air.

probably still present just below the mp and finally disappear to give rise to LaPO$_4$ at the mp

At this stage, we may wonder what the chemical nature of these transient phases is. To address this point, we investigated alternately the reactivity of ADP toward (LiCl-KCl)$_e$ (system III$_a$), KCl (system III$_b$), and LiCl (system III$_c$). As previously, samples were heated at 300 °C in air for 5 min and air-quenched to RT before characterization by ^{31}P MAS NMR at RT. Corresponding ^{31}P-MAS NMR spectra are gathered in Figure 8 with that of system II$_b$ prepared in the same conditions as reference (Figure 8a). The spectrum of (LiCl-KCl)$_e$ and ADP compositions with and without LaCl$_3$ (i.e., system II$_b$ and III$_a$, respectively) are rigorously identical (Figure 8, panels a and b, respectively). Consequently, it may be concluded that LaCl$_3$ does not participate in any chemical reaction with ADP and phosphate derivative below the mp. Therefore, the ^{31}P-MAS NMR signals detected on samples II$_b$ heated in the 100−370 °C temperature range and quenched afterward (see Figure 5) may only originate from a hypothetical thermal decomposition of ADP or a significant reactivity of ADP toward the alkaline elements in a solid state. The decoupling of the effects of ADP on KCl and LiCl was carried out via the investigation of system III$_b$ and III$_c$. For the mixture KCl−ADP, the spectrum (Figure 8c) consists of only two peaks at −18.2 and −19.7 ppm. For LiCl−ADP mixture, the spectrum is characterized by eight different signals (Figure 8d). The number of ^{31}P NMR peaks relative to LiCl-ADP and KCl-ADP interactions $(8 + 2)$ and their position are exactly the same as those observed for system II$_b$. The two peaks at −18.2 and −19.7 pm of system III$_b$ can be attributed to the broad line in the same chemical shift range in the system II$_b$. Thus, for the chemical shift range −15/+15 ppm, it can be estimated that intermediate products are based on lithium and phosphorus ions. Signals in the −15/−30 ppm range can involve lithium as well as potassium even if their respective role is not clearly understood.

4.3. Suggestion of a Partial Mechanism. From this study, a partial mechanism accounting for the conversion of LaCl$_3$ and ADP into LaPO$_4$ in (LiCl-KCl)$_e$ may be

Scheme 1. Proposal of a Partial Multi-Step Mechanism for the La-Monazite Formation from LaCl$_3$ and ADP in LiCL-KCl Eutectic
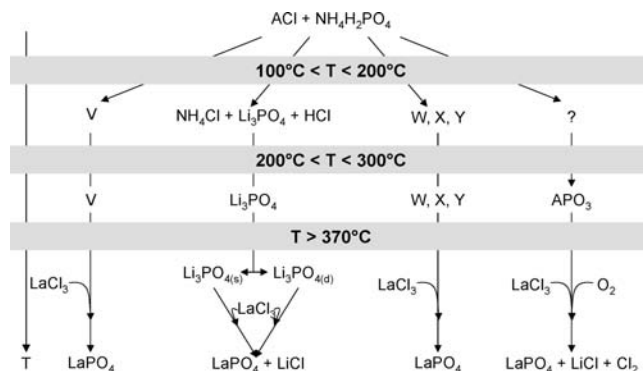

proposed. The different steps are summarized in Scheme 1.

Namely, according to the literature devoted to alkali metal (A) phosphates[56−62], orthophosphates (i.e., A$_3$PO$_4$) give rise to ^{31}P chemical shifts around 10 ppm while hydro- or dihydrophosphates (i.e., A$_2$HPO$_4$, AH$_2$PO$_4$) and pyrophosphates (i.e., A$_4$P$_2$O$_7$) exhibit δ_{iso} ranging approximately from −6 ppm to +6 ppm. Meta-phosphates (i.e., APO$_3$) have ^{31}P chemical shifts which may extend from −14 ppm to −32 ppm.
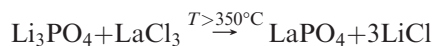
On the basis of these data, the peak at +10.7 ppm (Figure 8d) may be associated with the occurrence of Li$_3$PO$_4$ according to the following reaction:

$$3LiCl+NH_4H_2PO_4 \overset{100°C-200°C}{\rightarrow} Li_3PO_4+NH_4Cl+2\overset{\uparrow}{HCl}$$
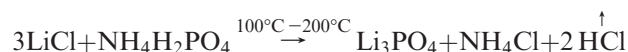
This assignment perfectly agrees with the chemical shift of Li$_3$PO$_4$ reported by several authors[58−61].The assignment of the peak at +9.8 ppm remains unknown. Formally, it cannot be explained by the existence of K$_3$PO$_4$ in the mixture supposed to display a δ_{iso} of +12 ± 0.5 ppm[58−62]. In fact, the presence of any potassium phosphate derivatives cannot be put forward since this signal is observed even for LiCl flux (system III$_c$). The formation of this unknown compound, labeled V, is proposed according to

