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Study of magnesium aluminate spinel formation from carbonate precursors

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Abstract

The aim of the presented work was to study formation of magnesium aluminate spinel precursor powder during the co-precipitation of magnesium and aluminium nitrate with ammonium carbonate and its thermal transformation to spinel powder. After precipitation, the only crystalline phase is $NH_4Al(OH)_2CO_3{\cdot}H_2O$ (ammonium dawsonite). The second one, $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ (hydrotalcite) appears during ageing. As found by DTA-MS and HT-XRD measurements, co-existence of both phases in very close contact results in their easier decomposition. On the base of the results obtained the scheme of phase transformations of co-precipitated precursor leading to formation of $MgAl_2O_4$ is proposed.

Keywords: Spinels; Powders-chemical preparation; Calcination; $MgAl_2O_4$

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1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is one of the best-known and widely used polycrystalline materials. It possesses a good combination of features like high melting point, good mechanical strength, low dielectric constant and high resistance against both alkali as well as acids.[1] This makes it popular in many industrial applications, e.g., in chemistry, metallurgy and electronics. Spinel ceramics is commonly used as isolative and refractory material. Chemical inertness makes it an ideal candidate for ultrafiltration membranes.[2] Polycrystalline $MgAl_2O_4$ also finds application as humidity sensor[3] or insulating material for fusion reaction cores.[4] Another field of possible uses opens fabrication of transparent $MgAl_2O_4$ ceramics. In this form it is attractive alternative to relatively expensive and difficult to produce $MgAl_2O_4$ monocrystals. Optical applications of transparent spinel include infra-red windows and passive Q-switch of lasers.[5]

It is well known that good properties of ceramics are the result of properly chosen formation processing and sintering conditions as well as the favorable properties of starting powder. It is not possible to obtain good, uniform and porosity-less ceramics, which is essential for optical applications without using very reactive, pure and non-agglomerated powder. As previous studies proved,[6–8] these characteristics are typical for $MgAl_2O_4$ powders prepared by co-precipitation with ammonium carbonate. Until now, there is no work describing in details the processes taking place during precursor formation by this method and its decomposition leading to nanometric spinel powder. The attempt to study this problem is undertaken in present work.

2. Experimental

2.1. Powders processing

Magnesium aluminate precursor powder was prepared by co-precipitation using carbonate route similarly to that proposed by Li et al.[6–8] Briefly, an aqueous solutions of 0.15 mol aluminum nitrate and 0.075 mol magnesium nitrate (analytical grade, purchased from Polskie Odczynniki Chemiczne) were prepared. 200 ml of both solutions were mixed and heated to

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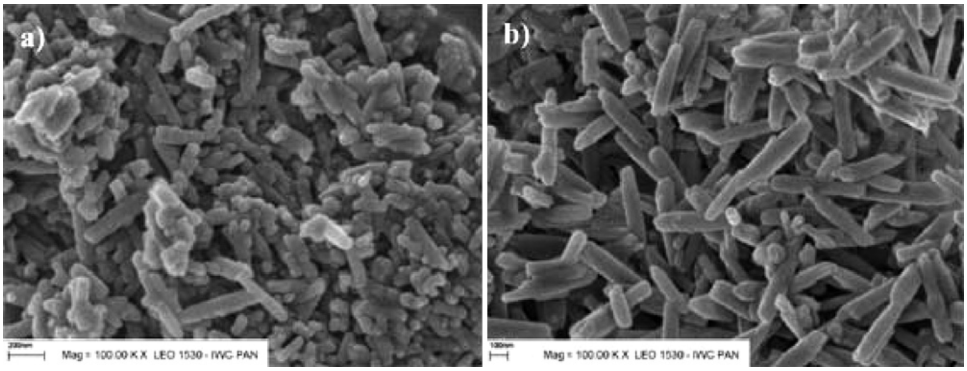

Fig. 1. SEM pictures of $MgAl_2O_4$ precursor powder (a) before ageing and (b) after ageing.

