



# Influence of Processing on Magnesium Aluminate Precursors Morphology Prepared by Co-Precipitation

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## Abstract

The aim of the presented work was to study the influence of processing conditions on the morphology of magnesium aluminate spinel precursor powders, co-precipitated using ammonium hydrogen carbonate at temperatures ranging from 10 to 70°C. XRD showed the same phase composition of precursor powders independent of precipitation temperature ( $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ ). However, a strong difference in powder morphologies was found. The precursor prepared at 10°C consisted of round particles, while increasing the co-precipitation temperature resulted in rod-like grains. Magnesium aluminate precursors were calcined in air and then pressure-free vacuum sintered (1750°C/2h) without any powder pre-treatment or sintering additives. The best relative density of 98.9 % was obtained for ceramics prepared from the powder obtained at the lowest co-precipitation temperature.

**Keywords:** Transparent ceramics,  $\text{MgAl}_2\text{O}_4$ , Powder morphology, Co-precipitation

## WPŁYW WARUNKÓW WYTWARZANIA NA MORFOLOGIĘ WSPÓŁSTRĄCANYCH PREKURSORÓW GLINIANU MAGNEZU

Celem prezentowanej pracy były badania nad wpływem warunków wytwarzania na morfologię proszków prekursora spinelu magnezo-glinowego, współstrąconych za pomocą wodorowęglanu amonowego w temperaturach z przedziału 10 do 70°C. Badania XRD pokazały ten sam skład fazowy proszków prekursora niezależnie od temperatury strącania: ( $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3 \cdot \text{H}_2\text{O}$  i  $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ ). Jednakże, stwierdzono mocną różnicę w morfologii proszków. Prekursor przygotowany w 10°C składał się z okrągłych cząstek, podczas gdy zwiększanie temperatury współstrącania prowadziło do cząstek o kształcie prętów. Prekursory glinianu magnezowego kalcynowano w powietrzu, a następnie spiekano swobodnie w (1750°C/2h) bez żadnej obróbki wstępnej ani dodatków do spiekania. Największą gęstość wynoszącą 98.9 % uzyskano w przypadku ceramiki wytworzonej z proszku otrzymanego w najniższej temperaturze współstrącania.

**Słowa kluczowe:** ceramika przezroczysta,  $\text{MgAl}_2\text{O}_4$ , morfologia proszku, współstrącanie

## 1. Introduction

Transparent polycrystalline magnesium aluminate spinels attain nowadays large interest due to versatile optoelectronic properties and possible armor related applications [1]. The most commonly used route to obtain transparent  $\text{MgAl}_2\text{O}_4$  ceramics consist is hot pressing (HP) with sintering aids (usually LiF) [2, 3]. Other methods include vacuum sintering followed by hot isostatic pressing (HIP) [4], air sintering with post-HIP [5] or spark plasma sintering (SPS) [6, 7].

Relatively rare reports show the possibility of pressure-free sintering of transparent/translucent spinel ceramics. One of the examples is the work of Li *et al.* who have synthesized the magnesium aluminate powder by co-precipitation using ammonium bicarbonate (AC) and sintering in vacuum to high translucency at 1750°C for 2 h [8]. The same group showed also that if the precursor powder consists of rod-like particles instead of semi-spherical ones (as in the case of [8]) the problems with powder compaction and sintering appear due to the undesirable particle morphology [9]. The density of ceramics sintered to 1530°C via constant rate heating (8 deg/

min), using powders obtained after calcinations of precursor consisting of semi-spherical particles, reached >99 % of the theoretical density [8] while sintering to 1550°C with the same heating rate of powder prepared using the precursor of rod-like particles gave ceramics of significantly lower density (96.4 %) [9]. Unfortunately, it was not described in detail, what the main difference between applied powder preparation routes was which resulted in a such strong morphology change and that it was not discussed if the morphology was crucial for strong differences of sinterability or other factors dominating the sintering behaviour of powders.

