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Sintering Conditions for $Al_2(WO_4)_3$ High-Dense Ceramic

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$Al_2(WO_4)_3$ nanoparticles with average particles size of 20, 90 and 200 nm are sintered by two methods: cold pressing with additional sintering at different temperatures and time durations and hot pressure sintering. Density, particles size dimensions and anisometricity are tested. The results show that optimal initial nanosized dimensions and an optimal pressing condition are needed to obtain compact ceramic. Hot pressure method gives possibilities of a ceramic with a density in order of 99.8% to be received, which possesses some level of transparency.

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1. Introduction

Aluminium tungstate $Al_2(WO_4)_3$ belongs to the class of compounds of the general formula $Me_2(WO_4)_3$ (Me = Al, Y, Sc, In), with orthorhombic structure, space group *Pnca* [1]. This class of compounds possesses Al^{3+} ion conductivity. Therefore, they can be used as solid electrolytes, sensors, etc. [2]. Some of the $Me_2(WO_4)_3$ compounds possess unusually low thermal expansion coefficients (including zero and even negative values) within a broad temperature range [3]. As a third potential application, $Me_2(WO_4)_3$ compounds doped by Cr^{3+} are very perspective laser media for tunable lasers. 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.

The potential application as ionic conductors and materials with tailored expansion coefficient requires a high density ceramic. The production of single crystals for laser active media from these tungstates is related with a number of problems — significant evaporation of WO_3 in the case of the Czochralski growth and low growth velocity and high anisometric of the crystals in the case of flux method [4, 5]. An effective approach to decide these problems is to produce high dense ceramics. If the density is near to the crystallographic one, the transparent ceramics could be obtained for replacing the single crystals as laser media.

The main aim of our research in recent years was the preparation of high dense (transparent) ceramics of tungstates with the general formula $Al_{1-x}Me_x(WO_4)_3$, where Me is Sc or In, and x varies from 0 to 2. To our knowledge preparation of tungstate high dense and transparent ceramic has not been published yet.

The technology of optical ceramics includes three main stages: (1) fabrication of nanopowders (2) preparing of highly dense compacts, and (3) sintering of the compact to the non-porous ceramics [6].

Preparation of tungstates with the general formula $Al_{1-x}Me_x(WO_4)_3$, Me = Sc or In nanopowders was previously investigated by us. Pure phase nanopowders with the mean size of the particles in the range of 10–200 nm was obtained and deeply characterized by X-ray, transmission and scanning electron microscopy (TEM, SEM), NMR, IR and Raman analysis [7–9].

In this article we present the next step of the investigation — sintering of high dense compact $Al_2(WO_4)_3$ ceramics as a main member of these tungstates by cold pressing and additional sintering as well as by hot pressure sintering.

2. Experimental

The nanosized powders of $Al_2(WO_4)_3$ were obtained using the co-precipitation method [8]. The amorphous precipitates of the samples were thermally treated at different temperatures and time durations due to obtaining nanosized particles with average particle size — 20, 90, and 200 nm. Tungstates obtained by classical solid state synthesis, with an average particles size of 2 μm, were used as a reference.

To obtain high-density ceramics from these tungstates there were used two methods: cold pressing with additional thermal sintering and hot pressure sintering with additional vacuum treatment.

In cold pressing process there was used laboratory press with pressure of 600 MPa. Pellets with a diameter of 10 mm and thickness of 1.5–2 mm were obtained. The preliminary tests showed that the temperature at which the initial shrinkage began is 780 °C. Therefore density of the pellets and particles size were measured after thermal treatment for 1, 5 and 10 h at 800, 900 and 1000 °C for all $Al_2(WO_4)_3$ nanoparticles with average particle size of 20 nm (Al20), 90 nm (Al90), 200 nm (Al200) and $Al_2(WO_4)_3$ powder from solid state synthesis with average particles size of 2 μm (Alss).

Density measurements were carried out using Archimedes' principle. As a liquid there was used distilled water (20 °C, density 0.99823 g/cm^3). The accuracy of the pellets mass measurement by the balance

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was ±0.001 g. In this way the accuracy of the density calculation was ±0.02 g/cm^3.

The densities of non-deformed pellets were calculated by the measured mass divided by pellets volume. The diameter and the thickness of the samples were measured by micrometer (2 μm accuracy). The accuracy of the density calculation measurement in this case was ±0.015 g/cm^3. Samples obtained by sintering were subjected to SEM micrographs with magnification of 200–5000. The SEM micrographs were obtained on a Philips SEM 515 device at an accelerating voltage of 20 kV. The powders were covered with a gold layer of 10–15 nm thickness. The average particle size and its anisometricity were determined using Lince v2.4 — Linear Intercept-program.

