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Preparation of nanosized sodium–aluminum tungstate, $NaAl(WO_4)_2$

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ABSTRACT

Investigations are carried out for preparing nanosized pure phase of $NaAl(WO_4)_2$ by means of solid state synthesis with mechanical activation, applying the sol–gel method (Pechini) and by co-precipitation. It is shown that it is not possible to obtain pure phase when the initial substances are in stoichiometric amounts due to the simultaneous formation of a number of accompanying tungstate phases. The reasons for their origin are discussed. A method is demonstrated for obtaining a pure phase of $NaAl(WO_4)_2$ by co-precipitation of aqueous Na_2WO_4 and $Al(NO_3)_3$ solutions with considerable excess of Na_2WO_4. It is proved that $NaAl(WO_4)_2$ with particle size 40–80 nm is obtained with final synthesis of the powders at temperature 600–650 °C and duration of thermal treatment of 1–2 h.

1. Introduction

An increasing interest in tunable and very short pulse solid-state lasers was observed during the last years due to their promising application in modern science and technology. This stimulated the studies on single crystal materials with a broadband emission in the near-infrared region between the different tungstates [1–4], molybdates [5,6], borates [7,8], garnets [9,10], forsterite [11], germanates [12], different oxides [13,14] alexandrite [15], galates [16], silicates [17,18] and fluorides [19,20]. Cr-doped $NaAl(WO_4)_2$ is a potential laser active media because of high absorption, efficient pumping with the use of visible-range semiconductor diode lasers and broad laser emission [2]. However, the production of single crystals as laser active media from this tungstate is related with a number of problems, first of all due to the low growth velocity and anisotropy [3]. An effective approach to overcoming the crystal growth problems is to produce transparent ceramics, replacing the single crystals. In addition, transparent ceramics production is low cost and possess higher chemical homogeneity and isotropy [21,22]. The technology of optical ceramics production includes three main stages:

- synthesize of nanopowders;
- preparing of highly dense compacts;
- sintering of the compact to the non-porous ceramics.

As a first step of $NaAl(WO_4)_2$ ceramic production is to obtain nanosized powder. $NaAl(WO_4)_2$ was synthesized by solid state reaction, sol–gel (modified Pechini), as well as co-precipitation methods. As we know this is a first attempt to obtain $NaAl(WO_4)_2$ as a nanopowder. The main aim of this investigation was to find a suitable method and way for preparation of nanosized $NaAl(WO_4)$, i.e. to have possibilities to obtain this compound with a require dimension of the powders, size distribution and particle shape. It is important to control these characteristics. The expectation is that the last powder characteristics will influence the result from the next stage of ceramic preparing.

The experiments show that sol–gel and solid state reaction methods are not suitable because of several secondary (mainly sodium tungstates) phases crystallize in parallel to $NaAl(WO_4)_2$. Co-precipitation method gives good possibilities pure nanosized $NaAl(WO_4)_2$ to be obtained. The purity of the products, size dimensions, size distribution, and morphology of the particles were tested using X-ray, DTA/TG, TEM and SEM analyses.

2. Experiment and characterization techniques

The main objective of these studies was to choose a synthesis method, ensuring reproducible formation of the pure $NaAl(WO_4)_2$ phase. As a preliminary investigations three methods of $NaAl(WO_4)_2$ preparation were tested—a solid state synthesis, a sol–gel method (modified Pechini) and co-precipitation of aqueous solutions.

Three series of experiments were carried out in the case of solid state synthesis with different initial reagents. The series were