In our previous study [10] we obtained the magnesium aluminate precursor of rod-like particles by the procedure similar to that proposed by Li *et al.* [8, 9]. After calcination, the agglomerates of magnesium aluminate grains keep initial elongated shape. Such a morphology of powder occurred to be strongly inconvenient for pressing and it causes inhomogeneous packing in green samples [9]. This makes the ceramics difficult (or even impossible) to be sintered to full density, despite small grain size and high reactivity of powder.

In this work a series of magnesium aluminate precursors

consisting of particles of spherical or rod-like shapes, but with the same phase composition (mixture of  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ ) were prepared by co-precipitation at different temperatures. The objective of this work was to study the relation between the morphology of the magnesium aluminate precursor, the properties of calcined spinel powders and the final density of ceramics.

## 2. Experimental procedure

Magnesium aluminate precursor powders of different morphologies were prepared by co-precipitation using the carbonate route, similarly to that proposed by Li *et al.* [8, 9]. Aqueous solutions of 0.15 mol aluminum nitrate and 0.075 mol magnesium nitrate (4N purity, purchased from Auer Remy) were prepared first, then 200 ml of both solutions were mixed. 1.5 mol ammonium carbonate solution was prepared using the Chempur reagent (analytical grade). The pH of ammonium carbonate solution was set to 11 by using ammonia (Chempur, analytical grade) and then it was heated/cooled to the set temperatures (10 to 70°C). Salts solution mixtures were added drop by drop with 7 ml/min speed to stirred 600 ml of 1.5 M ammonium carbonate solution. After precipitation, the suspension was aged for 17 h at reaction conditions. The resultant powders were twice washed by decantation using water and then centrifugally separated and rinsed with ethanol. This procedure was repeated twice. Finally, the precursor powder was dried at room temperature and calcinated in air at 1100°C for 2 h. As-received powders (without any milling or pre-treatment) were pressed into 20 mm diameter samples by uniaxial pressing (30 MPa) followed by isostatic pressing under 120 MPa. The samples were vacuum sintered at 1750°C with 2 h holding at sintering temperature.

The specific surface area of the powders was measured by BET method (Nova 1200e, Quantachrome Instruments). Apparent density of the samples was measured by Archimedes' method. Pore size distribution in pressed samples was evaluated by the mercury porosimetry (Poremaster 60, Quantachrome Instruments). Powders morphology was observed by the scanning electron microscope (LEO1530). X-ray diffraction measurements were performed on the powder samples, using a Siemens D500 diffractometer in Bragg-Brentano geometry, equipped with a high-resolution, semiconductor Si:Li detector and  $\text{CuK}\alpha$  radiation. The diffraction pattern was measured in a  $\theta/2\theta$  step-scanning mode with a  $2\theta$  step of 0.05°, counting time of 4sec/step and  $2\theta$  range 10-70°. The experimental data were analyzed by the XRAYAN phase analysis program and ICDD PDF4+ 2008 data base package.

## 3. Results and discussion

As it was found, co-precipitation of magnesium and aluminium nitrates using ammonium hydrogen carbonate (AHC) at 10 to 70°C leads to the magnesium aluminate precursor powders, consisting of two crystalline phases:  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3 \cdot \text{H}_2\text{O}$  (ammonium dawsonite) and  $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  (hydrotalcite), independent of co-precipitation temperature. Higher co-precipitation temperature favours better crystallization of ammonium dawsonite

and hydrotalcite, which manifests in sharper and stronger XRD peaks (Fig. 1). The crystallite size of ammonium dawsonite  $d_{\text{XRD}}$ , estimated from the broadening of the main XRD peak, is presented in Table 1.

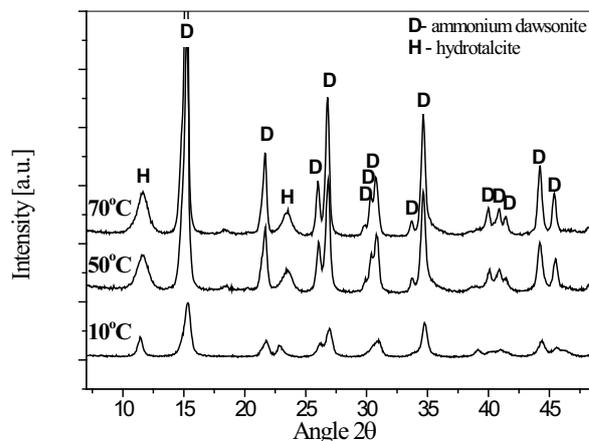


Fig. 1. XRD spectra of magnesium-aluminate spinel precursor powders prepared at 10°C, 50°C and 70°C.