50 °C. Mixture was added drop by drop with 7 ml/min speed to stirred 600 ml of 1.5 mol ammonium carbonate (analytical grade, Chempur) solution at the same temperature. To maintain pH of solution equaled 9.8, ammonia water was added. After precipitation, suspension was aged for 17 h at processing conditions. The resultant powder was two times washed by decantation using water and then centrifugally separated and rinsed with ethanol (Alchem LINE-Etoh CLEAR). This procedure was repeated two times. Finally, the precursor powder was dried at room temperature.

$NH_4Al(OH)_2CO_3{\cdot}H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ separately as well as its mixtures with different mass ratios (2.1:1 and 1:1) than for magnesium aluminate spinel stoichiometry (2.6:1) were also prepared in similar way. In all cases precipitation temperature was set on 50 °C and pH on 9.8. Aluminum nitrate solution of 0.15 mol concentration (for $NH_4Al(OH)_2CO_3{\cdot}H_2O$) or its mixture with 0.075 mol magnesium nitrate water solution (for $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ and $NH_4Al(OH)_2CO_3{\cdot}H_2O$–$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ mixtures) were added dropwise to 1.5 mol ammonium carbonate solution. After precipitation all suspensions were aged for 17 h, washed with water and rinsed with ethanol.

2.2. *Powders characterization*

Specific surface of precursor powder was measured by BET method (Nova 1200e, Quantachrome Instruments). Differential thermal analysis coupled with thermogravimetry and mass spectroscopy of evolved gasses (SDT 2960, TA Instruments with QMS Thermostar, Balzers) were conducted in He atmosphere (5N purity). Powders morphology was observed by scanning electron microscope (LEO1530).

The XRD ex situ measurements were carried out on Siemens D5005 diffractometer using Ni filtered Cu Kα radiation (=1.5418 A), scintillation detector and commercial DiffracPlus Software. The X-ray tube was operated at 40 kV and 40 mA settings. The *in situ* diffraction measurements employed INEL CPS 120 position sensitive detector with a flat graphite monochromator and in-lab designed environmental XRD camera.[9] The camera used a flat sample mounting with a sample powder spread over porous glass slab mounted on a steel heater. The measurements used asymmetrical geometry with incident angle set between 10° and 20°. Data conversion and analysis of pattern evolution with time was done using a laboratory written software INEL. The *in situ* measurements employed XRD camera fed with helium (5N purity) with the sample heated up to 773 K using linear temperature program and the heating rate of 1 K/min. A series of XRD patterns were collected starting from room temperature with each pattern collected for 5 min, every 5 min.

3. Results and discussion

As a result of co-precipitation and ageing of suspension, a white and loose precursor powder of high ($389\ m^2/g$) specific surface has been obtained. Powder consisted of two crystalline phases: $NH_4Al(OH)_2CO_3{\cdot}H_2O$ (ammonium dawsonite) and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ (hydrotalcite) with molar ratio equal to 10:1. As it was found, crystalline powder particles were formed in two steps. After co-precipitation only ammonium dawsonite was detected by XRD as a crystalline phase. Chemical analysis of powder and a filtrate proved that in the applied conditions precipitation was complete for both cations. Crystalline hydrotalcite appeared after ageing of suspension at reaction conditions (pH 9.8, $T = 50$ °C). Phase change of precursor powder was followed by its morphology change. As seen in Fig. 1a two kinds of particles were found before ageing: the spherical ones with diameter of 50–80 nm approximately and rod-like particles with thickness below 100 nm and length of 200–400 nm. After ageing, spherical particles almost disappeared and the rod-like particles were found (Fig. 1b).