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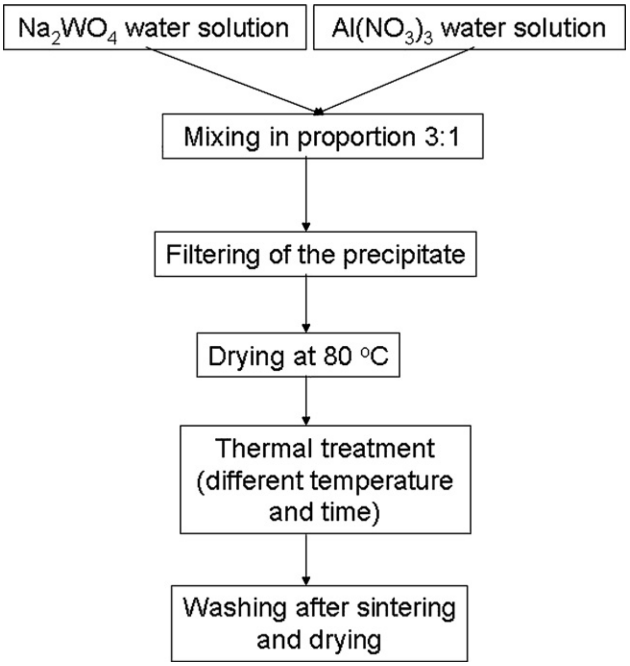

Fig. 1. A scheme for producing $NaAl(WO_4)_2$ by co-precipitation of aqueous solutions of Na_2WO_4 and $Al(NO_3)_3$ from non-stoichiometric proportion between the initial reagents.

composed with the following reagents: Na_2CO_3, Al_2O_3 and WO_3; Na_2WO_4, Al_2O_3 and WO_3 or Na_2WO_4 and $Al_2(WO_4)_3$. All reactant substances were with purity p.a. Within the range of each series variation was realized of the temperature of synthesis (500, 600 and 700 °C as the highest temperature, because $NaAl(WO_4)_2$ melts incongruently at 775 °C [23]), time of synthesis (6, 12, 24 and 48 h), as well as of the conditions of mechanical treatment. The latter was conducted either on a mechanical mixture of the initial reagents or on the intermediate products after the thermal treatment at the already mentioned temperatures after 6 h of treatment.

A standard procedure for synthesis of $NaAl(WO_4)_2$ according to the method of Pechini was applied with initial reagents $Na_2WO_4{\cdot}2H_2O$, $Al(OH)_3$ and H_2WO_4 (p.a.). Citric acid or EDTANa were applied as chelating agent and ethylene glycol–as forming agent. The ratio between the ions, the chelating and forming agent was 1:4:4. A standard drying procedure was applied at 80 °C in the course of 5 days with subsequent heating to the final temperature for 2 h. The final temperatures of synthesis were 600 and 700 °C with retention time of 24 h.

The initial reagents for the synthesis of $NaAl(WO_4)_2$ according to the co-precipitation method were $Na_2WO_4{\cdot}2H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$. Aqueous solution of $Al(NO_3)_3{\cdot}9H_2O$ was added at room temperature with intensive mixing to aqueous solution of $Na_2WO_4{\cdot}2H_2O$, with molar ratio of the substances 2:1. The expected reaction of synthesis was

$$2Na_2WO_4 + Al(NO_3)_3 \rightarrow NaAl(WO_4)_2 + 3NaNO_3$$

The obtained precipitate was washed and dried at 80 °C. The dry product was heated at temperatures between 500 and 700 °C in the course of 6, 12 and 24 h.

Taking into account the result from as described preliminary investigations the basic investigation on the $NaAl(WO_4)_2$ synthesis by co-precipitation method were made.

These experiments were carried out according to the scheme, given in Fig. 1.

The principal difference from the preliminary and basic syntheses by co-precipitation method is the mixing of solutions of Na_2WO_4 and $Al(NO_3)_3$ not in the ratio 2:1 (the stoichiometric ratio), but in the amount 3:1 with the objective of obtaining more rich in sodium additional undesired phases, water soluble Na_2WO_4 or $Na_2W_2O_7$. Then the undesired phases could be easily removed by washing the product of temperature synthesis with water and so pure $NaAl(WO_4)_2$ may be obtained. The main part of the temperature syntheses was carried out at temperatures 550, 600, 650 and 720 °C and treatment time of 1, 2, 5 and 24 h for each of these temperatures. As obtained solid-phase products, washed with water was dried and then analyzed and characterized by different methods.

Powder X-ray diffraction patterns were collected at room temperature on Bruker D8 Advance diffractometer using CuKα radiation and LynxEye PSD detector within the range 10–80° 2θ. The X-ray pattern of a ground sample of single crystal $NaAl(WO_4)_2$, obtained by us by means of the flux method in previous investigations, was used as a reference in these analyses [23]. The mean crystallite size and unit cell parameters were calculated from the integral breadth of all peaks (Pawley fit) using the TOPAS 3 program [24].

