

Metal nitrate/fuel mixture reactivity and its influence on the solution combustion synthesis of γ -LiAlO₂

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Abstract The reactivity of LiNO₃ and Al(NO₃)₃ with respect to urea and β -alanine was investigated. Experimental results proved that β -alanine is a more suitable fuel for LiNO₃, whereas urea seems to be more adequate for Al(NO₃)₃. Based on the different metal nitrate/fuel mixture reactivity, nanocrystalline γ -LiAlO₂ powders were prepared by solution combustion synthesis using a fuel mixture of urea and β -alanine. This fuel mixture yielded single-phase nanocrystalline γ -LiAlO₂ (32.6 nm) directly from the combustion reaction. The resulted powder had a specific surface area of 3.2 m²/g and no supplementary annealing was required. On the other hand, pure γ -LiAlO₂ could not be obtained by using a single fuel (urea, β -alanine) unless annealing at 900 °C for 1 h was performed.

Keywords Combustion synthesis · Fuel mixture · Lithium aluminate · Metal nitrate · Urea · β -alanine

Introduction

Lithium aluminate, LiAlO₂, possesses a number of valuable properties, which makes it a first choice material for many applications [1]. Lithium aluminate exhibits three allotropic forms, namely: α -LiAlO₂ (hexagonal), β -LiAlO₂ (monoclinic) and γ -LiAlO₂ (tetragonal). Among all polymorph modifications of LiAlO₂, γ -LiAlO₂ is the most stable one, so that at elevated temperature (above 750 °C) α -LiAlO₂ and β -LiAlO₂ turn into γ -LiAlO₂ [2]. Some of

the applications of lithium aluminate, such as tritium breeder for fusion nuclear reactor [3, 4] or electrolyte matrix for molten carbonate fuel cells [5, 6] rely on the excellent thermo-mechanical, chemical and low radiation damage susceptibility of γ -LiAlO₂. Other applications of LiAlO₂ aim the synthesis of various phosphor materials [7, 8] and substrates for microelectronics [9].

The traditional method of lithium aluminate preparation is based on solid-state reactions between different polymorph forms of Al₂O₃ and various lithium containing compounds, such as Li₂CO₃ or LiOH [10]. In this case, elevated temperatures and long soaking times are required to ensure the formation of pure γ -LiAlO₂. The situation is even more complicated due to the high volatility of lithium component. In order to overcome the problems related to the preparation of single-phase γ -LiAlO₂ powders, several synthesis methods have been reported: coprecipitation [11], mechanochemical synthesis [12], gel to crystallite conversion [13], Pechini [2], spray pyrolysis [6], hydrothermal method [14], sol-gel [15] etc.

Although these methods are able to ensure the formation of pure γ -LiAlO₂, many sophisticated techniques and time-consuming procedures are required, which are not cost effective and represent obstacles to reproducibility and reliability of the final powder.

In the past 20 years, combustion synthesis merged as an innovative and promising powder preparation method [16, 17]. The method relies on the strong exothermic self-propagating reaction, which takes place during the rapid heating up to 500 °C of an aqueous solution of metal nitrates and a suitable fuel. The temperature reached during combustion reaction enables the formation and crystallization of the designed oxide compound without any additional annealing [18]. However, we have shown in our previous papers [19–21] that in the case of combustion

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synthesis of mixed metal oxides, the use of a single fuel yields amorphous powders or mixtures of crystalline phases. As a result, the formation of the desired compound demands additional thermal treatments.

Considering the individual behaviour of metal nitrate/fuel binary mixtures as well as the particular case of γ -LiAlO₂ preparation, an explanation is given for the difficulty related to the formation of pure γ -LiAlO₂ by using a single fuel. The solution of using fuel mixtures instead of a single fuel is suggested, showing that in this case, pure γ -LiAlO₂ powders can be obtained directly from the combustion reaction.

Experimental

LiNO₃ (Merck), Al(NO₃)₃·9H₂O (Merck), urea (CO (NH₂)₂) (Merck) and β -alanine (NH₂(CH₂)₂COOH) (Merck) were used as starting materials.