Table 1. Crystallite size,  $d_{\text{XRD}}$ , of ammonium dawsonite calculated on the basis of the X-ray diffraction method.

Precipitation temperature [°C]	10	25	40	50	60	70
$d_{\text{XRD}}$ [nm]	16.0	18.3	19.8	20.3	20.3	23.3

The Change of powder crystallinity is accompanied by the change of its morphology. As it can be seen in Fig. 2 the higher precipitation temperature is, the more elongated particles are present in the precursor powder.

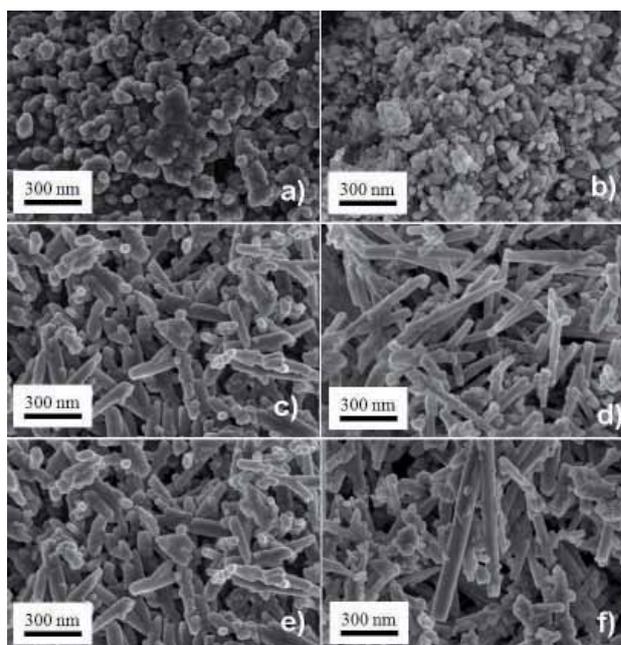


Fig. 2. Scanning electron micrographs of magnesium-aluminate precursor powders co-precipitated at: a) 10°C, b) 25°C, c) 40°C, d) 50°C, e) 60°C and f) 70°C.

Only co-precipitation at 10°C gives the precursor of nearly spherical grains, while even at 25°C some elongated forms can be noticed. After calcination at 1100°C, the majority of rod-like particles collapse into spherical ones, but some round  $\text{MgAl}_2\text{O}_4$  powder particles are still connected in elongated agglomerates, resembling the shape of the initial precursor rod (Fig. 3).

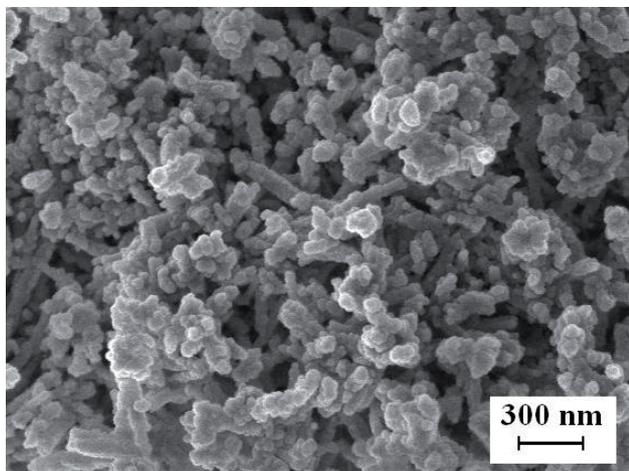


Fig. 3. Scanning electron micrograph of magnesium-aluminate powder calcinated at 1100°C in air using precursor co-precipitated at 40°C.