DTA/TG was applied for additional analysis of some of the syntheses. For this LABSYS^{TM} EVO DTA/TG device of the SETARAM Company, France was used. The samples were investigated at a heating rate of 10 °C/min in Ar flow at a flow rate of 20 ml/min.

An idea about the size and shape of the particles of some of the samples was obtained by TEM and SEM analyses. A TEM JEOL 2100 at 200 kV was used. For this purpose specimens were prepared by grinding the samples in agate mortar and dispersing them in methanol by ultrasonic treatment for 6 min. A droplet of suspension was dispersed on holey carbon films on Cu grids. The SEM analyses were realized by Philips SEM 515 device. An accelerating voltage of 30 kV was applied. The powders were covered with gold with a thickness of 10–15 nm.

3. Results and discussion

The results of the preliminary investigations showed that it is impossible to obtain a pure phase of $NaAl(WO_4)_2$ according to the described methods and conditions. It turned out that parallel with $NaAl(WO_4)_2$, in all cases there were one or more additional phases. Fig. 2(a–d) illustrates the impossibility of obtaining pure phase of $NaAl(WO_4)_2$ according to each of these applied methods and conditions. The result of the solid state syntheses, regardless of the conditions of mechanical activation and conditions of synthesis, represents a product, containing $NaAl(WO_4)_2$ and other phases. The amount and type of these phases change depending on the particular conditions. These phases are sodium tungstates—Na_2WO_4, $Na_2W_2O_7$, $Na_2W_3O_{10}$, $Na_2W_4O_{13}$, as well as free WO_3. An example for a similar result is shown in Fig. 2b. The synthesis by co-precipitation for stoichiometric ratio between Na_2WO_4 and $Al(NO_3)_3$ also does not yield a pure product of $NaAl(WO_4)_2$, the accompanying products being most often sodium tungstates with various ratio between sodium and aluminum, as well as WO_3 (Fig. 2c). Fig. 2d shows an example of a product, synthesized according to the Pechini method. In this case the additional undesired phases are most often sodium–aluminum tungstates with other ratios between sodium and aluminum, sodium tungstates, WO_3 and other phases, which have not been identified.

The formation of undesired additional phases parallel to $NaAl(WO_4)_2$ regardless of the methods and conditions for synthesis may be explained with the presence of a great number of sodium tungstates, whose formation is kinetically more facilitated by the existence of double sodium–aluminum tungstate. In addition, once formed, these tungstates are relatively stable and could not be decomposed back at temperatures close to the tempera-