The reactivity of LiNO₃ and Al(NO₃)₃ with respect to urea and β -alanine

In the first part of the experiments, the combustion reaction between each metal nitrate and each fuel was investigated. For this purpose stoichiometric metal nitrate/fuel combinations were designed and the phase composition of the resulted powders was determined. Recipes were calculated in order to obtain 0.150 moles of Li₂O and 0.150 moles of Al₂O₃, respectively. It was assumed that the gaseous by-products of the combustion reactions are: CO₂, H₂O and N₂.

Preparation of LiAlO₂ powders

After determining the most suitable fuel for each metal nitrate, the preparation of γ -LiAlO₂ was aimed. The first two samples were designed using a single fuel, urea (sample 1) or β -alanine (sample 2), whereas sample 3 represents the innovative concept, involving the use of urea and β -alanine fuel mixture. Batches were calculated for 0.150 moles of LiAlO₂. Stoichiometric metal nitrate/fuel molar ratios were also used in all samples. Appropriate amounts of LiNO₃ and Al(NO₃)₃·9H₂O were dissolved in distilled water in a porcelain-evaporating dish. Then stoichiometric amount of fuel was added according to each recipe. The resulting solution was rapidly heated to 300 °C in a preheated electric nest causing water evaporation and the ignition of a self-sustaining combustion reaction, except for sample 1 which failed to ignite. The space of time between the initiation of the combustion reaction and its finalization was measured.

Characterization methods

Heating behaviour of the precursor mixtures (samples 1–3) were monitored by thermal analysis, using a NETZSCH STA 449 C instrument. The investigated temperature range was 30–900 °C, with a 10 °C min⁻¹ heating rate, in N₂ atmosphere (20 mL min⁻¹) and alumina crucibles. Losses on ignition (L.O.I.) were determined after annealing the combustion residue at 900 °C for 1 h. The evolution of the crystalline phases was monitored by XRD, using a Bruker D8 Advance System, Cu_{K α} monochromated radiation. The crystallite size was determined based on the XRD patterns using the Sherrer's Eq. 1. The peaks used for the crystallite size determination were the ones corresponding to 101 (22.246°), 102 (33.321°) and 200 (34.645°) *hkl* planes.

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

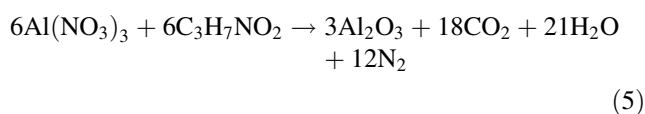
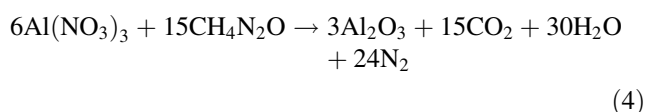
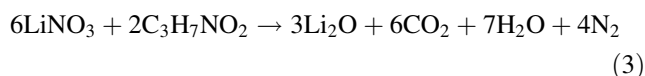
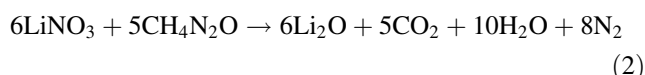
where *D* is the crystallites size in nm, λ is the radiation wavelength (Cu_{K α} , 0.15406 nm), β is the full width at half of the maximum in radians and θ is the Bragg-angle.

BET (Brunauer, Emmett and Teller) surface area measurements were performed using a Micromeritics ASAP 2020 instrument and nitrogen as adsorption gas. The powder morphology was investigated by scanning electron microscopy (SEM) using a FEI Inspect S electron microscope.

Results and discussion

The individual reactivity of LiNO₃ and Al(NO₃)₃ with respect to urea and β -alanine

Combustion reactions assumed to take place in the case of metal nitrate/fuel binary mixtures are represented by the Eqs. 2–5



As seen in Table 1, LiNO₃ and Al(NO₃)₃ react very different with β -alanine and urea. In the case of LiNO₃/urea binary mixture (Eq. 2) no combustion reaction was

Table 1 The individual reactivity of LiNO₃ and Al(NO₃)₃ with respect to urea and β-alanine

Metal nitrate	Combustion reaction duration/s		Phase composition of the resulted powder	
	Urea	β-alanine	Urea	β-alanine
LiNO ₃	No combustion	<1	LiNO ₃	Li ₂ O
Al(NO ₃) ₃	10	240	α-Al ₂ O ₃	Amorphous

