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Preparation of uniform lithium tantalate spherical particles by two different aerosol processes

O. AMIEL, P. CAZEAU*, R. SALMON‡
Institute de Chimie de la Matière, Condensée de Bordeaux, Château Brivazac,
Avenue du Dr. A. Schweitzer, 33 600 Pessac, France
** Laboratoire de Chimie Organique et Organométallique, Université de Bordeaux I - 351,*
Cours de la Libération 33 405 Talence Cedex France

The preparation of spherical particles of controlled size by chemical reactions in aerosol has been extended to the elaboration of mixed binary oxides. Two elaboration routes have been investigated: an aerosol route and a mixed aerosol–organometallic route. In the two cases, lithium tantalate compounds have been prepared but the chemical reactions involved are different for the two routes. Reaction mechanisms which enable an interpretation of the experimental results are proposed.

1. Introduction

The requirement of synthesis routes allowing the preparation of controlled size and morphology particles has been felt, mainly in ceramic science, but also in many research fields such as catalysis, optics and magnetism [1–4].

Among the many elaboration methods developed during these last years (controlled precipitation, solvothermal synthesis, sol–gel, gaseous routes) [5–21], this study focuses on the aerosol technique of powder elaboration. Previous works have shown that the chemical reactions between droplets constituting the aerosol and a reactive vapour led to spherical particles of controlled size. For example, this elaboration technique has already been used to prepare monodisperse particles of single oxide such as SiO_2 [22], TiO_2 [23], Al_2O_3 [24], SnO_2 [25] and Ta_2O_5 [26–27]. A few papers, however, only deal with the preparation of mixed oxides [28–29] or composite oxides such as SiO_2/TiO_2 [30] or TiO_2/Al_2O_3 [31].

The aim of this paper is to demonstrate that the aerosol process is a versatile technique, which is also valuable in the preparation of mixed oxides with the form of spherical particles of controlled size. Two elaboration routes have been investigated: (a) an aerosol route in which the alkoxide precursor of the desired oxide is nebulized. The precursor can be a mixed alkoxide or a solution of simple alkoxides mixed in the appropriate stoichiometric ratio; (b) a mixed aerosol–organometallic route in which hydrous and amorphous oxide particles obtained by the aerosol process react with the organometallic precursor of the additional cation.

To illustrate the difference of reaction mechanisms involved in these two preparation routes, we present results concerning the preparation of lithium tantalate compounds.

2. Experimental procedure

2.1. Preparation of lithium tantalum alkoxides

The tantalum pentaethoxide $Ta(OC_2H_5)_5$ was of 99.999% purity and lithium ethoxide $LiOC_2H_5$ was prepared by reacting *n*-butyl lithium with pure ethanol. These two alkoxides were then mixed by stirring with a controlled excess of pure ethanol at room temperature for one hour in a dry N_2 atmosphere [32]. The molar ratio $Ta(OC_2H_5)_5/LiOC_2H_5$ varies with the desired oxide.

2.2. Preparation of lithium tantalate particles

2.2.1. *Aerosol route*

An improved version of the apparatus previously described by Salmon and Matijevic [28] has been used to prepare particles (Fig. 1). To produce the aerosol, the mixed alkoxide solution was introduced into the pneumatic nebulizer (Fig. 1), the nitrogen flow rate was $207\,l\,h^{-1}$. The aerosol so formed was then vaporized inside the sphere (Fig. 1), the temperature, T_S, of which was regulated to 250 °C. The introduction of any foreign bodies in the vapour phase caused the aerosol to reform by homogeneous nucleation in the condensation tube (Fig. 1) also under a controlled temperature ($T_C = 50\,°C$). The role of the evaporation–condensation sequence was to sharpen the size distribution of the droplets constituting the initial spray [33]. The aerosol, thus reformed, was brought into contact with water vapour inside the hydrolysis cell ($T_h = 100\,°C$) (Fig. 1). The resulting lithium tantalate particles were collected in ethanol, filtered and then calcined at different temperatures.