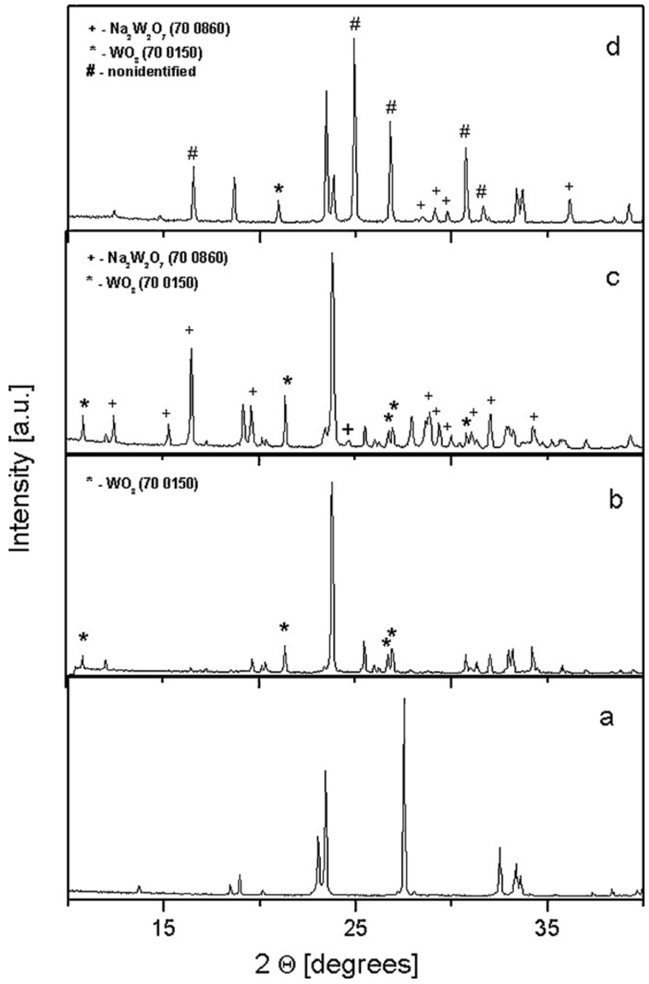

Fig. 2. X-ray diffraction patterns of products obtained by: solid state synthesis products with preliminary mechanical activation (b); co-precipitation (c); and sol–gel method (d) treated at 700 °C for 24 h, compared with powder diffraction pattern of single crystals (a).

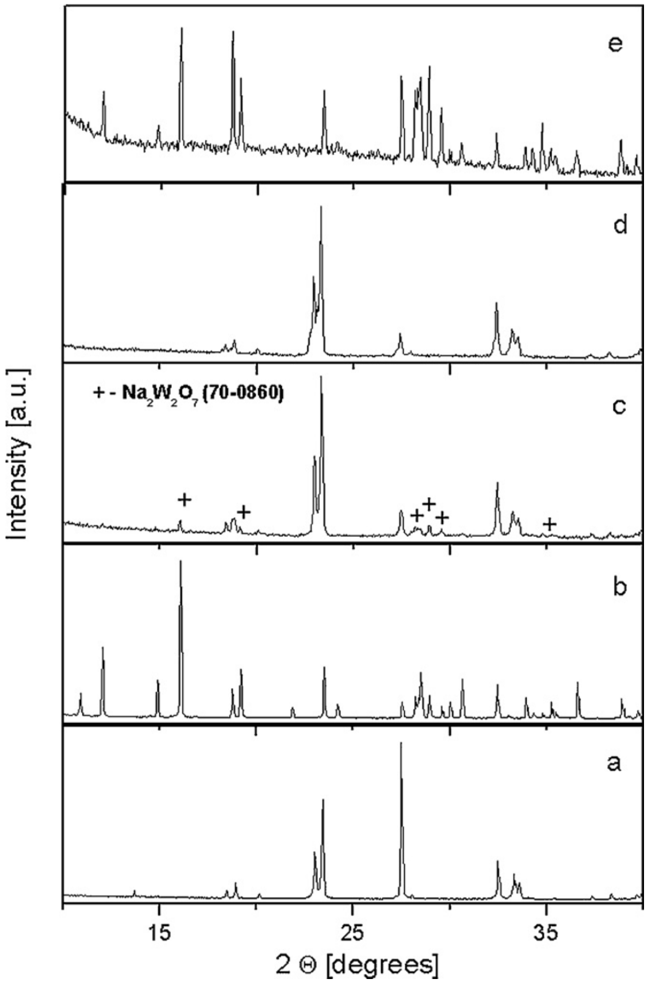

Fig. 3. X-ray diffraction patterns of the products of co-precipitation after synthesis at 650 °C for 5 h (c), after synthesis at 650 °C for 5 h and washing of the product (d) and of the residue after evaporation of the washing water (e), compared with the X-ray diffraction pattern of $NaAl(WO_4)_2$ single crystals (a) and $Na_2W_2O_7$ (b) (ICDD 70 0860).

ture of peritectic decomposition of $NaAl(WO_4)_2$ itself (775 °C) [23]. The temperatures of congruent melting or peritectic decomposition of sodium tungstates according to reference literature data are 700 °C, 746 °C, 700 °C, 770 °C and 913 °C for Na_2WO_4, $Na_2W_2O_7$, $Na_2W_4O_{13}$, $Na_2W_5O_{16}$ and $Na_2W_6O_{19}$, respectively [25].