Table 2 Characteristics of the combustion-synthesized powders

Sample	Fuel	Combustion reaction duration/s	Gas velocity ^a /L/s	Powder colour	L.O.I./%
1	Urea	No visible combustion	–	Yellowish	47.0
2	β-alanine	35	1.09	Grey	8.4
3	Urea + β-alanine	60	0.80	White	0.1

^a The velocity of the combustion generated gases calculated under normal conditions for 0.150 moles of LiAlO₂

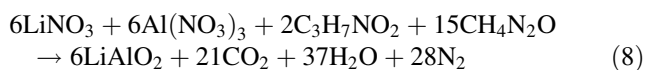
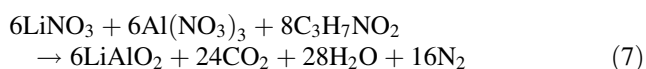
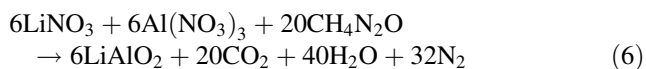
observed. At the same time, the presence of LiNO₃ peaks on the XRD pattern of the resulted powder indicates that reaction (2) did not take place. On the other hand, LiNO₃ reacted extremely fast (explosively) with β-alanine (Eq. 3) leading to the formation of a white crystalline Li₂O powder.

In the case of Al(NO₃)₃ the situation is quite opposite. The reaction of Al(NO₃)₃ with urea (Eq. 4) was an intense and rather fast flaming combustion process. XRD investigations evidenced that the resulted powder consisted of single-phase α-Al₂O₃. On the other hand, the reaction between Al(NO₃)₃ and β-alanine (Eq. 5) was a slow and smouldering combustion process, which yield an amorphous black powder.

Considering the individual reactivity of LiNO₃ and Al(NO₃)₃ with respect to urea and β-alanine (Table 1) the conclusion can be drawn that there is a predilection of these metal nitrate with respect to urea and β-alanine. While β-alanine seems to be an excellent fuel for LiNO₃, urea seems to react better with Al(NO₃)₃.

Combustion synthesis of γ-LiAlO₂ powders

For the preparation of γ-LiAlO₂ powders, the following reactions (6–8) were considered:



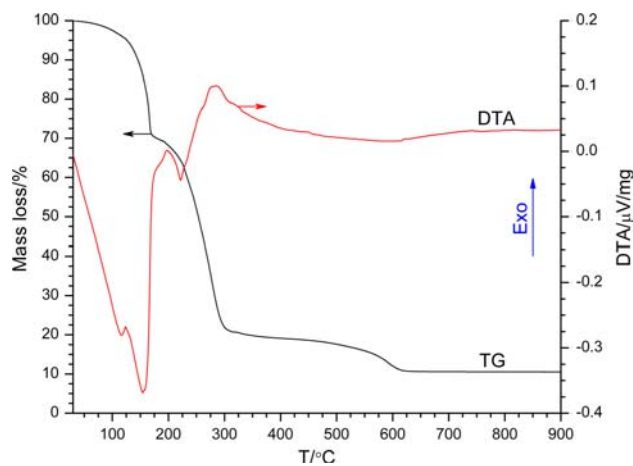
In the first two cases (Eqs. 6, 7) the traditional version of the combustion synthesis was used. This means that a single fuel, either urea (Eq. 6) or β-alanine (Eq. 7), is expected to react with both metal nitrates. Obviously, this

concept does not take into consideration that the two metal nitrates react quite different with urea and β-alanine, as it was already shown.

The different reactivity LiNO₃ and Al(NO₃)₃ manifest with respect to urea and β-alanine leads to the rational conclusion that in the case of γ-LiAlO₂ a mixture of fuels should be used (Eq. 8). In this case urea was assumed to react with Al(NO₃)₃, whereas β-alanine was assumed to react with LiNO₃.

As seen in Table 2, in the case of sample 1, the combustion reaction failed to occur. The absence of the combustion reaction, which is confirmed by the elevated loss on ignition of the resulted powder, can be correlated with the absence of the combustion reaction in the LiNO₃/urea system.