DTA and MS results of $NH_4Al(OH)_2CO_3{\cdot}H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ powders obtained separately and $MgAl_2O_4$ precursor are presented in Figs. 2 and 3. DTA of hydrotalcite (Fig. 2) is similar to described by Yang et al.[10] There are two wide endothermic effects with minima at 210 and 390 °C. MS results (Fig. 3) show that in the first decomposition step mostly H_2O is lost. At this moment metastable phase of structure similar to hydrotalcite (interlayer distance changed from 3.0 to 1.8 Å) named by Kanezaki "phase II" is formed.[11] Second endothermic effect is strongly asymmetric, which suggests two processes overlapping. It is confirmed by MS results. While the water is being removed evenly and gradually, much more complicated is ionic current course of CO_2. CO_2 starts to evolve together with H_2O, however, the maximum of its

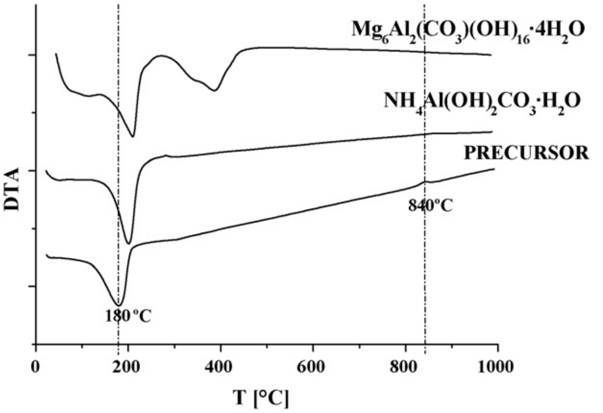

Fig. 2. DTA curves of precursor, ammonium dawsonite and hydrotalcite.

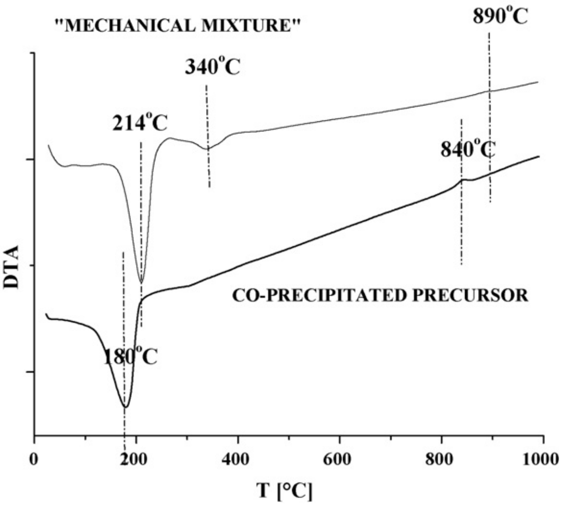

Fig. 4. Comparison of DTA profiles of co-precipitated precursor and "mechanical mixture".

removal is observed at temperature 30 °C higher than observed for maximum of H_2O.

There is only one endothermic peak at DTA curve of ammonium dawsonite with minimum at 200 °C. MS results show that around this temperature CO_2, NH_3 and H_2O are evolved simultaneously. This is in agreement with the one-step decomposition of $NH_4Al(OH)_2CO_3$ H_2O proposed by Yalfani et al.[12]

If DTA and MS results of precursor are compared and its components are annealed separately, it is easy to notice several important differences between them. First of all, precursor decomposition starts earlier than it is observed for ammonium dawsonite or hydrotalcite. Minimum of endothermic peak for precursor is situated at temperature about 20 °C lower than the same peak minimum for $NH_4Al(OH)_2CO_3·H_2O$ or $Mg_6Al_2(CO_3)(OH)_{16}·4H_2O$ obtained separately. For the second, there is no strong endothermic effect around 300–400 °C at DTA of precursor powder, which exists in case of hydrotalcite. It can mean that in the close co-existence of components in precursor powder obtained by co-precipitation, ammonium dawsonite and hydrotalcite influence of one on another during decomposition. This consumption is confirmed by mass spectra. H_2O and NH_3 evolve from precursor powder below 200 °C. The major amount of carbon dioxide evolves simultaneously with them, but small peak of CO_2 on ionic current profile