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‡ Author to whom correspondence should be addressed.

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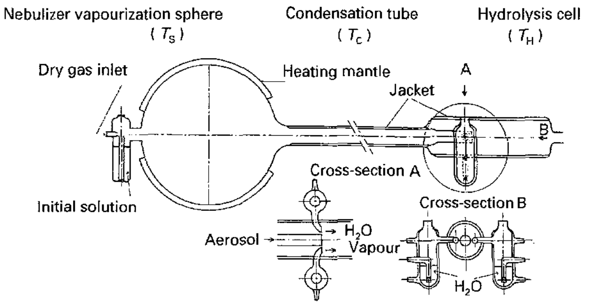

Figure 1 Schematic diagram of the apparatus used to prepare oxide particles by the aerosol process.

2.2.2. Mixed aerosol–organometallic route

The hydrous amorphous $Ta_2O_5 \cdot nH_2O$ particles were obtained by the classical aerosol route using tantalum pentaethoxide diluted in 2-propanol as a liquid precursor [26, 34]. The experimental parameters (gas flow rate, temperatures of the sphere, condensation tube and hydrolysis cell) were kept unchanged, in comparison with the aerosol route. These particles were then washed with cyclohexane in order to eliminate residual ethanol coming from the collecting bath. Stoichiometric amounts of *n*-butyl lithium 1.6 M were added to $Ta_2O_5 \cdot nH_2O$ particles, in suspension into cyclohexane (Fig. 2). This reaction took place at room temperature and in a dry N_2 atmosphere and led to the formation of lithium tantalate particles. The powder so obtained was calcined at different temperatures and then characterized by crystallographic analysis.

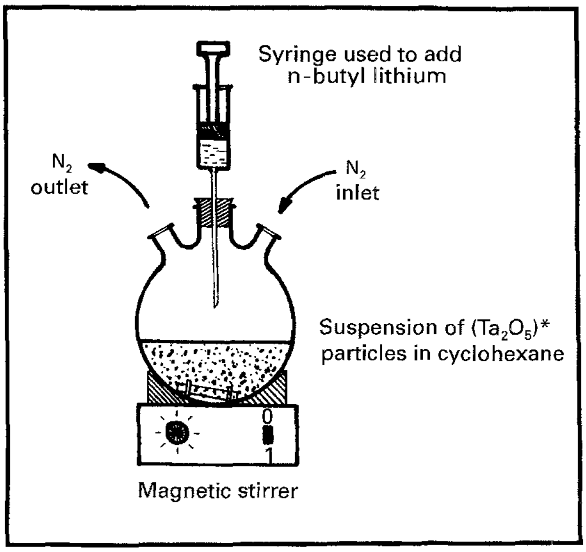

Figure 2 Schematic diagram of the experimental set-up used to prepare lithium tantalate particles following the mixed aerosol–organometallic route.

2.3. Analysis

The powder micrographs were obtained with a scanning electron microscope (Jeol JSM 840A). The powder X-ray diffraction experiments were performed using the CuK_α line of a Philips PW1710 instrument.

3. Results and discussion

3.1. Aerosol route

We define the factor α as the ratio of the mole number of $LiOC_2H_5$ to that of $Ta(OC_2H_5)_5$. A detailed experimental study showed that $LiTa(OC_2H_5)_6$ was the only stable mixed alkoxide of the system $LiOC_2H_5$–$Ta(OC_2H_5)_5$ [35]. As a consequence, a solution corresponding to an α value not equal to 1 leads to a solution constituted of $LiTa(OC_2H_5)_5$ and of the alkoxide in excess.

For all cases, particles were spherical, non-agglomerated and of narrow size distribution (average diameter is around 1 μm, the exact value depending on the experimental parameters). For example, Fig. 3 presents $LiTaO_3$ oxide particles obtained by hydrolysis of a $LiTa(OC_2H_5)_5$ aerosol.