Thermal analysis investigation of the precursor mixture consisting of LiNO₃, Al(NO₃)₃ and CH₄N₂O (sample 1) suggests that LiNO₃ does not participate in the combustion reaction, but it acts as an inert material, hindering the development of the combustion reaction (Fig. 1).

**Fig. 1** TG and DTA curves of precursor mixture 1

Below 200 °C dehydration, hydrolysis and destruction of nitrate groups from aluminium nitrate take place as well as the partial decomposition of urea [22]. The endothermic effect from 222 °C accompanied by a mass loss is associated with the dehydroxylation of aluminium hydroxy salts (resulted from the hydrolytic processes) as well as the LiNO₃ melting. The very weak exothermic effect from 285 °C might be related with the combustion reaction between Al(NO₃)₃ and urea in the presence of inert LiNO₃ melt. The mass loss on the TG curve between 500 °C and 600 °C is due to the thermal decomposition of unreacted LiNO₃. The presence of unreacted LiNO₃ in the final powder was confirmed by the XRD analysis (Fig. 2).

Due to the retarding effect of LiNO₃ the combustion reaction between urea and aluminium nitrate is so much downgraded that instead of α -Al₂O₃ (which is formed in the case of Al(NO₃)₃/urea binary system), poor crystalline γ -Al₂O₃ could be identified on the XRD pattern (Fig. 2).

β -alanine (sample 2) gave a fast combustion reaction (Table 2), leading to the formation of a very voluminous grey powder, with a surface area of 32.0 m²/g (Table 3). The combustion reaction duration is in agreement with the individual reactivity of metal nitrate/fuel combinations. This reaction is faster than the reaction of Al(NO₃)₃ with β -alanine but at the same time is slower than the reaction of

LiNO₃ with β -alanine (Table 1). Such behaviour points out that LiNO₃ accelerates the combustion reaction of Al(NO₃)₃ with β -alanine, or, Al(NO₃)₃ decelerates the combustion reaction of LiNO₃ with β -alanine.

The colour of the sample indicates that the temperature reached during combustion was not very high, so that some carbon impurities originating from the incomplete oxidation of β -alanine contaminated the powder. As shown in Fig. 3, the DTA curve of the precursor mixture containing LiNO₃, Al(NO₃)₃ and C₃H₇NO₂ (sample 2) exhibits an endothermic effect at 170 °C, which is accompanied by a mass loss.

As in the case of sample 1, partial aluminium nitrate decomposition might be responsible for this effect. The development of the combustion reaction is evidenced on the DTA curve by a strong exothermic effect (245 °C) corroborated with a very rapid mass loss on the TG curve. At the same time one can see that the sample still losses about 8 mass% up to 600 °C, which agrees very well with the loss on ignition determination (Table 2). This process might be due to the burning out of carbon impurities. The crystalline phases identified on the XRD pattern of the powder prepared by using β -alanine are β -LiAlO₂ and γ -LiAlO₂ (Fig. 2). The formation of LiAlO₂ proves that combustion reaction (7) occurred; however, the temperature was not high enough to ensure the complete conversion of β -LiAlO₂ to γ -LiAlO₂ and carbon oxidation.

In the case of sample 3, where a mixture of urea and β -alanine was used, the combustion reaction was extremely intense, resulting in a white powder, with a surface area of 3.2 m²/g (Table 3). XRD analysis confirmed that in this case the only crystalline phase present on the diffraction patterns was γ -LiAlO₂ (Fig. 2), with an average crystallite size of 32.6 nm. SEM investigations of the γ -LiAlO₂ powder prepared by using the urea and β -alanine fuel

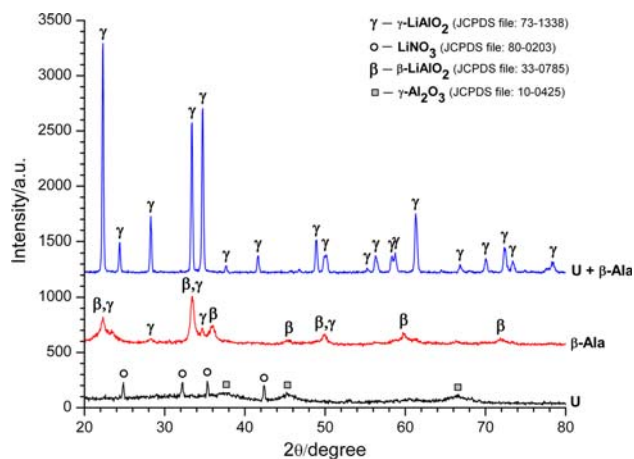


Fig. 2 XRD patterns of the powders resulted from the combustion reactions

Table 3 Characteristics of the combustion-synthesized powders before and after annealing