In hot pressure sintering there was used laboratory press with possibilities of simultaneous or separate pressure applying up to 100 MPa and temperature applying up to 800 °C. The pressure could be applied in step mode (25, 50, or 100 MPa) and temperature could be programmed with speeds from 20 to 500 °C per h. Ceramic press with diameter of 10 mm was used. Samples with different particle size were hot pressed at different pressure (50–100 MPa), different temperature (400, 600, and 800 °C) and different pressing time (30 min, 1 h and 2 h). Some of the obtained nanosized powders were subjected to step mode applying of pressure and temperature — 25 MPa and 400 °C for 15 min, followed by 50 MPa and 600 °C for 15 min and 100 MPa and 800 °C for 30 min. Density measurements were carried out by the methods used after "cold pressing". Samples with densities exceeding 98% from the crystallographic one were subjected to additional vacuum sintering — 1000 °C for 2 h with a constant vacuum 1 mm Hg.

3. Cold pressing

In Fig. 1 pellets' density was presented as relative density to crystallographic one, which for $Al_2(WO_4)_3$ is 5.079. Figure 1a shows that $Al_2(WO_4)_3$, obtained by co-

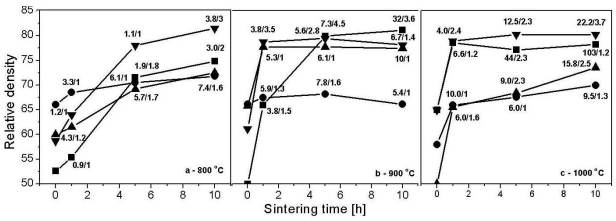

Fig. 1. Variation of the relative density of $Al_2(WO_4)_3$ pellets, depending on the sintering temperature (800, 900, and 1000 °C), sintering time (1, 5, and 10 h) and the average particle size in the raw pellets (-■- 20 nm, -▼- 90 nm, -▲- 200 nm and -●- > 1 μm). Explanation: 3.8/3 means 3.8 μm average particle size and ratio between the largest and the smallest particle size equal to 3.

-precipitation method with particle size of 20 nm (Al20) and 90 nm (Al90), were compacted progressively with time, achieving 74%, respectively 81% of the crystallographic density. The compaction level is significantly lower for Al200 particles size and for one obtained by classic solid state synthesis Alss. The last one has only 68% of the crystallographic density. The time required for maximum sintering at 900 °C for all samples was 1 h, except for Al20 (Fig. 1b). Al20 and Al90 achieved highest density — 79–81% of the crystallographic one. In Fig. 1c there are presented samples after thermal treatment at 1000 °C. Highest density again was achieved for Al20 and Al90 after one hour of thermal treatment — 75–80%.

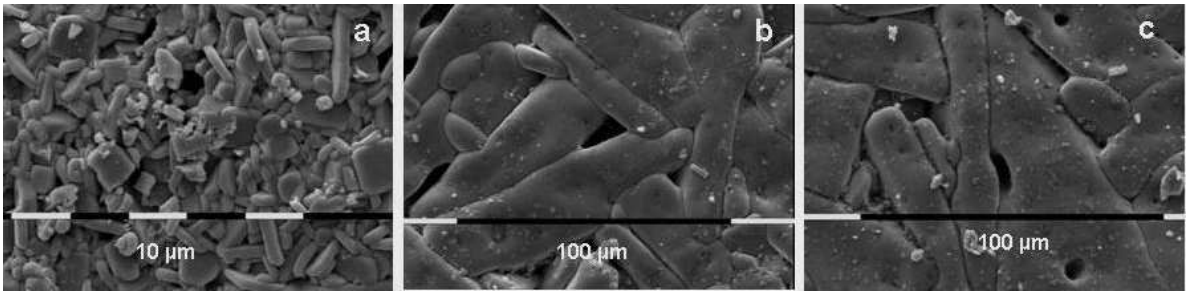

Fig. 2. SEM photographs of the surfaces of the $Al_2(WO_4)_3$ pellets with initial average particle size of 20 nm after cold pressing and thermal treatment during 10 h at 800 °C (a), 900 °C (b), and 100 °C (c).

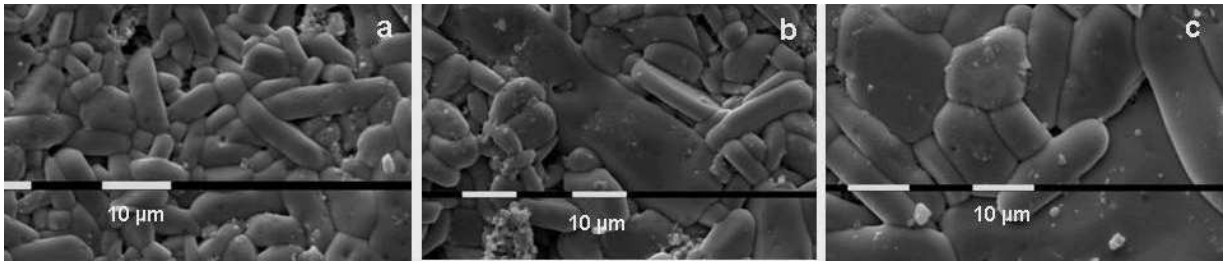

Fig. 3. SEM photographs of the surfaces of the $Al_2(WO_4)_3$ pellets with initial average particle size of 90 nm after cold pressing and thermal treatment during 10 h at 800 °C (a), 900 °C (b), and 100 °C (c).