The detailed analysis of the described preliminary investigations shows that one possible alternative for the formation of pure $NaAl(WO_4)_2$ is to use the co-precipitation method in such a manner that the accompanying additional phase are only water soluble tungstates—Na_2WO_4 or $Na_2W_2O_7$. The basic investigations described further on confirm this possibility.

The X-ray diffraction patterns of the products of one experiment are shown in Fig. 3, where Fig. 3c is the pattern of the product after temperature synthesis before washing, Fig. 3d—after washing and Fig. 3e—after water evaporation from the residue of the washing solution.

As can be seen in Fig. 3c, the result after temperature synthesis before washing of the sample represents a two-phase system, consisting mainly of $NaAl(WO_4)_2$ and relatively small part of $Na_2W_2O_7$. The X-ray diffraction patterns of these phases according to reference literature data are given in Fig. 3a and b. After washing the synthesized product with water, the result is pure $NaAl(WO_4)_2$ (Fig. 3d), and the residue product from the washing fluid after water evaporation is $Na_2W_2O_7$ (Fig. 3e).

The X-ray diffraction patterns of the products after their synthesis at different temperatures in the course of 5 h and after their subsequent washing are shown in Fig. 4. It is seen that peaks of $NaAl(WO_4)_2$ appear after synthesis at 500 °C (Fig. 4c). The treatment at temperatures lower than 500 °C in the course of 5 h (even 24 h) does not yield a pure product. An amorphous part, as well as several peaks belonging to $Na_3AlW_5O_{18}$ (ICDD 50 0961), are available, which decrease with increasing the temperature. At 550 °C the amount of the amorphous part and $Na_3AlW_5O_{18}$ is reduced (Fig. 4d). A pure $NaAl(WO_4)_2$ product is obtained after synthesis at 600 °C or higher temperature (Fig. 4e–g). The formation of the pure phase of $NaAl(WO_4)_2$ according to the described procedure is confirmed also by the comparison of the DTA curves with the curves of $NaAl(WO_4)_2$ single crystals (Fig. 5). An endothermic peak of peritectic decomposition of $NaAl(WO_4)_2$ is observed at 764 °C according to the reaction

$$NaAl(WO_4)_2 \rightarrow Al_2(WO_4)_3 + \text{threecomponentmelt}$$

After cooling of the specimens, in both cases an inverse reaction takes place at 705 °C for the single crystals or at 694 °C for the product of co-precipitation (a metastable region about 60 °C). The second exothermic peak is related to the full crystallization of the residue melt. A small endothermic peak at 690 °C is observed for some samples before the peritectic decomposition at 764 °C. The