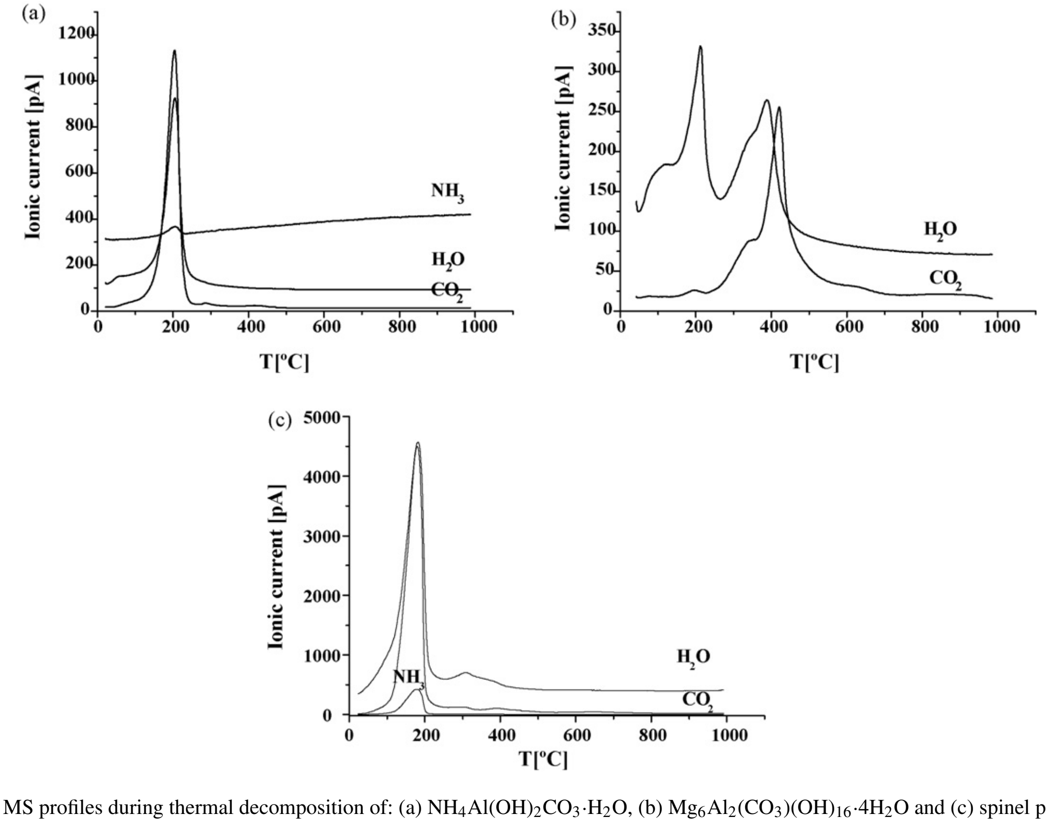

Fig. 3. MS profiles during thermal decomposition of: (a) $NH_4Al(OH)_2CO_3·H_2O$, (b) $Mg_6Al_2(CO_3)(OH)_{16}·4H_2O$ and (c) spinel precursor.