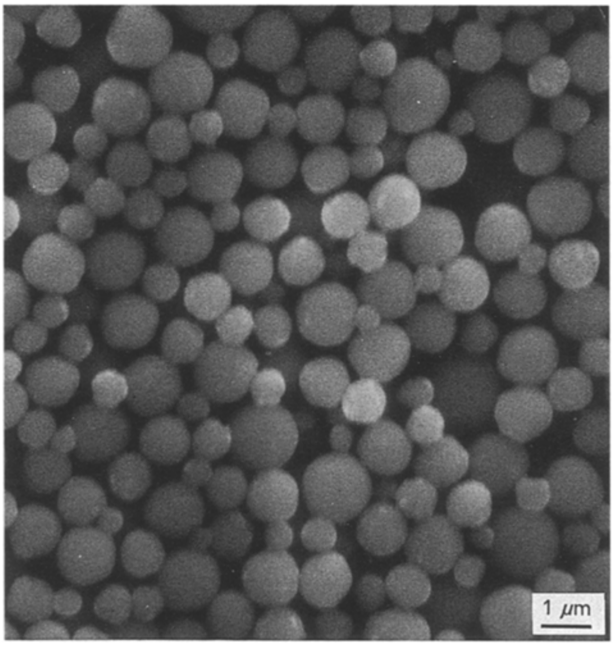

Figure 3 Scanning electron micrograph of $LiTaO_3$ particles obtained by hydrolysis of an aerosol of $LiTa(OC_2H_5)_6$ (aerosol route).

Table I indicates, for different values of α, the crystallographic structure of the oxide as a function of the calcination temperature. Three peculiar values of α corresponding to three stoichiometric compounds of the system Li_2O–Ta_2O_5 are highlighted, namely:

$$\alpha_1 = 3 \rightarrow \text{compound } Li_3TaO_4$$

$$\alpha_2 = 1 \rightarrow \text{compound } LiTaO_3$$

$$\alpha_3 = 0.33 \rightarrow \text{compound } LiTa_3O_8$$

To explain the experimental results displayed in Table I, the formation process of crystallized solid particles needs to be decomposed into three stages: (i) mixing of the alkoxides; (ii) hydrolysis reaction between aerosol droplets and water vapour; and (iii) calcination of the so-prepared particles.

In considering these three stages, two cases must be distinguished:

TABLE I Evolution of the crystallographic structure of the oxide as a function of the calcination temperature, for different α values

T (°C)	$\alpha = 3.85$	$\alpha_1 = 3.00$ Li_3TaO_4	$\alpha = 2.04$	$\alpha_2 = 1.00$ $LiTaO_3$	$\alpha = 0.40$	$\alpha_3 = 0.33$ $LiTa_3O_8$	$\alpha = 0.30$
400 °C	Amorphous						
600 °C	$LiTaO_3$				Amorphous		
800 °C					$LiTaO_3 + Ta_2O_5$		
1000 °C					$LiTa_3O_8$ + $LiTaO_3$	$LiTa_3O_8$	$LiTa_3O_8$ + Ta_2O_5

(a) $\alpha \geqslant 1$ (x is assigned to the excess of $LiOC_2H_5$)

Mixing: $Ta(OC_2H_5)_5 + (1 + x)LiOC_2H_5 \rightarrow LiTa(OC_2H_5)_6 + xLiOC_2H_5$.

Hydrolysis: $LiTa(OC_2H_5)_6 + xLiOC_2H_5 \xrightarrow{+H_2O} LiTaO_3 \cdot nH_2O + xLiOH$.

LiOH is soluble and remains in solution, inside the collection bath. As a consequence $LiTaO_3$ is always formed whatever the excess value is. This is the reason why the compound Li_3TaO_4 cannot be obtained by this route.

Calcination: $LiTaO_3 \cdot nH_2O \rightarrow LiTaO_3 + nH_2O$.