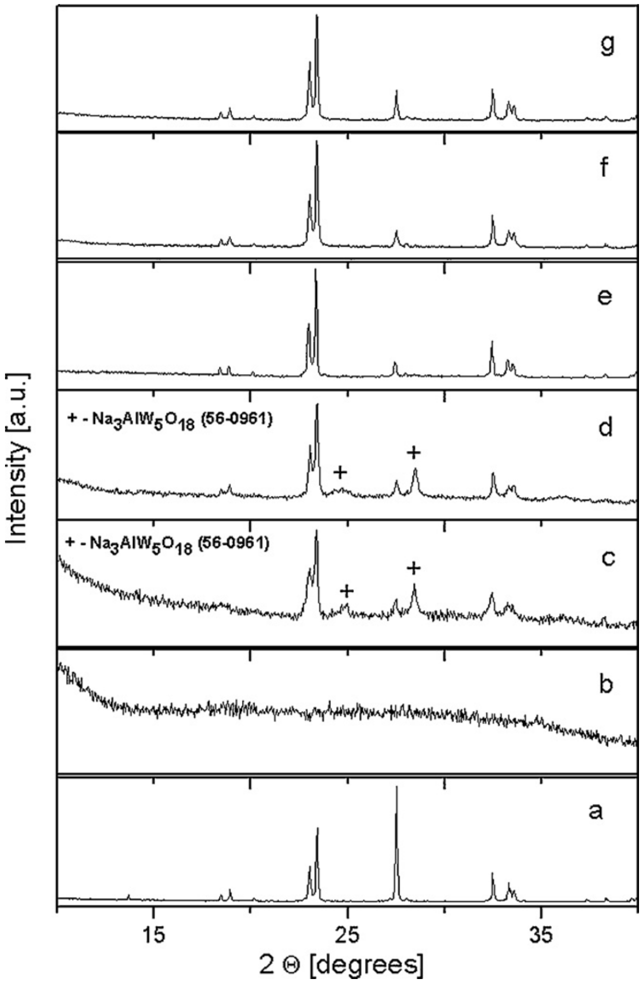

Fig. 4. X-ray diffraction patterns of the $NaAl(WO_4)_2$ product after 5 h of thermal treatment at different temperatures and subsequent washing: single crystals of $NaAl(WO_4)_2$ (a), 400 °C (b), 500 °C (c), 550 °C (d), 600 °C (e), 650 °C (f) and 720 °C (g).

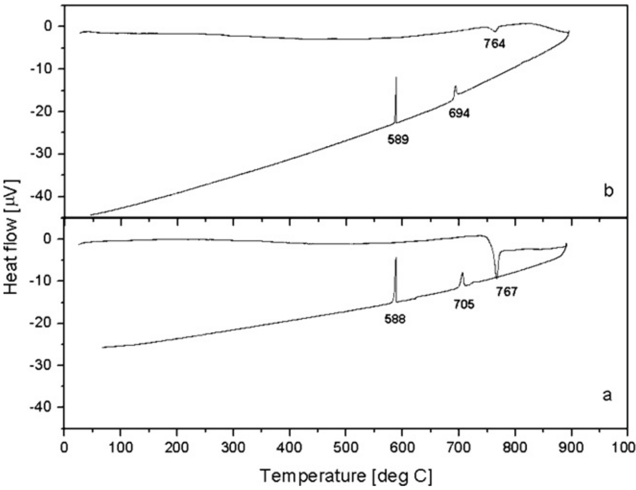

Fig. 5. DTA analysis of: single crystal $NaAl(WO_4)_2$ (a) and $NaAl(WO_4)_2$ obtained by co-precipitation (b).

additional investigations show that this peak disappears after second washing of the synthesized product. It has been also elucidated that this peak is related with a $Na_2W_2O_7$ residue, which is undistinguishable by X-ray phase analysis. During the interaction of this residue with the basic phase, a compound is formed, which is peritectically decomposed at 690 °C. Probably this compound represents $Na_3AlW_4O_{15}$, which is not described in reference literature. To establish its composition and to characterize its structure is another scientific task.

Information about the particle size of the produced $NaAl(WO_4)_2$ phase at different temperature (550, 600, 650, 720 °C) and time of thermal treatment (1, 2, 5 and 24 h) is obtained using the TOPAS 3 software program. The results are given in Table 1. As it could be expected, the particle size increases with the temperature thermal treatment time increases. The results show that pure crystal phase of $NaAl(WO_4)_2$ with average particle size from 40 to 80 nm may be obtained by synthesis in the temperature range 600–650 °C for synthesis duration up to 2 h. It has to be noted that the time for producing well crystallized nanosized particles at these temperatures is only 1 or 2 h, which is an indication for the high reaction capacity of the material.

