Rheological properties of $Y_3Al_5O_{12}$ powder obtained by preceramic organoyttrioxanealumoxanes

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Abstract. Submicron powder $Y_3Al_5O_{12}$ (YAG) aluminium yttrium garnet was synthesized from an Al-Y-ceramic-forming precursor, according to the method developed in the State Research Institute for Chemistry and Technology of Organoelement Compounds (SRICTO). The advantage of the method is the possibility of obtaining close to the stoichiometric phase and obtaining high purity nanopowder. In this work, we studied the effect of the pyrolysis temperature of the polymer (700°, 800° and 900°C) and grinding time on the rheological properties of the powder. It was shown that after pyrolysis at 700° and 800°C, the powder has an amorphous structure, the ultimate strain, in this case, being 6.1 and 8.1% of the initial size. The compressibility modulus decreases with increasing temperature from 34.5 to 19.4 MPa. Due to the formation of YAG crystals after pyrolysis at 900°C, the compressibility of the powder increases and the compacts become denser.

1. Introduction
The need for modern technology, as well as the development and improvement of the production of ceramics from pure oxides, requires researchers to develop new methods for producing highly pure raw materials. One of the possible applications of such materials is the production of optically transparent ceramic materials, which in many physicomechanical properties can surpass opaque ceramics, and in some parameters single crystal materials. A special place among such materials is occupied by optically transparent ceramics from $Y_3Al_5O_{12}$ (YAG) yttrium aluminium garnet. YAG belongs to a group of minerals which have a complex cubic crystallographic structure. The YAG structure is particularly resistant to creep and is much less sensitive to orientation [1]. Ceramics based on it has a wide range of applications in various fields: nanophotonics, optoelectronics, aerospace engineering and other fields [2]. Yttrium aluminium garnet has high mechanical strength, excellent optical and thermal characteristics. Materials based on yttrium aluminium garnet are used for the manufacture of active elements of solid-state lasers in the near and middle IR ranges [3]. Due to the complex of unique properties of yttrium aluminium garnet and spinel, ceramics based on them are of great interest to industry.
In recent years, a new method for the synthesis of YAG from a ceramic-forming oligomer has been developed at the Research Institute for Chemistry and Technology of Organoelement Compounds (SRICTO). For the first time, hydrolytically stable in air soluble inorganic solvents keramo-forming organo-yttrioxanaluminoxoxanes, which are the organo-yttrioxanaluminoxoxanes, were the first oligomer to produce \( \text{Y}_3\text{Al}_5\text{O}_{12} \) (YAG) [4]. The advantage of this method is the possibility of obtaining close to the stoichiometric phase, and obtaining high purity nano-powder (99.99 wt.%) [5], which is an essential criterion for optically transparent ceramics.

The work aim is to study the rheological properties of spinel and YAG powders. Namely, the study of the microstructure of the powders, the study of the influence of the pyrolysis temperature of the ceramic-forming oligomer and the grinding time on the rheological parameters of these powders during pressing.

2. Experimental part

2.1. Materials

The general scheme for the synthesis of ceramic-forming organoyttrioxanealumoxanesiloxanes can be represented by the following equation [6]:

\[
[(\text{R}^{**}\text{O})_{s}\text{Y}((\text{OH})_{t}\text{O}r)\cdot [\text{Al(OR)l(OR*)x(OH)zOy}]m\cdot [(\text{EtO)2SiO}]p,
\]

where \( k, m, p = 3–12; s + t + 2r = 3; 1 + x + 2y + z = 3; \text{R} = \text{CnH}_{2n} + 1 \text{ with } n = 2–4; \text{R}^{*} = \text{C(CH3)=CHC(O)}\text{CH3} \); and \( \text{R}^{**} = \text{C(CH3)}=\text{CHC(O)CH3} \).

The synthesized ceramic-forming oligomer was then subjected to pyrolysis for 2 hours in a muffle furnace at 700°, 800° and 900°C in air. Next, the resulting powder was crushed. The grinding of the initial powder was carried out in a planetary mill for two hours at 250 rpm in a solution of isopropyl alcohol. The powder was ground before and after pyrolysis to compare rheological properties. After grinding, the powder was dried in an oven at 130 °C until the alcohol was completely removed. The resulting spinel powder was characterized by particle size analysis, x-ray phase analysis, and using scanning electron microscopy.