The $LiTaO_3 \cdot nH_2O$ phase is already crystallized at 600 °C because it results from the hydrolysis reaction of its own alkoxide precursor $LiTa(OC_2H_5)_6$. Although the oxide is amorphous just after elaboration, Li–O–Ta bonds probably pre-exist allowing to reach the crystallization state at lower temperature. As an illustration, $LiTaO_3$ prepared by solid state reaction between Li_2O and Ta_2O_5 crystallizes only from 800 °C [36].

(b) $\alpha < 1$ (x is assigned to the excess of $Ta(OC_2H_5)_5$).

Mixing: $(1 + x)\ Ta(OC_2H_5)_5 + LiOC_2H_5 \rightarrow$

$LiTa(OC_2H_5)_6 + x\ Ta(OC_2H_5)_5$.

Hydrolysis: $LiTa(OC_2H_5)_6 + xTa(OC_2H_5)_5 \xrightarrow{+H_2O} LiTaO_3 \cdot nH_2O + (x/2)Ta_2O_5 \cdot nH_2O$.

A mixture of amorphous $LiTaO_3$ and Ta_2O_5 is formed. Three cases have to be considered depending on the value of α:

Calcination: (i) $x > 2$ ($0 < \alpha < 0.33$).

In this range of composition, the existence of an excess of Ta_2O_5 with respect to $LiTaO_3$ lead to the formation of $LiTa_3O_8$ and Ta_2O_5 mixture. At 800 °C, $LiTaO_3 \cdot nH_2O + (x/2)\ Ta_2O_5 \cdot nH_2O \rightarrow LiTaO_3 + (x/2)\ Ta_2O_5$ which gives at 1000 °C: $LiTaO_3 + (x/2)\ Ta_2O_5 \rightarrow LiTa_3O_8 + (-1 + x/2)\ Ta_2O_5$.

(ii) $x = 2$ ($\alpha = 0.33$).

In this case, the 800 °C heating stage gives $LiTaO_3 \cdot nH_2O + Ta_2O_5 \cdot nH_2O \rightarrow LiTaO_3 + Ta_2O_5$ which transforms at 1000 °C into $LiTaO_3 + Ta_2O_5 \rightarrow LiTa_3O_8$.

(iii) $x < 2$ ($0.33 < \alpha < 1$).

This domain is characterized by an excess of $LiTaO_3$ compared to Ta_2O_5, causing the formation of a mixture of $LiTa_3O_8$ and $LiTaO_3$.

At 800 °C $LiTaO_3 \cdot nH_2O + (x/2)Ta_2O_5 \cdot nH_2O \rightarrow LiTaO_3 + (x/2)Ta_2O_5$.

At 1000 °C $LiTaO_3 + (x/2)Ta_2O_5 \rightarrow (x/2)LiTa_3O_8 + (1 - x/2)LiTaO_3$.

For the three cases, $LiTa_3O_8$ compound only appears from 1000 °C because it results from an intragrain solid state reaction between $LiTaO_3$ and Ta_2O_5. This oxide is never formed directly at low temperature (in contrast to $LiTaO_3$) since its own alkoxide precursor does not exist.

3.2. Mixed aerosol–organometallic route

3.2.1. Introduction

The preparation of a mixed oxide by the aerosol route requires as a precursor the corresponding mixed liquid alkoxide. Many simple metal alkoxides exist, however mixed ones are few and not always very well characterized because of their complex structure [37]. An alternative solution is to use a mixture of simple alkoxides. Unfortunately, due to their physical state (liquid or solid), the mixing of simple alkoxides is not always possible and the stoichiometry of the resulting particles may be difficult to control if the simple alkoxides have different hydrolysis rates. For these reasons, it appeared interesting to develop a preparation process involving the reactivity of simple oxide particles obtained by the aerosol route to elaborate mixed oxide particles.