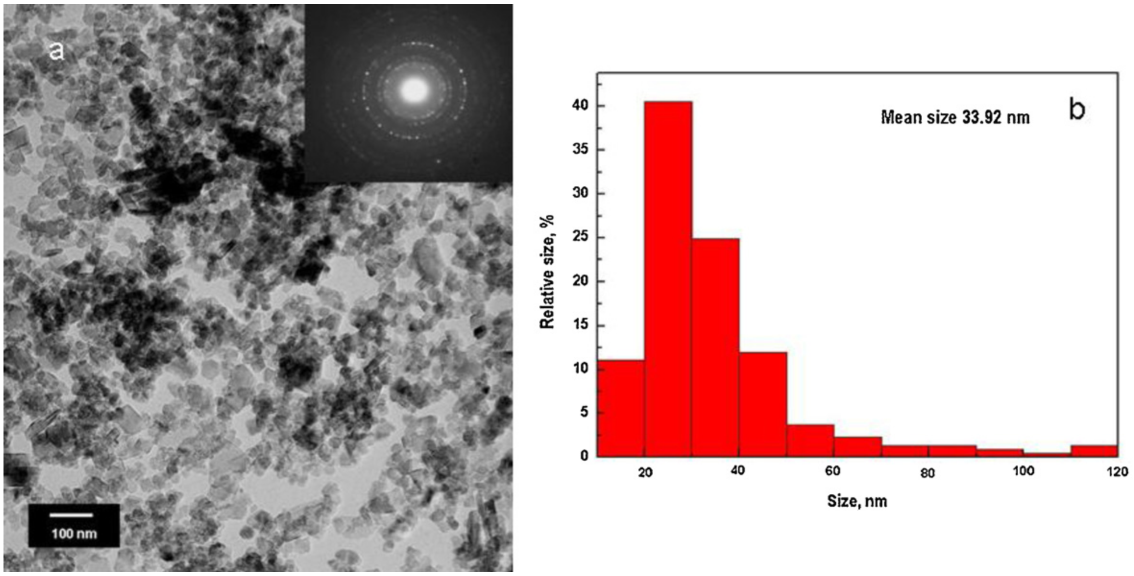

Fig. 6. TEM bright field micrograph and SAED of the sample (a) and size distribution (b) of the powder treated at 650 °C for 2 h.

Table 1
Particle size [nm] of the produced NaAl$(WO_4)_2$ phase at different temperature (550, 600, 650 and 720 °C) and time of thermal treatment (1, 2, 5 and 24 h), obtained using the TOPAS 3 software program.

T [°C]	Treatment time [h]			
	1	2	5	24
550			50	60
600		60	108	
650	40	77	120	
720	102		168	

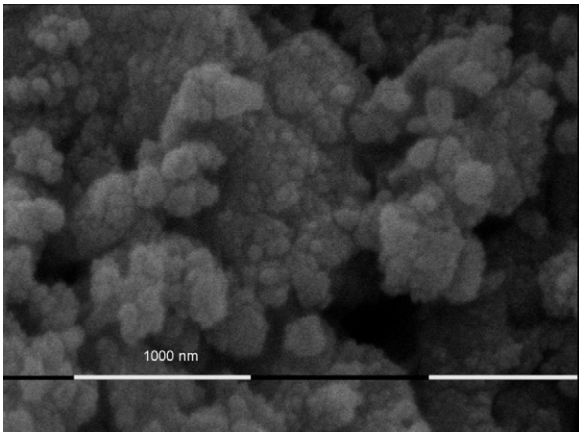

Fig. 7. SEM photograph of the powder treated at 650 °C for 2 h.

The TEM bright field micrographs of the sample and the size distribution of the powder treated at 650 °C for 2 h are shown in Fig. 6. As seen in Fig. 6a, the majority of the particles with small sizes are well shaped, almost spherical. A considerably lower number of larger particles with clearly defined habit are available. The SAED of the particles shows well crystallized phase. The size distribution of the particles, determined by means of the Lince v 2.4 software program (Linear Intercept program) shows that 65% of them are with sizes between 20 and 40 nm and 90% are with sizes up to 50 nm, i.e. a product has been obtained with particles having sufficiently close size, Fig. 6b.

The SEM photograph of the same sample is shown in Fig. 7. The volumetric isometric particles form single aggregates.

4. Conclusion

The investigations carried out for producing NaAl$(WO_4)_2$ by solid-phase synthesis, sol–gel (modified Pechini) method and coprecipitation have shown that the formation of pure NaAl$(WO_4)_2$ phase is strongly hampered by the simultaneous origin of a number of sodium tungstates. The predominant part of these tungstates are more stable than NaAl$(WO_4)_2$ and are insoluble, which makes their decomposition or separation of the once formed undesired additional phases impossible. As a result of the investigations, a simple and reliable method has been established for reproducible production of a pure NaAl$(WO_4)_2$ phase, based on ensuring conditions for yielding accompanying phases that are only rich in sodium water soluble sodium tungstates and their subsequent dissolution (washing) after the synthesis. The results proved that for the formation of nanosized NaAl$(WO_4)_2$ with dimensions from 40 to 80 nm the temperature of synthesis should be in the range 600–650 °C and the treatment time should be from 1 to 2 h.

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