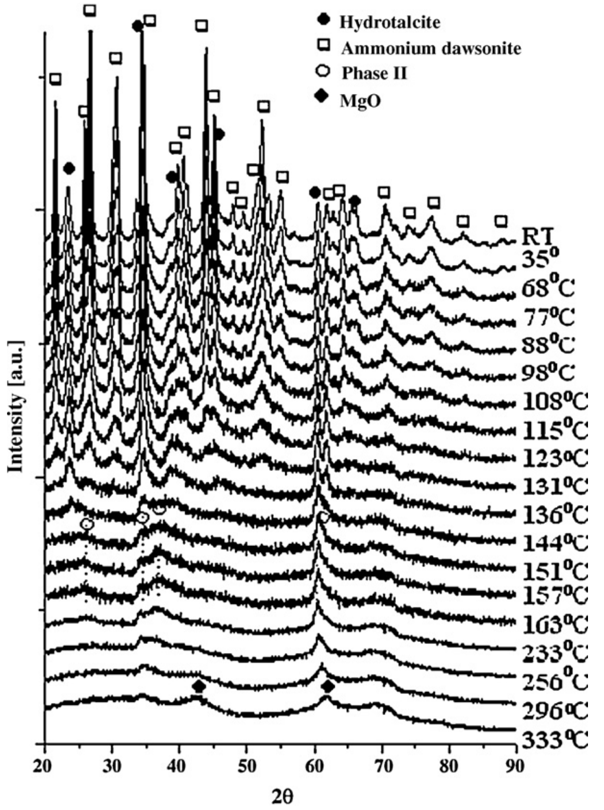

Fig. 5. *In situ* XRD patterns during thermal decoposition of magnesium aluminate spinel precursor.

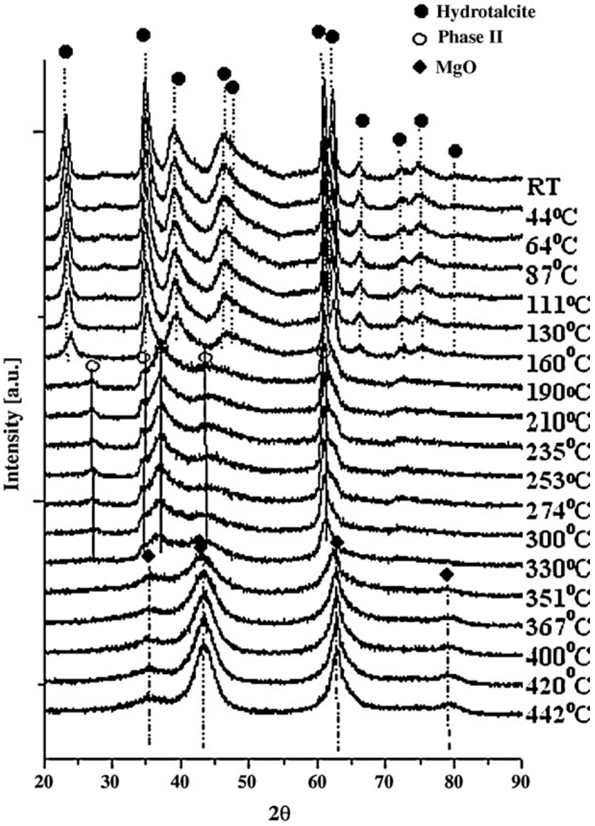

Fig. 6. *In situ* XRD patterns during thermal decomposition of hydrotalcite.

