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Preparation of aluminium tungstate $Al_2(WO_4)_3$ using sol-gel modified Pechini method

I. I. Koseva*, V. S. Nikolov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Aluminium tungstate $Al_2(WO_4)_3$ pure phase with nanosized particles was prepared using modified Pechini method. Citric acid was used as chelating agent and ethylene glycol was used for sterification. Dried resin was treated at different temperatures and different heating time. The pure phase $Al_2(WO_4)_3$ appears after treatment at 830 ^{o}C for 36 h. Increasing the heating temperature to higher than 830 ^{o}C leads to obtaining of the pure $Al_2(WO_4)_3$ phase for a shorter time. The TEM bright field micrographics of the samples show that the size varies between 50 and 200 nm, and strongly depends on the time and the treating temperature. Heating of the polymeric resin in oxygen flow leads to obtaining of the pure $Al_2(WO_4)_3$ phase at significant lower temperature and significant shorter treating time.

Keywords: ceramics, tungstates, sol-gel processes, nanostructured materials, transmission electron microscopy, X-ray diffraction

INTRODUCTION

In the recent years several compounds of the $M_2W_3O_{12}$ family, where M is a trivalent cation (Al, Sc, Zr, Y, Cr, etc.), have been investigated due to their interesting physical and chemical properties. One of them is the temperature-induced ferroelastic phase transition from orthorhombic (D14 2h, Pnca) to monoclinic (C5 2h, P21/a) structure [1, 2, 3]. The orthorhombic phase shows thermal expansion, strongly depending on the chemical substitution in the basic phase [2, 4, 5, 6]. Some reports demonstrated production of ceramics in this way with negative, positive or zero thermal expansion coefficients [5, 6]. Another feature of these materials is the unusual anisotropic high trivalent ion conduction [7, 8, 9]. A pressure-induced amorphization phenomena (PIA) were reported recently also [3, 10, 11]. Due to the acentric site symmetry of the Cr^{3+} laser ions, in place for M^{3+} into the $M_2W_3O_{12}$, these compounds exhibit strong absorption and emission cross sections in the $10^{-19}cm^2$ range and therefore belong to the class of high-gain Cr materials with potential application as tunable laser active media [12]. All these features make these compounds suitable for a wide variety of applications in fuel cell electrolytes, gas sensors, and lasers.

Aluminium tungstate $Al_2(WO_4)_3$ which is a member of this family (being with orthorhombic symmetry, point group Pnca), shows all above mentioned properties and perspective applications [2, 6, 11, 13, 14, 15, 16].

Most of the $Al_2(WO_4)_3$ properties reported in the literature have been measured on polycrystalline samples, prepared using the conventional solid-state reaction. Mainly XRD-control of the phase has been used [7, 8, 10, 15].

Some optical and ion conductivity measurements have been made on single crystal samples, obtained via Czochralski or Bridgman methods [12, 13, 14, 16, 17, 18, 19, 20, 21, 22]. However, the crystal growth process, involving these methods, is strongly limited due to the WO_3 evaporation. Flux growth process is demonstrated also [23]. In this case the process takes a long period of time and the crystal dimensions are small. In addition, high anisotropy of single crystal growth velocity is detected.

In the last years more attention has been paid to the nanosized transparent ceramics [24, 25, 26, 27]. The samples hold the same chemical composition, but they are isotropic in the different crystallographic directions. Nanosized ceramics are the main key for the improvement of the material physical properties. Therefore, the transparent ceramics can be used in place for single crystal elements in the fields of optics and electronics to improve the optical homogeneity, the high threshold of the materials, as well as to obtain elements of specific size and shape.

One of the main requirements for obtaining transparent ceramics is to control the powder grain

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* To whom all correspondence should be sent:
E-mail: E-mail: ikosseva@svr.igic.bas.bg

size. Obtaining powders by a conventional solid state synthesis does not allow grain size control. Generally the size of the particles depends on the sintering temperature and the process duration. Synthesis of KRE$(WO_4)_2$ samples, where RE is rare-earth element, with controlled grain size, obtained via sol-gel method (the so called modified Pechini method), has been reported [28]. The particle size here depends on the correlation between the compound components, the chelating agent, and the sterification agent, as well as on the chelating agent nature. [24]. Citric acid has been used as chelating agent for obtaining aluminium molybdates [27]. Citric acid and EDTA have been used as chelating agent for obtaining potassium gadolinium tungstate. [26]. Ethylene glycol has been used for sterification.

Taking into consideration the above papers we report on the preparation of aluminium tungstate for a first time ever, using modified Pechini method.