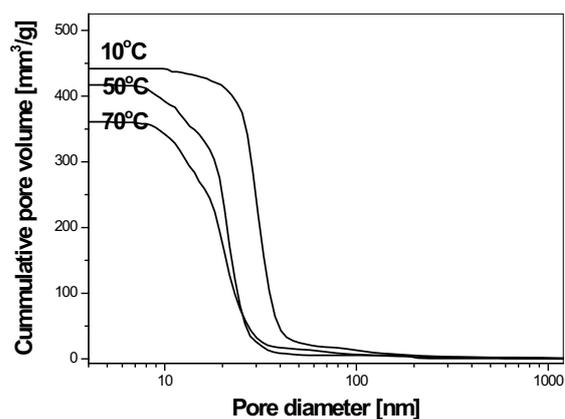
The results of specific surface area measurements (BET method) of calcined powders are collected in Table 2.

Table 2. The specific surface area of the powders co-precipitated at 10 to 70°C, measured by BET method.

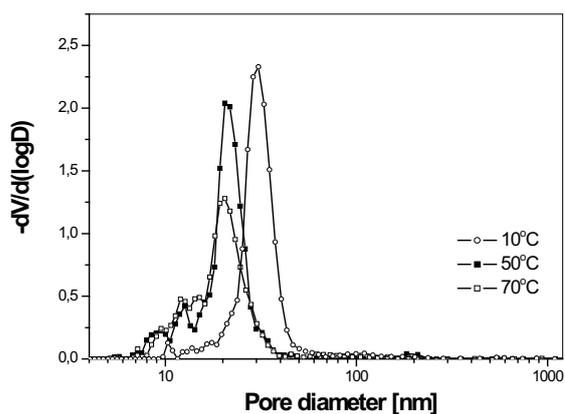
Precipitation temperature [°C]	10	25	40	50	60	70
$S_{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	52.5	61.2	61.2	59.6	59.4	68.2

As it can be seen, the specific surface areas of powders obtained after calcination of precursors prepared at 25–60°C are very similar. The smallest  $S_{\text{BET}}$  exhibits the powder prepared at 10°C, which as the only one was of initial spherical morphology. This phenomenon can be explained by the fact that round particles are well packed in the precursor and due to the better contact create stronger agglomerates after calcination. On the contrary, the precursor precipitated at 70°C consist of relatively big, elongated particles which form a porous structure and remain in a very limited contact between each other. It results in the highest specific surface area of powder after calcination.

The influence of precursors morphology on the compactibility (isostatic pressing, 120 MPa) of calcined magnesium-aluminate powders was studied by mercury porosimetry (Fig. 4). Surprisingly, the powder prepared from the precursor precipitated at the highest temperature (and, as a result, of the biggest rod-like particles) densifies most effectively. Both the pore size as well as its total volume are the smallest in this case. On the contrary, a green sample prepared at the same pressure from powder co-precipitated at 10°C is more porous and the pore size is also significantly larger.



a)



b)

Fig. 4. Pore size distribution in the isostatically (120 MPa) pressed samples, prepared using the powders co-precipitated at 10°C, 50°C and 70°C: a) cumulative curves, b) frequency curves.

The observed differences seem to be the result of the same phenomenon which was mentioned above with respect to specific surface area. Small, round particles of the precursor prepared at 10°C are well packed and due to the better contact create stronger agglomerates after calcination. Higher precipitation temperature favours less agglomerated powder. Elongated forms of powder precipitated at 70°C with probably weak contacts look to be less detrimental for pressing behaviour of powder a strong agglomerates of powder prepared at 10°C.

Elongated precursor particles of the powder co-precipitated at 70°C have an impact on sinterability of calcined powder. Due to the higher crystallinity and bigger sizes of ammonium dawsonite and hydrotalcite particles, the reaction between residual periclase (from hydrotalcite decomposition) and alumina (after ammonium dawsonite decomposition) is limited. MgO peak at  $\sim 43^\circ 2\theta$  for powder prepared at 70°C is present and well formed (Fig. 5), which confirms the above thesis. For comparison, there is not MgO peak at the X-ray diagram of powder prepared at 10°C.