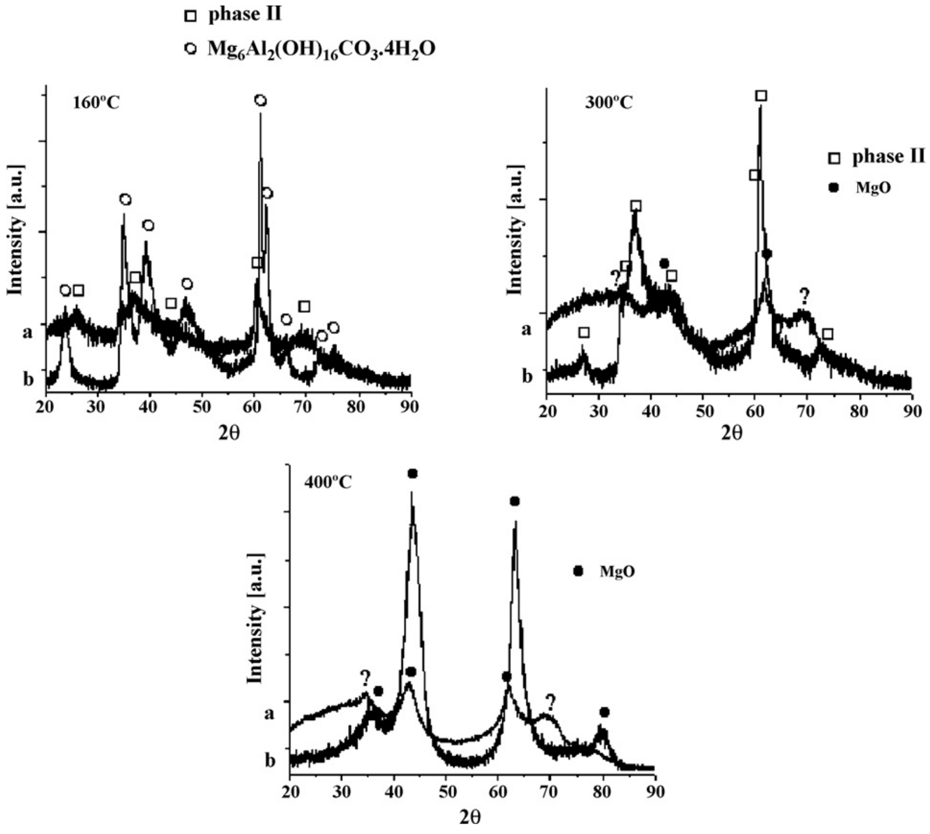

Fig. 7. Comparison of *in situ* XRD spectra of spinel precursor (more diffused spectra) and hydrotalcite (stronger and better defined peaks) collected at 160, 300 and 400 °C.

between 250 and 400 °C still remains. Moreover, there is a small exothermic peak around 840 °C in the case of spinel precursor, which is not observed for neither $NH_4Al(OH)_2CO_3{\cdot}H_2O$ nor $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ decomposed separately.

To check if the above-mentioned differences are related to the close contact of component phases obtained during co-precipitation a mixture (called hereafter "mechanical mixture") of these compounds (precipitated separately, with similar crystallite size as found in precursor powder) was prepared by mixing with ratio typical for spinel precursor. The comparison of DTA profiles of co-precipitated powder and "mechanical mixture" is shown in Fig. 4.

As is seen there is a strong shift of peaks position to higher temperature found in "mechanical mixture". Minimum of endothermic effect for co-precipitated powder observed at 180 °C and maximum of exothermic peak position at 840 °C shift to 214 and 890 °C, respectively, in case of "mechanical mixture". Another new feature of "mechanical mixture" is the second endothermic effect around 340 °C which can be associated with the carbon dioxide loss similarly to the same effect observed in pure hydrotalcite. But DTA profile of this mixture is not simply sum of the DTA profiles of individual components. Strong shift of the second peak position on DTA curve of hydrotalcite from ∼390 to ∼340 °C in case of "mechanical mixture" can be explained by the impact of ammonium dawsonite presence and its interaction with hydrotalcite. When the mixture of components is not ideal like in case of "mechanical mixture", ammonium dawsonite and hydrotalcite decompose more independently. In contrary, when ammonium dawsonite and hydrotalcite are in very close contact the interactions between them are much easier. This results in the change of hydrotalcite decomposition path, manifested by second endothermic peak disappearance. To check if this phenomenon has an explanation in different phase transitions of hydrotalcite and/or ammonium dawsonite in precursor powder during heating, *in situ* XRD measurements were performed (Figs. 5 and 6). As it occurred these measurements correlate well with DTA results. There is also shift of temperature of ammonium dawsonite and hydrotalcite decomposition. Fig. 7 presents XRD spectra of spinel precursor and pure hydrotalcite collected at three selected temperatures.

According to Morinaga et al.[13] ammonium dawsonite undergoes transformation to amorphous phase around 194 °C. But as found in this work, in close contact with hydrotalcite, in precursor powder obtained by co-precipitation, already at 160 °C ammonium dawsonite peaks disappear. Similar observation can be done for hydrotalcite. While independent heating of hydrotalcite gives results similar to that described by Kanezaki,[11] in contact with ammonium dawsonite its phase transformations shift also to lower temperatures. At 160 °C instead of hydrotalcite, phase II is detected, and at 300 °C MgO is already observed. On XRD spectra of spinel precursor heated to 300 and 400 °C two new unknown broad peaks appear. These peaks cannot be assigned to any known phase and needs more studies to be described. We suppose that this unknown phase is a result of reaction between phase II and amorphous alumina. During this reaction CO_2 is evolved.