EXPERIMENTAL PART

Powders of $Al(OH)_3$ (p.a.), and H_2WO_4 (p.a.) were used as starting materials. Citric acid (p.a.) was used as a chelating agent, and ethylene glycol (pure) for sterification.

$Al(OH)_3$ was dissolved at a room temperature in concentrated citric acid solution in metal ions to citric acid molar ratio of 1:2.

H_2WO_4 was dissolved at a room temperature in 25% NH_3, and than was added to the metal solution under stirring.

Ethylene glycol was added after to citric acid and ethylene glycol in 1:1 molar ratio.

The formation of resin occurs at 80ºC, and the resin transforms to gel. Afterwards, the resin was dried at 90 ºC for 5 days.

The resultant product was heated at 300 ºC for 30 minutes to obtain a brown powder, than the temperature was increased to 600 ºC by a 150 ºC/h step. The powder becomes of light brown color during the last procedure.

The light brown powder was hold at different temperatures in the range between 620 and 900 ºC, and at different heating time to obtain a pure phase. The final sintering product was of white or pale yellow colour, depending on the thermal conditions.

Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu Ka radiation and SolX detector. XRD spectra were recorded at room temperature. Data were collected in the 2θ range within 10 to 80 deg. with a step of 0.04 deg. and 1s/step counting time. XRD spectra were identified using Diffractplus EVA program. The presence of the $Al_2(WO_4)_3$ phase in the different specimens was estimated by a comparison with JCPDS card N 24-1101 for pure $Al_2(WO_4)_3$.

The particle size and morphology were performed using TEM JEOL 2100 at 200 kV. For this purpose, the specimens were prepared by grinding the samples in agate mortar and dispersing in methanol via ultrasonic treatment for 6 minutes. A droplet of suspension was dispersed on holey carbon films placed over Cu grids.

RESULTS AND DISCUSSIONS

The X-ray diffraction patterns of the samples, treated at different temperatures and constant heating time, are shown on Fig. 1. The lines of the additional phases are marked by stars. As can be seen, pure $Al_2(WO_4)_3$ phase appears after heating at 860ºC. The amount of the additional phases decreases with temperature increase.

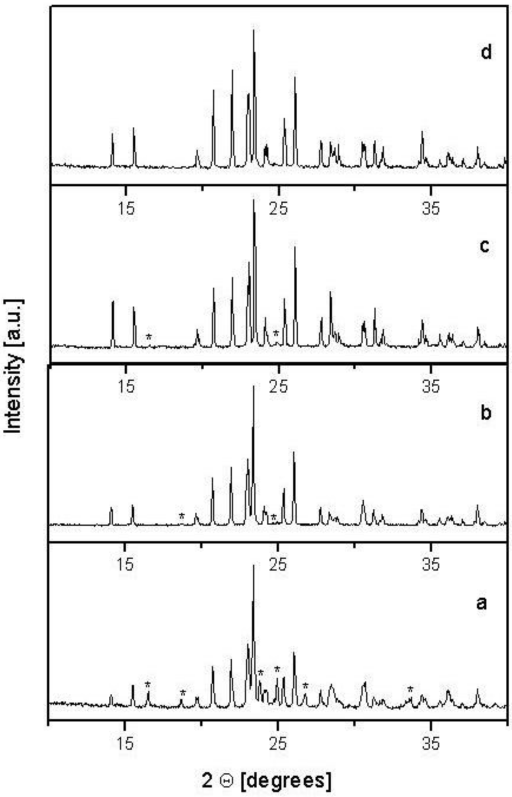

Fig. 1. X-ray diffraction patterns of the samples, treated at different temperatures, and at12 h constant heating time: a) at 620 ºC, b) at 800 ºC, c) at 830 ºC, and d) at 860 ºC.

Taking into account our final aim, i.e. to prepare a transparent ceramic, it was important to find out what the conditions are for obtaining $Al_2(WO_4)_3$ powder with smaller particle size. For this reason, the second series of experiments was done where the samples were treated at different temperature and different heating time.

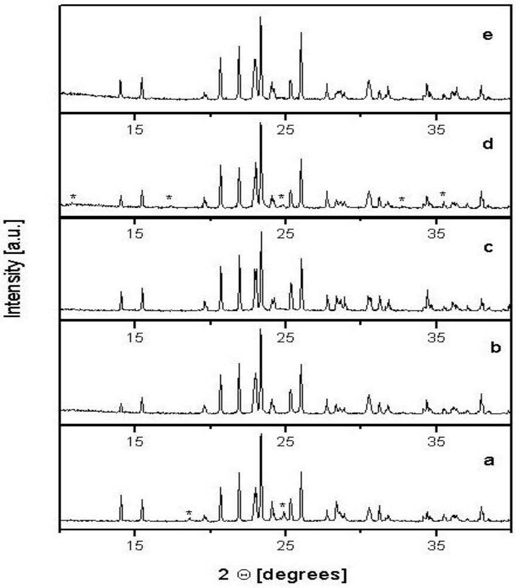

Fig. 2. X-ray diffraction patterns of the samples, treated at different temperatures, and at different heating time: a) at 760 ºC for 72 h, b) at 830 ºC for 36 h, c) at 860 ºC for 12 h, d) at 900 ºC for 2 h, and e) at 900 ºC for 6 h.