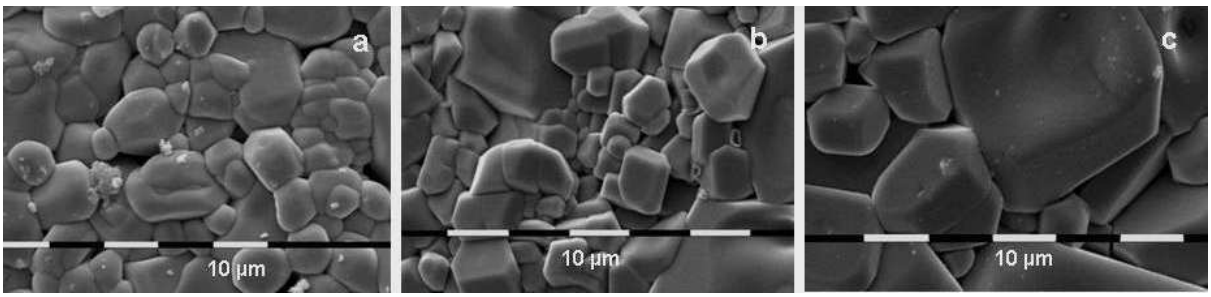

Fig. 4. SEM photographs of the surfaces of the $Al_2(WO_4)_3$ pellets with initial average particle size of 2 μm after cold pressing and thermal treatment during 10 h at 800 °C (a), 900 °C (b) and 100 °C (c).

The SEM micrographs of the samples are shown in Figs. 2, 3 and 4. From these figures it can be observed that samples Al20 and Al90 have very high sintering ability, compared to Al200 and Alss. This ability is demonstrated with a very high speed of particles size grown during the thermal treatment.

For example, particles size of Al20 grow to 3.0, 32, 103 μm, when they were treated for 10 h at 800, 900, and 1000 °C, respectively (Fig. 2). The particles A90 grow to 4.8, 6.7, and 22.2 μm at 800, 900, and 1000 °C (Fig. 3). In other words, the dimensions of the particles arise in range of 100–5000 times. Significantly lower sintering ability possesses samples Al200 and Alss. Figure 4 illustrates particles' growth of Alss. They grow from 2 μm to 5–10 μm.

The SEM micrographs show another feature for Al20 and Al90 samples. There is clear tendency for anisometrical growth — growth of the grain in the preferable crystallographic direction. This tendency is more obvious for Al20 than for Al90 (Figs. 2, 3). The SEM micrographs show tendency of habit growth for Alss (Fig. 4). This feature could be an explanation of the results about pellets compaction. Al20 and Al90 are with high sintering ability, which leads to a rapid particles growth and compaction. Higher tendency of anisometric growth of Al20 compared with Al90 could explain the relatively high compact of Al90 than Al20. Lower sintering ability of Al200 and Alss and tendency of habit growth are reason for low density of these samples.

The important result is that density of the samples is not proportional to the particles sizes. As rule, a maximal density was obtained when the particles size is about 10 μm. Further growth of the particles size does not lead to increase of the density.

4. Hot pressure sintering

Al20, Al90, and Al200 were also subjected on hot pressure sintering. Several combinations of applied temperature and pressure were used, as well as pressure sintering with stepwise increase of the temperature and pressure — 400 °C and 25 Pa during 15 min; 600 °C and 50 Pa during 15 min, and 800 °C and 100 Pa during 15 min.

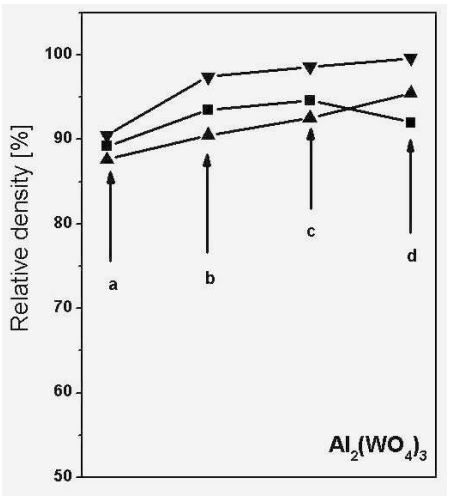

Fig. 5. Variation of the relative density of $Al_2(WO_4)_3$ pellets depending on the average particle size in the initial pellets (-■- 20 nm, -▼- 90 nm, and -▲- 200 nm) after the hot pressing conditions: *a* — 400 °C and 25 MPa, *b* — 600 °C and 50 MPa, *c* — 800 °C and 100 MPa after 1 h pressing, and *d* — stepwise increasing the temperature and pressure 400 °C and 25 MPa — 15 min, 600 °C and 50 MPa — 15 min, 800 °C and 100 MPa — 30 min.