3.2.2. Principles of the preparation method

When n-butyl lithium, BuLi, is added to the suspension of hydrous amorphous Ta_2O_5 oxide particles, a regiospecific reaction occurs between BuLi and the water molecules localized on the particle surface $BuLi + H_2O \rightarrow LiOH + BuH$. LiOH is formed only at the surface of the particles and *in situ* which avoids any carbonation problems. Lithium hydroxide then becomes fixed on the amorphous and hydrous Ta_2O_5 network by polycondensation processes, i.e. formation of Li–O–Ta bridges with elimination of water molecules.

Similar reactions between TiO_2 powder obtained by the aerosol route and strontium hydroxide solution were performed by Ocana [38]. When the precursor of the additional cation is an aqueous hydroxide solution, the formation of the desired oxide depends on many experimental parameters such as the reaction time but also the pH and the temperature of the hydroxide solution. As the hydroxide is dispersed in the suspension, the stoichiometry is difficult to control as the amount of hydroxide actually involved in the reaction is unknown. Moreover, as the presence of carbonates inhibits titanate formation, the water used to prepare the hydroxide solution must be preheated in order to eliminate CO_2 and later cooled in a CO_2-free atmosphere [39].

Using BuLi therefore offers many advantages: control of the stoichiometry since the hydroxide is only formed at the particle surface, formation of LiOH *in situ* (avoiding carbonation process) and ease of preparation (no problem of pH and temperature of the solution).

3.2.3. Experimental results

The chemical composition of the Ta_2O_5 hydrous oxide particles obtained by the aerosol route can be expressed as Ta_2O_5 ($n H_2O$, $n'OH$, $n''OC_2H_5$), labelled $(Ta_2O_5)^*$, where n is assigned to solvated water, n' to water issued from condensation reactions of Ta–OH groups and n'' to ethanol resulting from the condensation of unreacted $Ta–OC_2H_5$ groups. Thermogravimetric analysis (TGA) showed two weight losses, the first one ($T \approx 100\,°C$) corresponding to the elimination of the n-type water and the second one to the release of structural water and ethanol between 150 and 400 °C. The existence of Ta–OH, $Ta–OC_2H_5$ and solvated water was also confirmed by spectroscopic analyses (diffuse reflectance infrared Fourier transform and H-nuclear magnetic resonance spectroscopy) [40].

We now introduce the factor β defined as the ratio of the mole number of BuLi to that of $(Ta_2O_5)^*$. The three peculiar values of β become:

$$\beta_1 = 6 \rightarrow \text{compound } Li_3TaO_4$$

$$\beta_2 = 2 \rightarrow \text{compound } LiTaO_3$$

$$\beta_3 = 0.66 \rightarrow \text{compound } LiTa_3O_8$$

This route also leads to the formation of spherical and non-agglomerated particles, proving the action of BuLi does not affect either the morphology or the agglomeration state of the particles so prepared. As an example, Fig. 4 exhibits a scanning electron micrograph (SEM) of $LiTaO_3$ oxide particles obtained by reaction of Ta_2O_5 hydrous particles with n-butyl lithium, in the appropriate molar ratio. Table II indicates, for different values of β, the crystallographic structure of the oxide as a function of the calcination temperature. Three domains of composition can be considered. Overall reactions describing these experimental results are the following:

