INTRODUCTION

Indium tungstate $\text{In}_2(\text{WO}_4)_3$ belongs to the class of compounds of the general formula $\text{Me}_2(\text{WO}_4)_3$ ($\text{Me} = \text{Al}, \text{Y}, \text{Sc}, \text{In}$). Normally, these compounds crystallize in an orthorhombic structure, space group $\text{Pnca}$ [1]. As a result of a phase transition at lower temperatures, the structure transforms to monoclinic, space group $\text{P2}_1/\text{a}$. The phase transition of $\text{In}_2(\text{WO}_4)_3$ occurs at $250^\circ\text{C}$, while that of $\text{Al}_2(\text{WO}_4)_3$ takes place at $-6^\circ\text{C}$ [3].

The specific features of the orthorhombic structure determine a number of interesting properties and potential applications of the compounds. It includes $\text{MeO}_6$ octahedra, connected through $\text{WO}_4$ tetrahedra to form a pseudo layered structure with a large tunnel size. The $\text{Me}^{3+}$ ions are sufficiently mobile providing an ionic conductivity. Therefore, they can be used as solid electrolytes, sensors, etc. [4].

Some of the $\text{Me}_2(\text{WO}_4)_3$ compounds possess unusually low thermal expansion coefficients (having zero and even negative values) within a broad temperature range [5 - 8]. It is possible to tailor the thermal expansion coefficient to a desired value by varying the chemical composition of solid solutions of the structures mentioned. For example, a zero thermal expansion coefficient is reported for the $\text{Al}_{1.68}\text{Sc}_{0.02}\text{In}_{0.3}(\text{WO}_4)_3$ composition [9]. It is proved that the thermal expansion coefficient of $\text{Al}_{2-x}\text{In}_x(\text{WO}_4)_3$ solid solutions is slightly positive and increases with In content increase for $x$ value from 0.2 to 0.5. However, $\text{In}_2(\text{WO}_4)_3$ coefficient is negative at temperatures exceeding $250^\circ\text{C}$ (orthorhombic structure) and positive for temperatures lower than $250^\circ\text{C}$ (monoclinic structure) [9, 10].

As a third potential application, $\text{Me}_2(\text{WO}_4)_3$ compounds doped by $\text{Cr}^{3+}$ are very perspective laser media for tunable lasers. The $\text{Me}^{3+}$ situated in an octahedral coordination may be easily substituted by a $\text{Cr}^{3+}$ active ion. This active ion, being incorporated in a structure with a crystal field of weak or medium strength, as it is in the case the $\text{Me}_2(\text{WO}_4)_3$ tungstates [11 - 13], is characterized by a broad absorption cross section, as well as by a broad emission (in the $10^{-19}\text{cm}^2$ range).
Being isostructural, these tungstates can form solid solutions. This is a very important advantage because it enables varying widely the coefficient of expansion, the ionic conductivity and the laser properties by varying the chemical composition of the solid solution.

However, the production of single crystals on the ground of these tungstates is related to a number of problems, such as significant evaporation of WO$_3$ in the case of Czochralski growth [14 - 17] or low growth and anisotropic velocity when the flux method is applied [18 - 20].

An effective approach to overcome the crystal growth problems is to replace the single crystals through the production of high dense, transparent ceramics. If the density of the ceramics is close to the crystallographic one, transparent ceramics can be obtained. Moreover, the latter are low-cost products which possess high chemical homogeneity and isotropy [21]. Because of this, the focus of our research in recent years was the preparation of high-density ceramics from these tungstates. To our knowledge, preparation of high-density tungstate ceramics has not yet been published.

The technology of optical ceramics production includes three main stages: 1) fabrication of nanopowders; 2) preparation of high-density pellets and 3) sintering the pellets in order to obtain non-porous ceramics [22].

EXPERIMENTAL

Nanosized powders of Al$_2$(WO$_4$)$_3$, In$_2$(WO$_4$)$_3$ and solid solution of Al$_{2-x}$In$_x$(WO$_4$)$_3$ (x = 1) were obtained using the co-precipitation method. Each of the samples was synthesized using two preliminarily prepared separate aqueous solutions: first solution was that of Na$_2$WO$_4$ dissolved in 50 ml of distilled water using Na$_2$WO$_4·2$H$_2$O (p.a.) as a reagent, while the second one was that of Al(NO$_3$)$_3$ and In(NO$_3$)$_3$ dissolved in 50 ml of distilled water using Al(NO$_3$)$_3·9$H$_2$O (p.a.) and In(NO$_3$)$_3·7$H$_2$O (p.a.) as reagents. The quantity of the tungstate in the first solution and the total amount of the nitrates in the second one corresponded to the stoichiometric composition for the progress of the co-precipitation reaction:

\[(2-x)\text{Al(NO}_3\text{)}_3 + x\text{In(NO}_3\text{)}_3 + 3\text{Na}_2\text{WO}_4 \rightarrow \text{Al}_{2-x}\text{In}_x(\text{WO}_4)_3 + 6\text{NaNO}_3\]

After stirring at room temperature for 1 h, the precipitate was collected, washed with distilled water and dried at 80°C for 5 h [23].