The relative density of the sintered samples of $Al_2(WO_4)_3$, depending on the conditions of hot pressure treatment, are shown in Fig. 5. It can be seen that the hot pressure treatment results in considerably higher density comparing with those of a cold pressure treatment. Even in the hot pressure sintering at 400 °C and pressure 50 MPa, the density reaches almost 90%, while the maximum density achieved in cold pressure treatment and subsequent sintering is in order of 80%. The density at hot pressure sintering increases with increasing the temperature and pressure and at 800 °C and 100 MPa reaches 98.6%. It is interesting to note that the stepwise raising of the temperature and pressure results in a further increase in the density and the maximum total density is 99.6%. The highest density is registered after treatment of nanosized powders with average particle size of 90 nm.

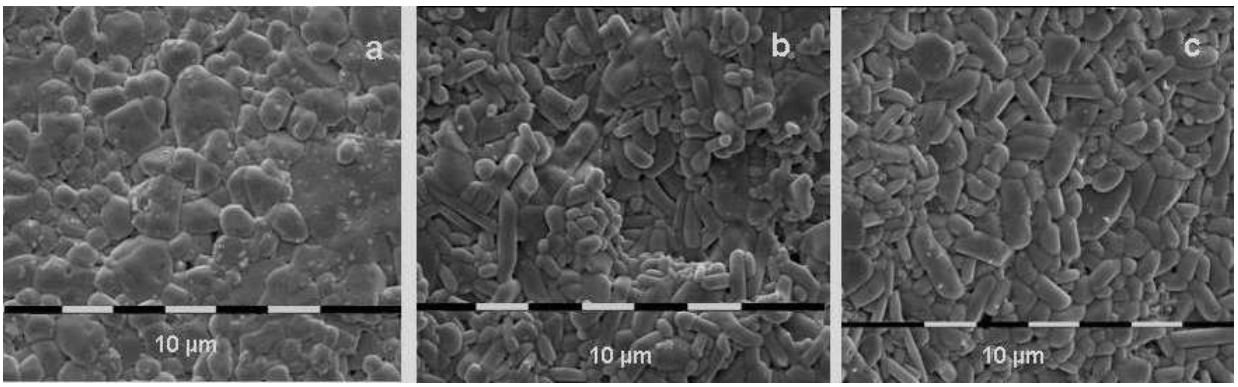

Fig. 6. SEM photographs of tungstate ceramics with 90 nm initial average particle size after hot pressing at 600 °C and 50 MPa (a); at 800 °C and 100 MPa (b) and after stepwise increasing the temperature and pressure 400 °C and 25 MPa — 15 min, 600 °C and 50 MPa — 15 min, 800 °C and 100 MPa — 30 min (c).

Figure 6 presents some typical photographs of the surface of the samples after hot pressure sintering. Compared with the already shown SEM photographs after cold pressing and further heat treatment, it can be seen that after hot pressure treatment the grains are considerably more uniform in size, more isometric, and more compact packed. It is particularly important to note that the 1 μm thick pellets with a density of over 98% are translucent. It was found that the transparency is further improved after additional vacuum sintering of the specimens at 1000 °C during 2 h. This result encourages further studies on the optimization of the hot pressure sintering of the tungstates.

5. Conclusion

From the results of obtaining high density ceramic from $Al_2(WO_4)_3$ powders, some general conclusions could be made. 1. Obligatory condition for obtaining high density tungstates ceramics is the initial samples to have nano-sized particles, having higher sintering abilities, causing faster grain growth and obtaining high level of compaction. 2. The optimal particles size for obtaining high density ceramics is about 90 nm. Below 90 nm grains have anisometricity growth, and above that value the particles have low sintering ability. Both are obstacles for obtaining high density ceramics. 3. Densities of 99.8% can be obtained by hot pressure sintering, which significantly exceeds the values obtained by cold pressure sintering (80%). 4. High density pellets (98%) have some level of transparency. It could be considered that the translucency can be increased by additional optimizing of hot pressure sintering. Investigations on the sintering conditions for $Sc_2(WO_4)_3$, $In_2(WO_4)_3$ as solid solutions tungstates are in progress.

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