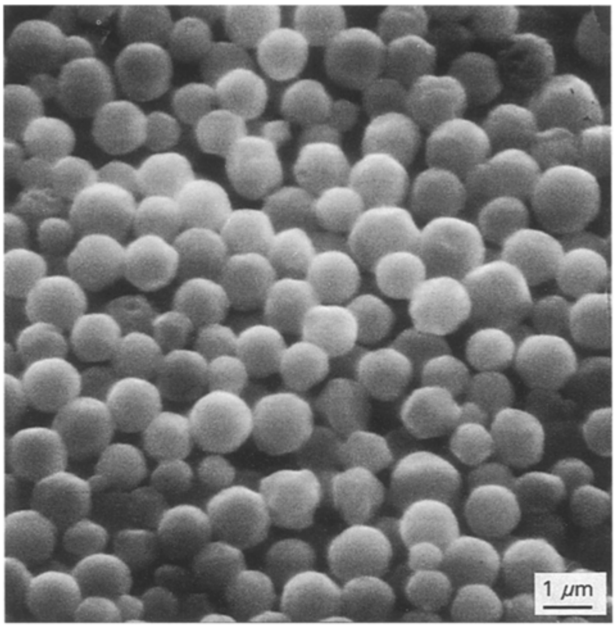

Figure 4 Scanning electron micrograph of $LiTaO_3$ particles obtained by reaction of hydrous Ta_2O_5 particles with n-butyl lithium (mixed aerosol–organometallic route).

(a) $\beta \geqslant 6$.

In this range of composition, the Li_3TaO_4 phase is exclusively present, which can be written $(Ta_2O_5)^* + \beta\ BuLi \rightarrow Li_3TaO_4$.

(b) $2 \leqslant \beta \leqslant 6$.

When $\beta = 2$, the phase prepared is $LiTaO_3$. For values of β between 2 and 6, a two phases mixture of $LiTaO_3$ and Li_3TaO_4 is obtained, the latter becoming the main phase as β increases. When $\beta = 6$, only the Li_3TaO_4 phase is present. These results can be summarized in the following descriptive equation

$$(Ta_2O_5)^* + \beta\ BuLi \rightarrow$$
$$(3 - \beta/2)LiTaO_3 + (-1 + \beta/2)Li_3TaO_4$$

(c) $\beta \leqslant 2$.

When the β value is less than 2, a two phases mixture of $LiTaO_3$ and Ta_2O_5 is obtained, the latter becoming the main phase as β decreases. The overall equation is the following $(Ta_2O_5) + \beta\ BuLi \rightarrow (1 - \beta/2)(Ta_2O_5)^* + \beta LiTaO_3$. The $LiTa_3O_8$ phase which appears at 1000 °C is issued from an intragrain solid state reaction between Ta_2O_5 and $LiTaO_3$.

TABLE II Evolution of the crystallographic structure of the oxide as a function of the calcination temperature, for different β values

T (°C)	$\beta = 50$	$\beta = 10$	$\beta_1 = 6$ Li_3TaO_4	$\beta = 4.17$	$\beta_2 = 2$ $LiTaO_3$	$\beta = 1.22$	$\beta = 0.86$	$\beta_3 = 0.67$ $LiTa_3O_8$	$\beta = 0.61$
400 °C	Amorphous								
600 °C	Amorphous			$LiTaO_3$ + Amorphous	$LiTaO_3$	Amorphous + $LiTaO_3$			
800 °C						TaO_2O_5 + $LiTaO_3$			
1000 °C	Li_3TaO_4			$LiTaO_3$ + Li_3TaO_4	$LiTaO_3$	Ta_2O_5 + $LiTaO_3$ + $LiTa_3O_8$			

3.2.4. *Interpretation of results and proposal of a reaction mechanism*

In order to explain the existence of these three domains of composition, we propose a reaction mechanism in which the reactivity of the so-prepared Ta_2O_5 particles may be decomposed into two steps.

First, for all cases, the amorphous hydrous tantalum oxide particles react with BuLi to form $(Ta_2O_5)^*$, 2LiOH species

$$(Ta_2O_5)^* + 2BuLi \rightarrow (Ta_2O_5)^*, 2LiOH + 2BuH \qquad (1)$$

One can reasonably consider that the solvation water, localized at the particle surface, reacts preferentially. However, this reaction needs the presence of two water molecules. This hypothesis seems possible as the observed weight loss at 100 °C is (11.0 + 0.2%), a value which is higher than that corresponding to the elimination of two water molecules (7.5%).

The polycondensation processes of the LiOH groups lead to the formation of hydrous and amorphous $LiTaO_3$ ($(Ta_2O_5)^*$, 2LiOH) which crystallizes during the calcination

$$(Ta_2O_5)^*, 2LiOH \rightarrow 2LiTaO_3 \qquad (2)$$

This first step explains the formation of $LiTaO_3$ (i.e. $\beta = 2$).