The amorphous precipitates of the samples were thermally treated at different temperatures (550°C and 700°C) and duration (1, 3 and 8 h) in order to obtain nanosized particles with average particles size of 20 nm and 90 nm [23]. The previous research on these tungstates densification showed that the optimal size should not exceed 100 nm [24, 25].

The cold pressing process, followed by thermal sintering at 800°C was applied to obtain high-density ceramics from these tungstates. A laboratory press providing pressure of 600 MPa was used. Pellets with a diameter of 10 mm and thickness of 1.5 - 2 mm were prepared. The densities of the non-deformed pellets were calculated by dividing the measured mass by the pellets volume. The diameter and the thickness of the samples were measured by a micrometer screw gauge (of 2 μm accuracy). The accuracy of the measurement in this case was ± 0.015 g cm$^{-3}$. The density measurements of the deformed pellets were carried out using Archimedes’ principle. In order to obtain comparable results by both methods, the pellets were covered in advance by a thin layer of film-forming polymer (nitrocellulose dissolved in an organic solvent (ethyl acetate)) in case of application of the Archimedes’ principle. Distilled water at 20°C (of density of 0.99823 g cm$^{-3}$) was used as a liquid. The density of the samples was calculated using the following formula:

\[
\rho(p) = \frac{M(p.a)}{M(p.a) - M(p.w)} \cdot \rho(w),
\]

where \(\rho(p)\) was the pellet density (g cm$^{-3}$), \(M(p.a)\) was the pellet weight measured at air (g), \(M(p.w)\) was the pellet weight measured after being dipped in water (g), while \(\rho(w)\) was the water density (g cm$^{-3}$). The accuracy of the pellets mass measurements was ± 0.001 g. Hence, the accuracy of the density calculations was ± 0.02 g cm$^{-3}$. The obtained pellets density was presented in a relation to that of the crystallographic one, i.e. 5.069 g cm$^{-3}$ for Al$_2$(WO$_4$)$_3$, 5.165 g cm$^{-3}$ for AlIn(WO$_4$)$_3$ and 5.173 g cm$^{-3}$ for In$_2$(WO$_4$)$_3$.

The phase characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu Kα radiation and SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2θ range from 10° to 80° with a step 0.04° and 1 s step − 1 counting time. X-ray diffractograms were identified using the
Diffractplus EVA program. The average crystallites size was calculated from the integral breadth of all peaks (Pawley fit) using the Scherrer equation and the TOPAS 3 program.

The samples obtained after sintering at 800°C without any additional treatment of the surface were subjected to SEM analysis. The SEM micrographs with magnification of 200 - 5000 were obtained on a Philips SEM 515 device at an accelerating voltage of 20 kV. The powders were covered by a gold layer of 10 nm - 15 nm thickness. The average particles size and the anisometricity were determined using the Lince v2.4-Linear Intercept Program.

RESULTS AND DISCUSSION

The preliminary tests showed that the temperature of the initial shrinkage depended mainly on the tungstate composition. These results were obtained by monitoring the pellets shrinkage with the application of micrometer measurements at gradually heating with a speed of 100°C h⁻¹. For Al₂(WO₄)₃, In₂(WO₄)₃, and AlIn(WO₄)₃, the initial shrinking temperature observed was at 780°C, 615°C, and 715°C, respectively. That is why, the density of the pellets and the particles size were measured after thermal treatment for 1, 5 and 10 hours at 800°C. In this study we compare the sintering ability of In₂(WO₄)₃ and AlIn(WO₄)₃ to that of Al₂(WO₄)₃.

Fig. 1 illustrates representative XRD patterns of the products after co-precipitation and subsequent thermal treatment at 800°C for 1 h. They show the presence of diffraction peaks characteristic for crystalline Al₂(WO₄)₃ (JCPDS Card No 24-1101) and In₂(WO₄)₃ (ICDD No. 74-4412). As the values of the sample d parameter corresponding to AlIn(WO₄)₃ composition were between those of Al₂(WO₄)₃ and In₂(WO₄)₃, we concluded that AlIn(WO₄)₃ solid solution was obtained.