$$3LiCl+NH_4H_2PO_4 \overset{100°C-200°C}{\rightarrow} V+product(s)$$
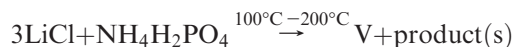
Signals at +10.7 and +9.8 ppm are maintained up to the mp. As a consequence, a direct interaction of Li$_3$PO$_4$ and V with LaCl$_3$ is assumed to give rise to LaPO$_4$ according to the two following reactions:

$$Li_3PO_4+LaCl_3 \overset{T>350°C}{\rightarrow} LaPO_4+3LiCl$$

$$V+LaCl_3 \overset{T>350°C}{\rightarrow} LaPO_4+product(s)$$

(58) Hayashi, S.; Hayamizu, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3061–3068.
(59) Grimmer, A.-R. *Chem. Phys. Lett.* **1983**, *99*, 487–490.
(60) Mudrakovskii, I. L.; Shmachkova, V. P.; Kotsarenko, N. S. *J. Phys. Chem. Sol.* **1986**, *47*, 335–339.
(61) Ben Nasr, C.; Rzaigui, M.; Sobrados, I.; Sanz, J. *J. Alloys Compd.* **2001**, *325*, 102–108.
(62) Voronin, V. I.; Posonov, Y.S.; Berger, I. F.; Proskurnina, N. V.; Zubkov, V. G.; Tyutyunnik, A. P.; Bushmeleva, S. N.; Balagurov, A. M.; Sheptyakov, D. V.; Burmakin, E. I.; Shekhtman, G.; Vovkotrub, E. G. *Neorg. Mater.* **2006**, *42*, 1001–1006 [Inorg. Mater. (2006 Engl. Transl.), 42, 8, 908−913].

Besides, since for a temperature higher than 370 °C our results do not show if all precursors (i.e., $LaCl_3$ and ADP) are dissolved, two different paths are suggested for the formation of $LaPO_4$. In the first, the dissolution of Li_3PO_4 is assumed whereas it is not in the second.

Moreover, in the 100−200 °C temperature range, the ADP signal completely disappears (see Figure 5) with a priori formation of two distinguishable groups of products (Scheme 1). The first group is composed of at least three unknown compounds, labeled W, X, and Y, which are thermally stable up to the mp. A second group would consist of a thermally unstable product, labeled Z, (Scheme 1) which disappears between 200 and 300 °C to trigger the appearance of APO_3 (A = Li and/or K).

Between 300 °C and the mp, the system is stable and six phosphate compounds coexist (Li_3PO_4, V, W, X, Y, and APO_3) with $LaCl_3$ and $(LiCl-KCl)_e$ which react to lead to $LaPO_4$. Finally, according to this mechanism, the only secondary products would be NH_4Cl, HCl, and Cl_2. Proof of NH_4Cl formation and assumptions concerning the production of HCl and Cl_2 have been described by Hudry et al.[29]. It is also interesting to notice that such a mechanism involves an external O_2 supply for the conversion of $LaCl_3$ in the corresponding phosphate by APO_3.

4.4. Influence of the Atmosphere Composition on the $LaPO_4$ Formation. To elucidate the importance of the O_2 partial pressure, the reactivity has also been investigated as a function of the atmosphere composition. Hence, three samples of system II_b (i.e., $(LiCl-KCl)_e + 5$ mol % $LaCl_3+$ADP with P/La = 1) heated at 500 °C during 5 h under different atmospheres (air, O_2, or Ar) were characterized at RT by ^{31}P MAS NMR. The corresponding spectra are presented in Figure 9, panels a, b, and c, respectively. The air condition is the only one which allows the formation of pure $LaPO_4$ (only one peak with a chemical shift at +4.4 ppm, Figure 9a) while the other atmospheres involve the formation of secondary phases previously identified to APO_3.

Actually, if O_2 is necessary for a reaction between APO_3 and $LaCl_3$, a too high O_2 partial pressure can induce an other type of reaction of $LaCl_3$. It can be converted into the corresponding LaOCl when heated under pure O_2 at 400 °C during 4 h (XRD pattern not showed). On the other hand, such a conversion is not dominating when heating is realized under air. Since LaOCl is insoluble in molten $(LiCl-KCl)_e$,[63,64] its formation may prevent the conversion of $LaCl_3$ into $LaPO_4$.