Fig. 2 includes the X-ray sample patterns of this series. Heating the samples for a time period longer than 12 h at below 830 ºC does not lead to obtaining of pure $Al_2(WO_4)_3$ phase. Increasing the heating temperature to higher than 830 ºC leads to obtaining of pure $Al_2(WO_4)_3$ phase for a shorter time (for 36 h at 830 ºC, for 12 h at 860 ºC, and for 6 h at 900 ºC).

An important result was obtained when the polymeric resin was treated in oxygen flow for 5 h at 620 ºC. As can be seen on Fig. 3, pure $Al_2(WO_4)_3$ phase was received in oxygen atmosphere at significant lower temperature and significant shorter treating time.

Thermal treatment conditions of the dried resin for the preparation of $Al_2(WO_4)_3$, and the results of the X-Ray phase analyses are summarized in Table 1. The quantity of the additional phases (marked by stars on the X-Ray diffraction pattern figures) was roughly evaluated as a correlation between the intensity of the highest pick of $Al_2(WO_4)_3$ (2θ = 23.27) and the highest pick of the additional phases (2θ = 24.88). The nature of the additional phases were not determined taking into account the JCPDS data for aluminium and tungstate phases.

The TEM bright field micrographics of the samples, treated at 620^{o}C for 12 hours and at 830 ^{o}C for 36 hours, are shown on Fig. 4. The particle size at the lower temperature is distributed in the narrow region from 50 to 80 nm without clear defined habit, while that at the higher temperature is distributed in a wide region from 50 to 200 nm with a clear defined habit according to the orthorhombic structure.

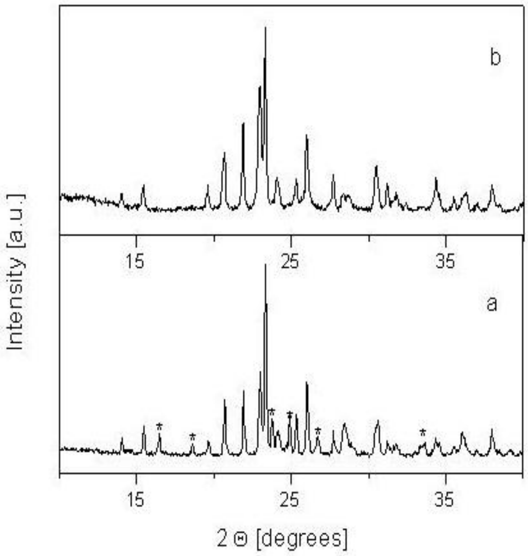

Fig. 3. X-ray diffraction patterns of the samples treated in air and in oxygen flow: a) in air at 620 ^{o}C for 12 h, and b) in oxygen flow at 620 ^{o}C for 5 h.

Thermal treatment conditions of the dried resin for the preparation of $Al_2(WO_4)_3$, and the results of the X-Ray phase analyses are summarized in Table 1. The quantity of the additional phases (marked by stars on the X-Ray diffraction pattern figures) was roughly evaluated as a correlation between the samples, treated at 620 ºC for 12 hours and at 830 ºC for 36 hours, are shown on Fig. 4.

The particle size at the lower temperature is distributed in the narrow region from 50 to 80 nm without clear defined habit, while that at the higher temperature is distributed in a wide region from 50 to 200 nm with clear defined habit according to the orthorhombic structure. TEM analysis shows that heating time decrease while temperature increase does not lead to a smaller particle size. Thus, the final and optimal result from the described experiments is pure $Al_2(WO_4)_3$ phase with particle size within 50 to 200 nm when the resin is treated at 830 ºC for 36 h.

The TEM bright field micrographics of the oxygen treated specimen show well separated particles with dimensions within 70 and 100 nm. The particle size is a little bigger than that of the air treated specimen (Fig. 5).