Based on our previous research on ceramic’s fabrication from tungstate solid solutions, it was established that the level of densification depended strongly on the particle’s size of the initial powders. We found that the samples of the highest density were those where the initial size was 20 nm and 90 nm. The level of densification was significantly lower for samples of particles size of 200 nm and for those obtained by the classic solid state synthesis, where the particles size was higher than 1 μm (only 68 % of the crystallographic density). The lower sintering ability and the tendency of habit growth of samples of larger particles size are the reasons for the low density of these samples [24, 25].

In₂(WO₄)₃, Al₂(WO₄)₃ and a solid solution of the general formula Al₂ₓInₓ(WO₄)₃, x = 1 were sintered at 800°C, and the level of densification was monitored at different sintering time (1, 5 and 10 h). Fig. 2 shows the pellets densification, the particles size and the level of anisometricity of In₂(WO₄)₃ (a), AlIn(WO₄)₃ (b) and Al₂(WO₄)₃ (c). The average particles size of the used raw pellets was 20 nm and 90 nm. The pellets density was presented as a relative value taking into consideration the crystallographic one. It can be seen that In₂(WO₄)₃, AlIn(WO₄)₃ and Al₂(WO₄)₃ were densified progressively with the sintering time increase. Samples of In₂(WO₄)₃, AlIn(WO₄)₃ and Al₂(WO₄)₃ of initial particles size of 20 nm achieved 83%, 77% and 75% of the crystallographic density, correspondingly. Samples of initial particles size of 90 nm achieved 85%, 78% and 81%, respectively. Density exceeding 85% was not obtained by cold pressure sintering. Our studies will be focused at further studying the sintering ability of In₂(WO₄)₃ and AlIn(WO₄)₃ at prolonged thermal treatment at 800°C, as well as at higher temperatures – at 900°C and at 1000°C in order to determine the conditions providing maximum density.

SEM micrographs of some samples are illustrated in Figs. 3 - 6. Fig. 3 shows that samples of Al₂(WO₄)₃ with initial particles size of 20 nm (Al20) (a) and 90 nm (Al90) (b) have a very high sintering ability. It is demonstrated by the very high speed of particles size growth
during the thermal treatment. For example, the particles
size grows from 20 nm to 3.0 μm upon treatment for 10
h at 800°C, while those of initial size of 90 nm grow to
3.8 μm under identical conditions. The relatively high
densification level can be most probably attributed to the
sintering ability, expressed by the high growth speed of
the particles. The latter isometricity is another feature
which can affect the level of densification. This is veri-

Fig. 2. Variation of the relative density of In_{2}(WO_{4})_{3} (a), AlIn(WO_{4})_{3} (b) and Al_{2}(WO_{4})_{3} (c) pellets, sintered at 800°C,
depending on sintering time (0, 1, 5 and 10 h) and average particles size in the raw pellets (●—20 nm, ▼—90 nm).
0.7/1.0 - 0.7 is the average particles size after appropriate sintering [μm]; 0.7 is the average ratio between the largest and
the smallest particle size.

Fig. 3. SEM photographs of the surfaces of the Al_{2}(WO_{4})_{3} after cold pressing, treated at: for 10 hours at 800°C (a) with
initial particle size of 20 nm and (b) with initial particle size of 90 nm.

CONCLUSIONS

The results referring to production of Al_{2−x}In_{x}(WO_{4})_{3}
density ceramics with x varying from 0 to 2 by cold
pressure sintering show that:

- the density of AlIn(WO_{4})_{3} and Al_{2}(WO_{4})_{3} increases with the sintering time increase;
- the average particles size increases with the sintering time increase;
- the highest density is achieved in case the starting material’s particles have a size of 90 nm.

Compared to Al_{2}(WO_{4})_{3} and AlIn(WO_{4})_{3}, In_{2}(WO_{4})_{3}
remains practically isometric and its particles size in-
creases more slowly. Most probably that is the reason
to achieve 85 % density with the application of cold
pressure sintering. The comparison carried out shows
that under identical conditions Al_{2}(WO_{4})_{3} has density
of 81 %, while that of AlIn(WO_{4})_{3} is 78 %.
high density tungstate ceramics can be obtained only if the initial powders contain nanosized particles; 

- $\text{Al}_{2-x}\text{In}_x(WO_4)_3$ powders have a high level of sintering ability because of the high speed of grain growth and the high level of densification; 

- the optimal particles size required to obtain high density ceramics refers to ca 90 nm. Grains sized below 90 nm display higher anisometricity; 

- $\text{In}_2(WO_4)_3$ has the lowest anisometrisity level and highest level of density which amounts to 85 % from the crystallographic one.

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