Second, two cases have to be distinguished depending on the value of β:

(a) $\beta < 2$. According to Equation 1, there is a lack of BuLi with respect to $(Ta_2O_5)^*$ which causes the formation of a two phases mixture consisting of $LiTaO_3$ and Ta_2O_5. The BuLi present transforms the corresponding and stoichiometric amount of Ta_2O_5 into $LiTaO_3$ following Equation 1, the excess of Ta_2O_5 remaining unreacted in the medium.

(b) $\beta > 2$. The excess of BuLi with respect to $(Ta_2O_5)^*$ reacts with the hydrous $LiTaO_3$ species (formed following Equation 2). Initially on the surface, the butyl lithium diffuses inside the particles [41]. These particles contain Ta–OH and Ta–OC_2H_5 bonds belonging to $(Ta_2O_5)^*$, but also LiOH groups. As a consequence, several reactions may be considered:

(i) *Reactions involving only bonds with the butyl lithium*

$$BuLi + H_2O \rightarrow Li\text{–}OH + BuH$$

$$BuLi + C_2H_5OH \rightarrow Li\text{–}OC_2H_5 + BuH$$

(ii) *Reactions involving only bonds between tantalum atoms and lithium atoms*

$$Ta\text{–}OH + HO\text{–}Li \rightarrow Ta\text{–}O\text{–}Li + H_2O$$

$$Ta\text{–}OC_2H_5 + HO\text{–}Li \rightarrow Ta\text{–}O\text{–}Li + C_2H_5OH$$

$$Ta\text{–}OH + C_2H_5O\text{–}Li \rightarrow Ta\text{–}O\text{–}Li + C_2H_5OH$$

(iii) *Reactions involving only bonds with lithium atoms*

$$Li\text{–}OH + HO\text{–}Li \rightarrow Li\text{–}O\text{–}Li + H_2O$$

$$Li\text{–}OH + C_2H_5O\text{–}Li \rightarrow Li\text{–}O\text{–}Li + C_2H_5OH$$

(iv) *Reactions involving only bonds with tantalum atoms*

$$Ta\text{–}OH + HO\text{–}Ta \rightarrow Ta\text{–}O\text{–}Ta + H_2O$$

$$Ta\text{–}OH + C_2H_5O\text{–}Ta \rightarrow Ta\text{–}O\text{–}Ta + C_2H_5OH$$

When the hydrous $LiTaO_3$ species react with BuLi in excess, these four reactions occur simultaneously and give as a final result Li_3TaO_4 by polycondensation of Li–OH, Li–OC_2H_5, Ta–OC_2H_5 and Ta–OH groups [42].

For $\beta = 6$, the total amount of $LiTaO_3$ is transformed into Li_3TaO_4 which then remains as a single phase. Because the Li_3TaO_4 compound is unreactive with respect to BuLi, any additional BuLi (when $\beta > 6$) has no effect on this compound. The *n*-butyl lithium in excess is eliminated by filtration.

4. Conclusion

The preparation of particles by chemical reactions in aerosol can be extended to the elaboration of mixed oxides, binary or ternary. Two elaboration routes have been studied: the first one consists of nebulizing the mixed alkoxide (which is characterized by the same atomic ratios as those of the desired oxide) and then to bring droplets constituting the aerosol into contact with the water vapour; the second one allows the fixation of an addition cation, firstly onto, and then inside amorphous and hydrous oxide particles obtained by the aerosol route. This second method is based on reactions between *n*-butyl lithium and water molecules but also hydroxy and ethoxy groups which exist inside the particles. Compounds belonging to the lithium tantalates were prepared this way but these two routes did not lead to the same results due to the difference in reaction mechanisms involved. For example, the $LiTa_3O_8$ phase obtained by the aerosol route could not be prepared by the mixed aerosol–organometallic route and conversely for the Li_3TaO_4 compound.

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