The similar observation was made for the precursor prepared at 50°C and additionally aged for 3 h at 90°C. This ageing resulted in the appearance of bigger and slightly more elongated particles (Fig. 6). After calcination at the same conditions the periclase phase was also observed at XRD spectrum (Fig. 7). If one compares this result with the diagram of the powder calcined from same precursor, but

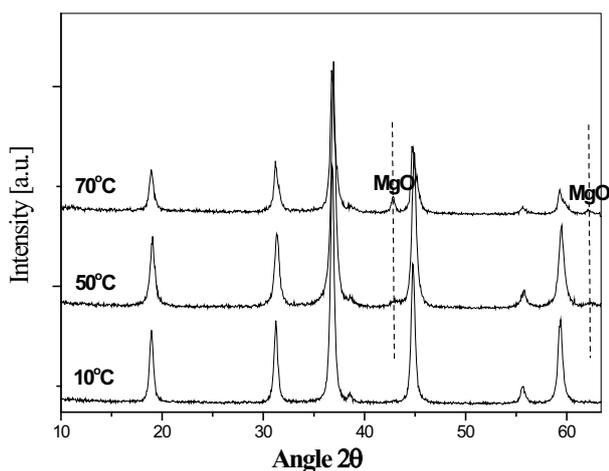


Fig. 5. XRD spectra of the powders obtained after calcination in air for 2 h of magnesium-aluminate spinel precursor co-precipitated at 10°C, 50°C and 70°C.

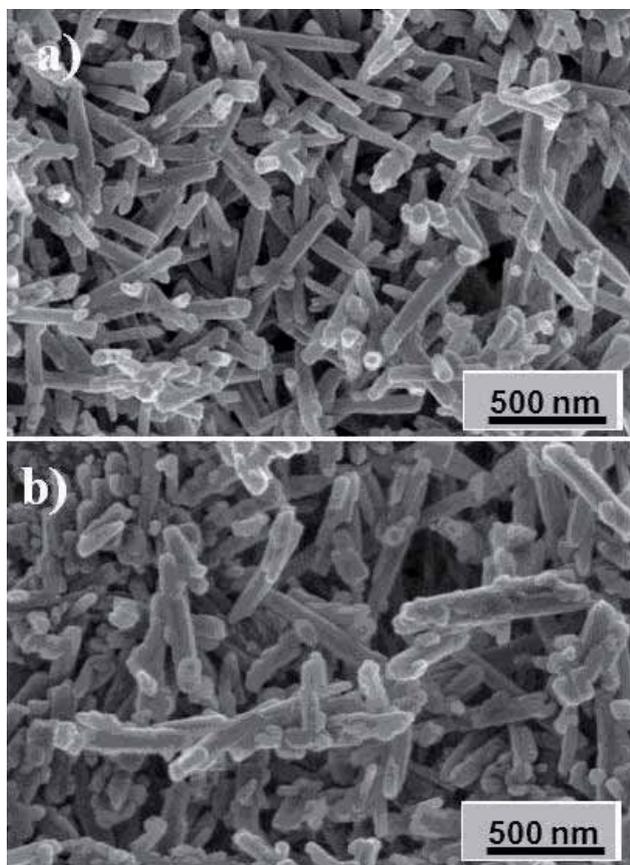


Fig. 6. Scanning electron micrographs of magnesium-aluminate powders: a) co-precipitated at 50°C and aged for 17 h at reaction conditions, b) additionally aged for 3 h at 90°C.

without additional ageing (Fig. 5, curve “50°C”), it is easy to notice a very strong increase in the intensity of MgO peak.