Sample	Before annealing		After annealing at 900 °C/1 h	
	D _{XRD} /nm	S _{BET} /m ² /g	D _{XRD} /nm	S _{BET} /m ² /g
1	–	–	32.3	2.1
2	12.4	32.0	27.5	16.0
3	32.6	3.2	33.1	1.8

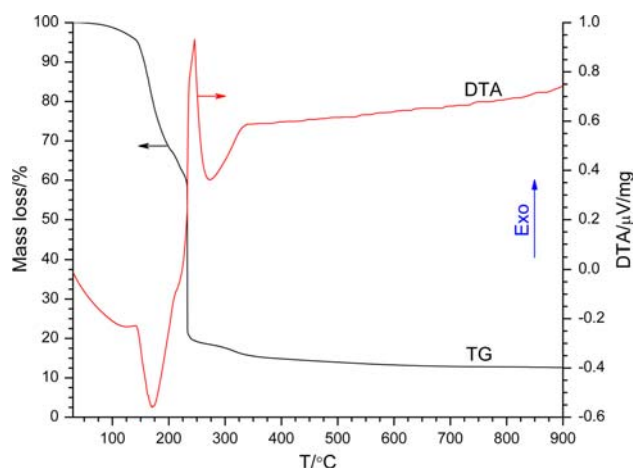


Fig. 3 TG and DTA curves of precursor mixture 2

mixture (Fig. 4) revealed that grains have an irregular shape and are smaller than 50 μm .

Sample 3 exhibits lower surface area and higher crystallite size than sample 2, which indicate that the temperature reached during the combustion reaction (8) was considerably higher than in the case of reaction (7). On the other hand, the lower surface area and larger crystallites size in the case of powder 3 could be also explained by the lower velocity of the combustion generated gases (Table 2).

Thermal analysis of the precursor mixture consisting of LiNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{CH}_4\text{N}_2\text{O}$ and $\text{C}_3\text{H}_7\text{NO}_2$ (Fig. 5) shows that below 200 $^\circ\text{C}$ the TG and DTA curves exhibit a similar profile with the other two precursors (Figs. 1, 3). The exothermic effect associated with the combustion

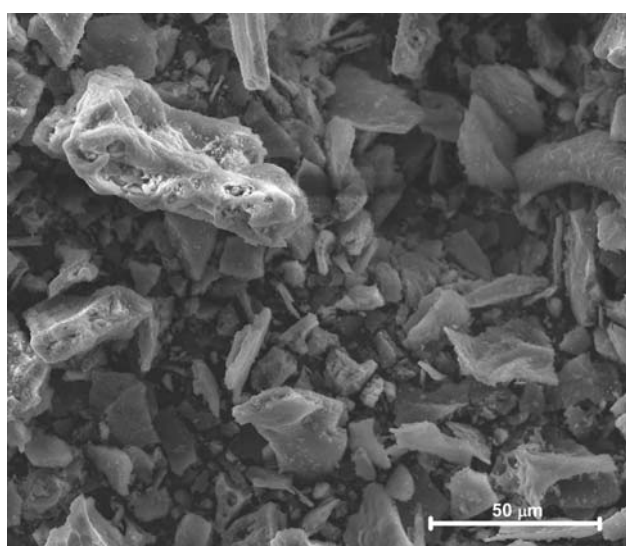


Fig. 4 SEM image of the $\gamma\text{-LiAlO}_2$ powder prepared by using the urea and β -alanine fuel mixture