In Figure 9c, corresponding with treatment under Argon, if we zoom in around −20 ppm, then we detect also a broad peak but with very small intensity. In our previous description (4.1.2Section 4.1.2) of spectra obtained on samples after high temperature experiments, we did not observe such a signal. It was due to the very small quantity of sample (50 mg) and the limited content of $LaPO_4$ (around 5 mol %). In that case, in spite of the favorable NMR properties of the^{31}P nucleus, it was very
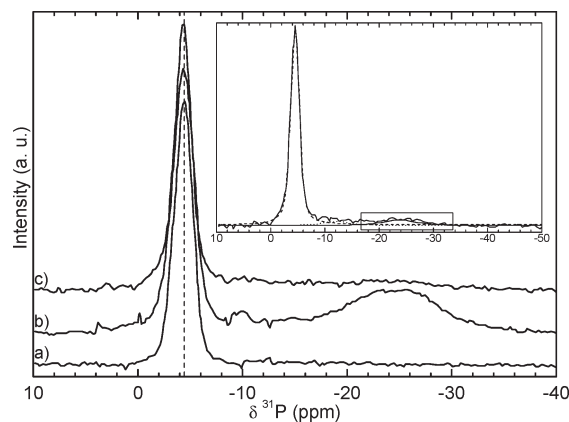
(63) Cho, Y.-J.; Yang, H.-C.; Eun, H.-C.; Kim, E.-H.; Kim, I.-T. *J. Nucl. Sci. Technol.* **2006**, *43*, 1280–1286.
(64) Cho, Y.-J.; Yang, H.-C.; Eun, H.-C.; Kim, E.-H.; Kim, J.-H. *J. Ind. Eng. Chem.* **2005**, *11*, 707–711.

Figure 9. RT ^{31}P MAS NMR spectra for samples of system II_b {(LiCl-KCl) + $LaCl_3$ + $NH_4H_2PO_4$, P/La = 1} after heating during 5 h under air at 500 °C under different atmosphere compositions (a) air, (b) O_2, and (c) Ar. Inset gives an enlargement of spectrum (c) with its associated deconvolution.

difficult to detect this signal (−20 ppm) for reasonable durations.

5. Conclusion

The mechanism of $LaPO_4$ formation in molten LiCl-KCl eutectic from $LaCl_3$ and ADP has been investigated by in situ HT-NMR by the evolution of ^{35}Cl and ^{139}La chemical shifts ("direct" approach) and by ^{31}P MAS NMR spectroscopy at RT ("indirect" approach).

In the in situ studies, the ^{35}Cl and ^{139}La chemical shift evolutions prove the formation of an insoluble lanthanum-based compound in molten LiCl-KCl at 370 °C/400 °C. This reaction seems to be very fast (only few minutes). Corresponding ex situ characterizations reveal the formation of pure $LaPO_4$ with a monazite structure.

^{35}Cl and ^{139}La HT-NMR give information on the structure of the liquid. The formation of at least three different chlorine environments in molten LiCl-KCl depending on $LaCl_3$ concentration has been shown. In addition we have proven that the coordination around the lanthanum in pure molten $LaCl_3$ is not 6 as it is claimed in the literature. The ^{139}La chemical shift measured in the melt lies at 567 ppm compared to 305 ppm in solid. We can thus argue that the average coordination in the melt should be higher than 6.

To describe the effect of ADP additions, the indirect approach by ^{31}P MAS NMR has proven to be well adapted and brought the proof of a complex multistep mechanism. Reactions start in the solid state at temperatures as low as 100 °C with no interruption until 300 °C. The total disappearance of ADP at 200 °C and the stability of $LaCl_3$ up to the mp of the mixture prove that the direct interaction between these two compounds cannot explain the $LaPO_4$ formation. In fact, various intermediary products are formed between 100 and 300 °C. Even if the role of potassium cannot be rejected, it seems that lithium and phosphorus are the main cationic elements involved in intermediary products. Finally, the system is stable between 300 °C and the mp of the mixture. When the temperature is raised above the mp, six intermediary products (Li_3PO_4, APO_3, and four unknown compounds) allow the conversion of $LaCl_3$ into $LaPO_4$.

The formation of pure $LaPO_4$ depends on the O_2 partial pressure. For a too high pressure, a competitive reaction of

LaOCl formation takes place. This compound is not reactive and cannot be converted into $LaPO_4$. Nevertheless, in the absence of oxygen, APO_3 cannot react with $LaCl_3$ to form $LaPO_4$. Thus, the O_2 partial pressure is very important to control the $LaPO_4$ purity.

Actually, if the chemically active role of the solvent is obvious, the influence of the molten state is still questionable. The identification of all intermediary products would allow to elucidate this question. Moreover, a comparison of the $LaCl_3$ conversion into the corresponding $LaPO_4$ in solvents free of LiCl would be interesting as well as an investigation of the properties of the so-synthesized $LaPO_4$.