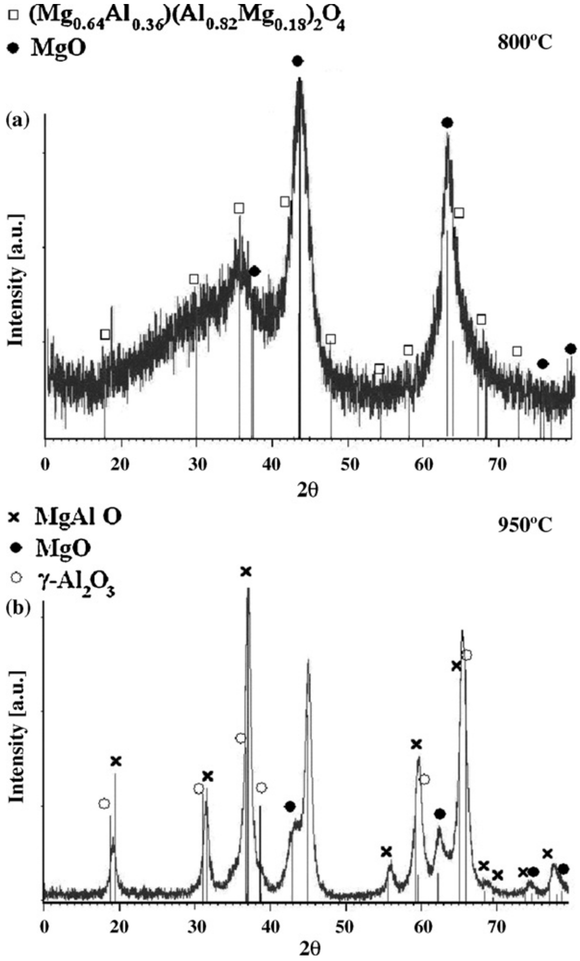

Fig. 8. XRD spectra of spinel precursor powder heated to: (a) 800 °C and (b) 950 °C.

Another interesting and worth explanation fact is appearance of exothermic peak at 840 °C in the co-precipitated mixture which does not exist neither in ammonium dawsonite nor hydrotalcite. This peak was observed also by Li et al.,[6–8] and in their works was assigned to MgO and γ-Al_2O_3 reaction leading to spinel phase. To check the origin of this peak XRD spectra was collected from powder annealed to temperature below and above peak position. Fig. 8 shows the result of this measurement. As seen at 800 °C dominating phase is periclase. Additionally observed broad peaks can correspond to $(Mg_{0.64}Al_{0.36})(Al_{0.82}Mg_{0.18})_2O_4$ phase. At 950 °C $MgAl_2O_4$ already dominates. Broadening of its reflections around 19°, 31°, 39° and 66° 2θ can suggest the presence of γ-Al_2O_3. For better explanation some additional DTA measurements of ammonium dawsonite with hydrotalcite co-precipitated mixtures with higher hydrotalcite content were performed. The results are shown in Fig. 9. It is easy to notice that when the hydrotalcite content increases the exothermic peak observed at 840 °C disappears. It suggests that this peak is connected rather with some phase transformations of alumina (originating from ammonium dawsonite) than with spinel formation. To prove it, mixture of ammonium dawsonite with spinel powder (30 wt%) was prepared. DTA profile of this mixture (Fig. 10) shows exothermic effect ∼890 °C. It looks that the presence of spinel