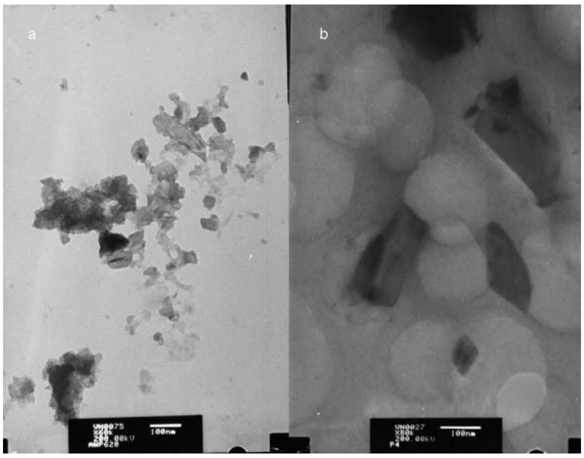

Fig. 4. TEM bright field micrographics of the samples, treated: a) at 620 ºC for 12 hours, and b) at 830 ºC for 36 hours

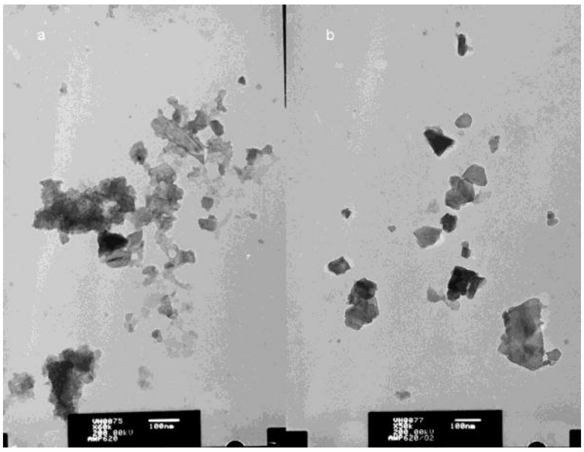

Fig. 5. TEM bright field micrographics of the samples, treated: a) in air at 620 °C for 12 h, and b) in oxygen flow at 620 °C for 5 h

Table 1. Thermal treatment conditions of the dried resign for the preparation of $Al_2(WO_4)_3$ and X-ray phase analyses results.

Sample	Heating temperature [ºC]	Heating time [hours]	Atmosphere	X-Ray results
1	620	12	Air	$Al_2(WO_4)_3$ + about 21% additional phases
2	800	12	Air	$Al_2(WO_4)_3$ + about 2% additional phases
3	830	12	Air	$Al_2(WO_4)_3$ + about 2% additional phases
4	860	12	Air	$Al_2(WO_4)_3$ Pure phase
5	760	72	Air	$Al_2(WO_4)_3$ + about 14% additional phases
6	830	36	Air	$Al_2(WO_4)_3$ Pure phase
7	900	2	Air	$Al_2(WO_4)_3$ + about 2% additional phases
8	900	6	Air	$Al_2(WO_4)_3$ Pure phase
9	620	5	Oxygen	$Al_2(WO_4)_3$ Pure phase

CONCLUSIONS

This study shows that the $Al_2(WO_4)_3$ pure phase with nanosized particles could be obtained by modified Pechini method.

The particle size and the morphology strongly depend on the time and treatment temperature. The size varies between 50 nm at 620 ºC for 12 h and 200 nm at 830 ºC for 36 h.

The treatment of the polymeric resin in oxygen flow leads to pure $Al_2(WO_4)_3$ phase at a significant lower temperature and a significant shorter treatment time but the particle size remains approximately the same.

Obtaining $Al_2(WO_4)_3$ pure phase via modified Pechini method with a particle size less than 50 nm seems to be problematic because of the formation of additional phases. The decomposition of these phases needs high temperature and long treatment time.

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Получаване на алуминиев волфрамат $Al_2(WO_4)_3$ по модифицирания зол-гел метод на Печини

Й.И. Косева*, В.С. Николов

Институт по обща и неорганична химия, Българска академия на науките, 1113 София, България

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(Резюме)

Получена е чиста фаза от алуминиев волфрамат $Al_2(WO_4)_3$ с наноразмерни частици по модифицирания метод на Печини. Като комплексообразуващи агенти са използвани лимонена киселина и етиленгликол. Полученият сух гел е нагряван при различни температури и различна продължителност. Установено е, че чистата фаза от $Al_2(WO_4)_3$ се получава след нагряване при 830 ºC в продължение на 36 часа. Повишаването на температурата над 830 ºC води до получаването на чист $Al_2(WO_4)_3$ за по-кратко време. Микрофотографии от TEM на различни образци показват, че размерът на частиците варира между 50 и 200 nm и силно зависи от температурата и продължителността на нагряването. При нагряването на гела в поток от кислород се получава чиста фаза от $Al_2(WO_4)_3$ при значително по-ниски температури и по-кратко време на третиране.