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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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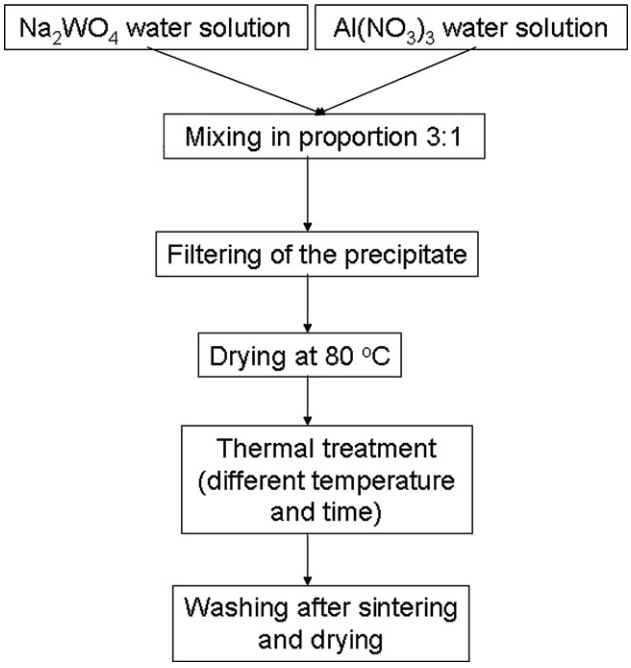

Fig. 1. A scheme for producing $NaAl(WO_4)_2$ by co-precipitation of aqueous solutions of Na_2WO_4 and $Al(NO_3)_3$ from non-stoichiometric proportion between the initial reagents.

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-