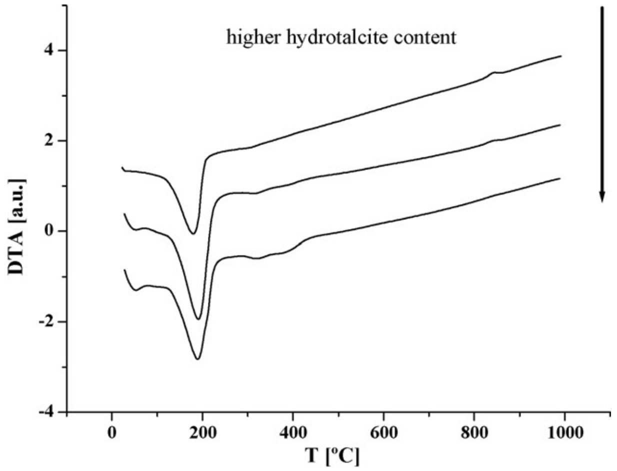

Fig. 9. Comparison DTA curves of ammonium dawsonite—hydrotalcite co-precipitated mixtures with mass ratios 2.6:1, 2.1:1 and 1:1.

nanocrystals serves as seeding phase for isostructural γ-Al_2O_3 crystallization.

Summarizing the obtained results, the decomposition of ammonium dawsonite and hydrotalcite in precursor powder can be described as follows. Below 200 °C, ammonium dawsonite evolves all the gases (CO_2, H_2O and NH_3) and decomposes to amorphous alumina but hydrotalcite evolves H_2O and undergoes transformation to phase II. Next, in the range of 200–300 °C CO_2 and H_2O are evolved and phase II peaks gradually disappear and crystalline periclase is formed. At the same time, two broad new peaks on XRD spectra appear, which in our opinion are probably connected to some not described in literature Mg–Al phase. Between 300 and 500 °C none significant phase changes are observed. In the range of 500–800 °C disordered spinel of $(Mg_{0.64}Al_{0.36})(Al_{0.82}Mg_{0.18})_2O_4$ composition appears as a result of reaction of MgO (from hydrotalcite) and amorphous alumina (from ammonium dawsonite), decomposition of MgO-based solid solution or the new Mg–Al phase mentioned above. The first crystalline alumina phase appears at 840 °C, and it is not θ-Al_2O_3 (as was observed for ammonium dawsonite annealed separately[13]) but γ-Al_2O_3. Crystallization of γ-Al_2O_3 is probably facilitated by the presence of nanocrystalline spinel of the same structure (seeding effect). At 950 °C dominating phase is $MgAl_2O_4$ but MgO and γ-Al_2O_3 are still present. Residual periclase and alumina react leading to spinel formation and finally, above 1100 °C, the only crystalline phase is $MgAl_2O_4$.

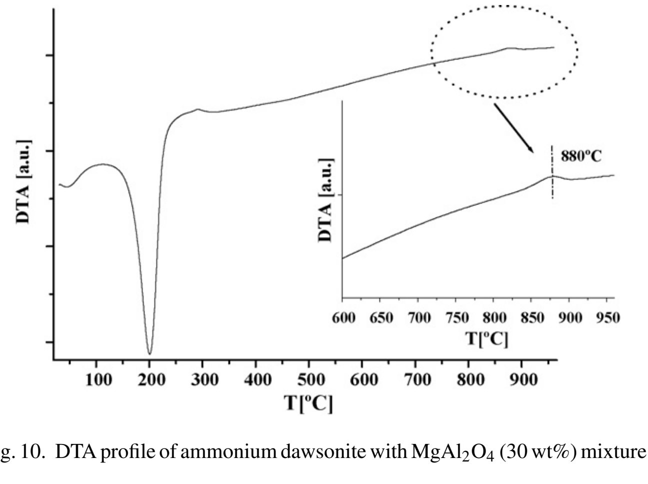

Fig. 10. DTA profile of ammonium dawsonite with $MgAl_2O_4$ (30 wt%) mixture.

4. Conclusions

During co-precipitation of magnesium and aluminium nitrate with ammonium carbonate the only crystalline phase which appear is ammonium dawsonite. Hydrotalcite crystallizes during prolonged ageing. Close co-existence of $NH_4Al(OH)_2CO_3 \cdot H_2O$ with $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$ enabled by co-precipitation significantly changes the decomposition path of both components. On the base of studies carried the scheme of phase transformations of co-precipitated precursor during annealing leading to the formation of $MgAl_2O_4$ is proposed.

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