Granulometric analysis of powders after pyrolysis was carried out on a Fritsch Particle Sizer ‘analysette 22’ laser diffraction analyzer. The dispersion was carried out in a liquid (laser wavelength 655 nm, incident beam diffraction 0.01–1000 μm, sample amount 0.1–2 cm³, measured particle size of the powder 0.16–1160 μm); the Fraunhofer optical method was used for calculation. Grain composition was presented on a differential particle distribution curve.

The microstructure of spinel powders was studied on a Supra 50 VP high-resolution scanning electron microscope (LEO, Germany, 2003) with an INCA Energy + Oxford microanalysis system with an attachment for local X-ray spectral analysis. In both cases, the electron beam source is a cathode with field emission, the voltage at the accelerating electrode - up to 20 kV. Used magnifications - from x 45 to x 20,000.

2.2. Rheology

Rheological properties were tested on the mechanical testing machine (Instron 5581, Great Britain). The stain velocity was 1 mm/min. A sample of the test sample weighing 0.15 g was placed in a steel mould. At least 5 measurements were carried out for each sample, then the values were averaged (the average value of the standard deviation of deformation in the entire interval of the experiment was \( \sigma_{700} = 0.03\% \) and \( \sigma_{800} = 0.05\% \) \( \sigma_{900} = 0.16\% \) for YAG powder after pyrolysis at 700°, 800° and 900°C, respectively), and calculations were carried out using the formulas below.

The deformation was calculated by the equation (1):

\[
\varepsilon = \frac{\Delta h}{h_0}
\]
where $\Delta h$ is the change in the height of the bulk layer over time; $h_0$ is the initial height of the bulk layer. The compressibility modulus is numerically equal to the tangent of the linear section slope angle of the diagram strain against deformation, and is calculated by the equation (2):

$$G = \frac{\Delta p'}{\varepsilon^*}$$

where $\Delta p'$ is the limiting change in the linear section pressure value; $\varepsilon^*$ is the final value of the linear section deformation. The compressibility coefficient ($k_c$) characterises the reversible decrease in the sample height (volume) under the pressure action and is quantitatively determined by equation (3):

$$k_c = -\frac{1}{h_0} \frac{\Delta h'}{\Delta p'}$$

where $\Delta h'$ and $\Delta p'$ are the limiting values of the height and the linear section pressure variation, $h_0$ is the initial height of the backfill.

The physical meaning of the compressibility coefficient is characterisation the material ability to compact at the initial (linear) stage, during which the compaction intensity is maximal [7,8].

3. Discussion of results

Kinetic curves were obtained, representing the pressure versus time for YAG powder. These values were rearranged in the stress-strain curve. To study the effect of powder grinding on rheological properties, the obtained data were used to plot the strain dependences of the strain after grinding (figure 1). On the stress-strain diagram after grinding, the dependence of the rheological properties on the pyrolysis temperature can be traced. With an increase in the pyrolysis temperature, the limiting value of the strain increases from 6.1 to 9.9%; a linear section indicates this at the initial stage, where the stress obeys Hooke's law. Further, a deviation from linearity begins, and particle accommodation occurs on this site. Figure 1B shows that it is in this section that the curves for the powder spread after 700° and 800°C of pyrolysis. This difference is due to the partial crystallisation of YAG at 800°C.

![Figure 1](image1.png)

**Figure 1.** The stress-strain curve of $Y_3Al_5O_{12}$ after pyrolysis at 700°, 800° and 900°C A — the linear section of deformation, B — the full curve of stress.

Interestingly, with a further increase in the load, the strain – load curves for the powder at 700°C and 800°C converge at one point. We attribute this to the similarity of the initial powder, since, unlike spinel [7], complete crystallisation occurs after 1000°C. For this reason, the curve for the powder after 900°C at equal pressure has a large deformation. It means that the particles have a more complex shape, and when filling the mould, many voids are filled during the accommodation of the powder in the second section of the deformation – load curve.