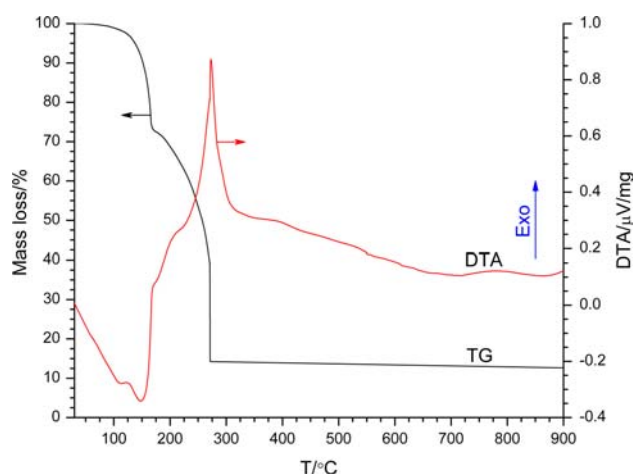


Fig. 5 TG and DTA curves of precursor mixture 3

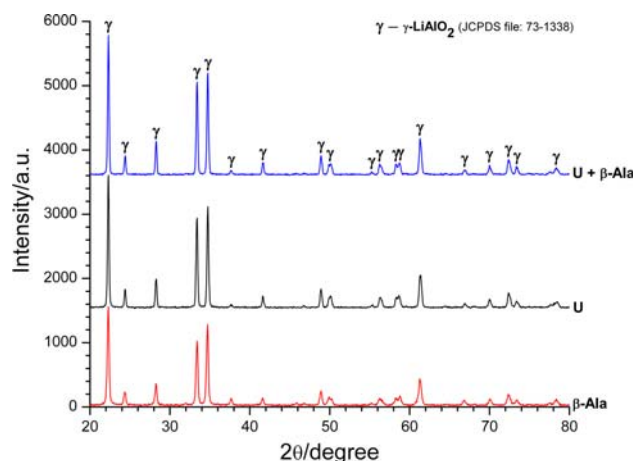


Fig. 6 XRD patterns of the powders after annealing at 900 $^\circ\text{C}$ for 1 h

process occurs at 273 $^\circ\text{C}$ and is also accompanied by a rapid mass loss. After combustion reaction ends, the resulting powder has no more mass loss, meaning that the reaction (8) was completed. Loss on ignition of powder 3 agrees with the results obtained by thermal analysis; in both cases the obtained value is practically negligible (Table 2).

In the case of sample 1, the formation of pure $\gamma\text{-LiAlO}_2$ with an average crystallite size of 32.3 nm requires annealing at 900 $^\circ\text{C}$ for 1 h (Fig. 6). In the case of sample 2 one can observe that after annealing $\gamma\text{-LiAlO}_2$ is the only crystalline phase identified on the XRD pattern. Moreover, a significant increase of the crystallites as well as the reduction of the surface area of the powder may be noticed (Table 3).

In the case of sample 3, where pure $\gamma\text{-LiAlO}_2$ was obtained directly from the combustion reaction no additional thermal treatment is needed. In this case, after annealing at 900 $^\circ\text{C}$ for 1 h the average crystallite size of the powder exhibits only a slight increase, whereas the surface area of the powder decreases below 2 m^2/g .

Conclusions

The reactivity of LiNO_3 and $\text{Al}(\text{NO}_3)_3$ with respect to urea and β -alanine was investigated. Experimental results proved that the above-mentioned metal nitrates have different affinities with respect to urea and β -alanine. LiNO_3 does not react with urea but gives an explosive combustion reaction with β -alanine. $\text{Al}(\text{NO}_3)_3$ gives a smouldering combustion reaction with β -alanine and a vigorous combustion reaction with urea.

Because of different behaviour of these metal nitrate/fuel binary combinations, in the case of $\gamma\text{-LiAlO}_2$ preparation, a mixture of urea and β -alanine is recommended,

instead of using a single fuel. The use of urea and β -alanine fuel mixture allowed the formation of pure nanocrystalline γ -LiAlO₂ powders directly from the combustion reaction. In this case no supplementary annealing was required.

On the other hand, pure γ -LiAlO₂ could not be obtained in the case of using only urea or only β -alanine as fuel, unless annealing at 900 °C for 1 h was performed. Urea failed to produce a combustion reaction; the resulting powder was a phase mixture of unreacted LiNO₃ and poorly crystalline γ -Al₂O₃. β -alanine led to the formation of a mixture of β -LiAlO₂ and γ -LiAlO₂.

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