The powders prepared at 10°C, 50°C and 70°C were pressed (isostatic pressing, 120 MPa) into pellets and sintered in vacuum at 1750°C with 2 h dwelling time. The best density of 3.54 g/cm<sup>3</sup> (98.9 % of theoretical Mg-Al spinel density) reached the sample prepared at 10°C (of semi-spherical precursor grains). On the contrary, ceramics produced from powders co-precipitated at 50°C and 70°C sintered to slightly lower density (3.52 g/cm<sup>3</sup>). A small difference (in the range

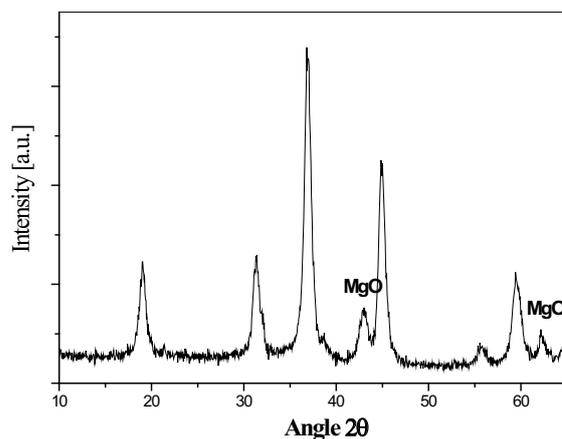


Fig. 7. XRD spectrum of the powder obtained after calcination in air for 2 h of magnesium-aluminate spinel precursor co-precipitated at 50°C and additionally aged for 3 h at 90°C.

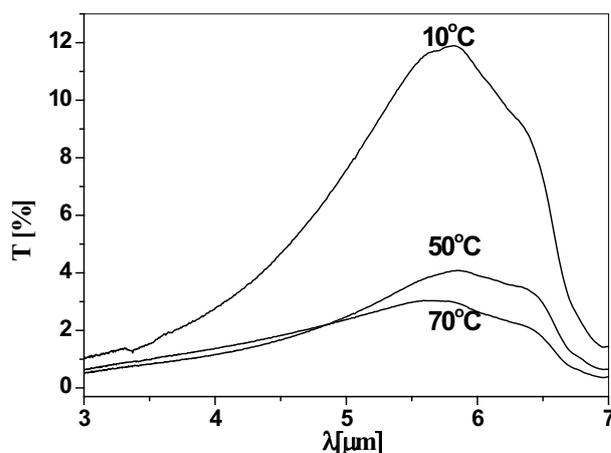


Fig. 8. Transmittance vs. wavelength dependence of the ceramics prepared using powders co-precipitated at 10°C, 50°C and 70°C.

of measurement accuracy) in density of samples is shown better by transmittance results (Fig. 8). Higher temperature of the precursor co-precipitation gave worse transmittance of ceramics.

The presence of non-reacted well crystallised magnesium oxide after calcination at 1100°C of the powder co-precipitated at 70°C can be the reason of its worse sintering behaviour. As it was found, the spinelisation reaction is accompanied by ~5 % volume expansion [11]. In the case of this precursor, higher calcination temperatures should be used to obtain the single phase spinel, but it would result in a creation of stronger agglomerates.

The presented work shows that morphology of the magnesium aluminate precursor, varied by co-precipitation temperature, influences morphology, agglomeration and phase composition of the calcined powder. Elongated particles of the precursor prepared at higher temperature create the loosely packed structure, which results in the less agglomerated powder than in the case of small, round and staying in the close contact particles of the precursor co-precipitated at low temperature. In the same time, a closer contact of particles favours an easier reaction between magnesium oxide (from hydrotalcite) and alumina (from ammonium dawsonite) which results in the lower calcination temperature needed for the calcination of single phase MgAl<sub>2</sub>O<sub>4</sub> powder.

## 4. Conclusions

AHC co-precipitation temperature strongly influences morphology of the magnesium-aluminate spinel precursor, but does not change its phase composition.

Higher temperature of co-precipitation results in better crystallization of precursors and pronounced elongated forms of particles.

The existence of elongated particles avoids strong agglomeration of powders during calcination.

Better crystallinity and bigger size of precursor prepared at higher temperatures slows the reaction between periclase (from hydrotalcite decomposition) and alumina (after ammonium dawsonite decomposition). It increases the calcination temperature needed to obtain the single phase  $\text{MgAl}_2\text{O}_4$  powder.

The best relative density of 98.9 % was obtained for the ceramics prepared using the powder prepared at the lowest co-precipitation temperature.

The results of the work show that the morphology of precursor significantly influences compactibility and sinterability of calcined spinel powders.

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