The XRD analysis for spinel powder after pyrolysis at 700°C showed the presence of an amorphous phase (Figure 2A). A fully crystallised phase is observed only after pyrolysis at 1000°C (Figure 2B). After 1000°C, two phases were detected in the powder: YAG - 98 wt.%, YAM - 2 wt%. Because the
non-crystallized phase remained in the powder after 700°C, the curve of the elastic deformation section for these powders is almost two times less than the powder for 900°C.

![XRD of Y₃Al₅O₁₂ powder after pyrolysis at 700° and 1000°C (YAG - 98 wt.%, YAM – 2 wt.%).](image)

**Figure 2.** XRD of Y₃Al₅O₁₂ powder after pyrolysis at 700° and 1000°C (YAG - 98 wt.%, YAM – 2 wt.%).

The SEM analysis results confirm after heat treatment of the polymer in the air environment, there remain polymer flakes 100-120 nm thick and crystallites from 0.1 μm to 2 μm (Figure 3). Here are the SEM of the powder at two magnifications: overall plan and enlarged with particle size. In fig. 3B, D, F, it can be seen that the agglomerates are composed of nanoparticles.
Figure 3. SEM analysis of Y₃Al₅O₁₂ powder after pyrolysis of A and B - 700°C, C and D - 800°C, E and F - 900°C.
The compressibility moduli for the powder after pyrolysis at 700 °C, 800 °C, and 900 °C were calculated from the slope of the linear section when the powder obeys Hooke's law. According to Eq. 3, the value of the compressibility coefficient was calculated (Table 1). With an increase in the pyrolysis temperature, the value of the compressibility modulus decreases from 31.5 to 19.4 MPa and an increase in the ultimate strain value, due to the transition from an amorphous to crystalline material, the elasticity of the particles increases. Due to the formation of nanoparticles close to spherical, better compaction of the powder occurs.

Table 1. The rheological parameters of Y₃Al₅O₁₂ powder

| Pyrolysis temperature | G, MPa | Kₐ, E* | ε*, % |
|-----------------------|--------|--------|-------|
| 700°C                 | 31.5   | 1.8    | 6.1   |
| 800°C                 | 25.3   | 2.3    | 8.1   |
| 900°C                 | 19.4   | 3.0    | 9.9   |

The data presented indicate the effect of grinding on the growth of the elastic modulus. This may be due to the destruction of particle agglomerates that form after pyrolysis. This once again proves that the particles created during the recrystallization process are brittle.

4. Conclusion

Yttrium aluminium garnet (YAG) powder was obtained after pyrolysis at 700°, 800°, and 900°C of the organotetroxanealumoxanesiloxanes ceramic-forming oligomer. X-ray diffraction analysis showed that YAG has an amorphous structure up to a pyrolysis temperature of 900°C. In the powder after 700°C, the shape of thin flakes with a thickness of up to 100 nm remaining after burning of the polymer is preserved. An increase in the pyrolysis temperature to 900°C leads to the formation of nanosized YAG crystals agglomerated into particles of 1-2 μm. It was shown that an increase in the pyrolysis temperature from 700° to 900°C leads to a decrease in the compressibility modulus from 31.5 to 19.4 MPa and an increase in the ultimate strain value, due to the transition from an amorphous to crystalline material, the elasticity of the particles increases. At the maximum pyrolysis temperature in the powder, polymer residues are no longer observed, and the powder has a narrow particle size distribution, due to this, the powder deformation at 200 MPa is 45% at a pyrolysis temperature of 900°C.

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References

[1] Bansal N P (Ed.) 2006. Handbook of ceramic composites 200 Springer Science & Business Media
[2] Senina M O, Lemeshev D O 2017 Successes in chemistry and chemical technology 31 182
[3] Aksenov D I, Zharikov E V, Faykov P P 2015 Advances in Chemistry and Chemical Technology 29 166 (in Russian)
[4] Shcherbakova G. I. et al. 2014 Inorganic Materials 50 636
[5] Storozhenko P A, Shcherbakova G I 2011 Inorganic Materials 47 167
[6] Shcherbakova G I, Storozhenko P A, Kutinova N B, et al. 2011 RF Patent 2 453 550
[7] E A Gumennikova et al 2019 J. Phys.: Conf. Ser. 1347 012062
[8] D D Titov et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 525 012077