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## INFLUENCE OF HOMOGENIZATION AND MICRO/NANO SOURCE OF STARTING POWDERS ON FORMATION OF THE SINGLE YAP PHASE

Manufacturing high purity polycrystalline  $\text{YAlO}_3$  (YAP) ceramics could replace monocrystalline YAP thus recently it is an interesting task for low cost producers of scintillators. The paper presents influence of different source of initial oxide powders (micro/nano powders of  $\text{Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) and the method of their homogenization on the formation of a YAP phase. The solid state reaction method was used to prepare YAP powder or ceramic pellets. After preheating, all samples in the form of powders and pellets were heat-treated in the temperature range of 1050-1650 °C. DTA method was applied for examination of the phase crystallization in the tested system. X-ray diffraction method (XRD) was used for characterization of the phase composition. X-ray microanalysis (EDS) was used to control homogeneity in the small areas. Morphology of the resultant samples are presented on SEM pictures. The results show a significant influence of the starting powders on the homogeneity, purity and temperature of formation of the main phase.

*Keywords:* YAP, scintillators, synthesis, polycrystalline ceramics

### 1. Introduction

Yttrium aluminum perovskite  $\text{YAlO}_3$  (YAP) is one of the three phases in the equilibrium binary  $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  system. Other phases in this system are: yttrium aluminum monoclinic (YAM) and a well-known yttrium aluminum garnet (YAG). Yttrium aluminium perovskite in the form of a monocrystal, doped with rare-earth or transition metal ions demonstrates the excellent optical properties and it is presently used in a range of application relevant to the applied doping. It has been successfully used as a host material for solid-state lasers [1] and scintillators [2-4]. The premium application of YAP:Ce into scintillator devices (e.g. PET camera) comprises X-ray computed tomography (CT) in the medical application. Commercially available YAP scintillators are manufactured by melting at high temperature (over 1950 °C) and grown by the Czochralski or modified Bridgman methods [5]. In order to obtain the high optical quality of crystals they must be produced in vacuum [6]. Thus, because of high costs of YAP-monocrystals manufacturing and the expected different behaviour of polycrystalline ceramics under the relevant excitation, manufacturing of RE-doped YAP powders or polycrystalline ceramics is a challenging task in nowadays research community. The results on preparation of YAP powders/nanopowders are scarce and they show complexity of that phase formation [7-14]. The topic of this work is to check the possibility of manufacturing the monophase YAP powder or polycrystalline ceramics by the solid-state reaction method using different particle size of starting powders and methods of homogenization.

### 2. Experimental

The samples with the general formula of  $\text{YAlO}_3$  were prepared by a solid-state reaction method using high purity commercial micro-powders of:  $\Theta$ - $\text{Al}_2\text{O}_3$  (Sasol, 99.96%, 2  $\mu\text{m}$ ),  $\text{Y}_2\text{O}_3$  (Aldrich, 99.99%, < 10  $\mu\text{m}$ ) and nano-powders:  $\Theta$ - $\text{Al}_2\text{O}_3$  (AlfaAesar, 99.5%, 40 - 50 nm),  $\text{Y}_2\text{O}_3$  (AlfaAesar, 99.995%, 50 - 70 nm). A stoichiometric amount of raw powders was mixed using different homogenization methods: hand-mixing in 100 ml agate mortar with acetone, roller mixing for 24 h in 125 ml PP bottles with ethanol, planetary milling (Fritsch PS7) in 80 ml corundum jar with corundum balls with ethanol for 1 h in 600 rpm. Deagglomeration step in rolled and milled suspensions was carried out in Branson Sonifier at an amplitude of 70% (400 W) for 1 h. Homogenized powders were dried at 60 °C for 24 h. A part of the powders was pressed in 2 stages, into 10 mm diameter pellets: first by uniaxial pressing at 30 MPa, followed by cold isostatic pressing at 250 MPa. Powders and pellets were placed in the corundum crucibles and were heat-treated for 8 h in an air atmosphere in a chamber furnace at temperatures in a range of 1050 to 1650 °C.

An Panalytical Xpert diffractometer was used for taking the powder diffraction patterns. The XRD patterns were collected in the  $2\Theta$  range of 10 - 80° with a step of 0.02° using  $\text{Cu K}_{\alpha 1}$  radiation with  $\lambda = 1.5406 \text{ \AA}$  with a nickel filter. Calculation of the phase weight fraction was done with the help of the Maud software. The grain size and morphologies of the samples were observed by a Hitachi 3400N scanning electron microscope (SEM) operated at 25 kV with energy-dispersive X-ray spectrometer (EDS). All measurements were carried out at room temperature. Differential thermal measurements

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List of the samples

Sample Name	Powder source	Homogenization Method	Synthesis temp.
M-M	Micro-powder Al <sub>2</sub> O <sub>3</sub> Sasol, 99.96%, 2 μm	Mortar	1650 °C
M-R		Roller	1650 °C
M-RD		Roller + Deagglomeration	1650 °C
M-PM		Planetary Mill	1650 °C
M-PMD		Planetary Mill + Deagglomeration	1650 °C
N-M	Nano-powder Al <sub>2</sub> O <sub>3</sub> AlfaAesar, 99.5%, 50 nm	Mortar	1650 °C
N-R		Roller	1650 °C
N-RD		Roller + Deagglomeration	1650 °C
N-PM		Planetary Mill	1050 - 1650 °C
N-PMD		Planetary Mill + Deagglomeration	1650 °C

(DTA) of the raw material were recorded on a Thermoanalyser Netzsch STA 409 with the heating rate of 10 K min<sup>-1</sup> in the atmosphere of flowing air.

### 3. Results and discussion

References of X-ray diffraction powder patterns of all phases in the Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> binary system are presented in Fig. 1. These include oxide substrates (Al<sub>2</sub>O<sub>3</sub> - ICSD #51687; Y<sub>2</sub>O<sub>3</sub> - ICSD #86815) and the three main phases: yttrium aluminium perovskite (YAlO<sub>3</sub> - ICSD #88261), yttrium aluminium monoclinic (Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> - ICSD #80039), yttrium aluminium garnet (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> - ICSD #280104). YAlO<sub>3</sub> crystallizes in the orthorhombic lattice with the space group Pbnm (No. 62). YAP is an expected phase in this work and the other phases are treated as the side phases. They appear if the temperature of synthesis is not suitable or the starting powders are not enough homogeneously mixed.

At the beginning, phase analysis of specimens, prepared with different homogenization methods and different size of the starting powders, was performed to choose suitable parameters for preventing the formation of phases with different than 1:1 ratio of Y-Al.

Fig. 2a shows influence of homogenization methods on the phase composition of YAP powders obtained from the micro-substrates. The purest final powders matching well the reference pattern of YAP were produced if homogenization in a mortar or milling in a planetary mill were applied. However, in both cases, a small amount of YAM phase was present. Calculated amount of YAM was found to be 3.94 wt% ± 0.23% for the specimen mixed in the mortar (M-M), and 2.90 wt% ± 0.42% for the planetary milling derived specimen (M-PM). In the case of the homogenization on the roller, the formation of secondary phases was advanced, with the domination of YAM phase and a small amount of overreacted substrates.

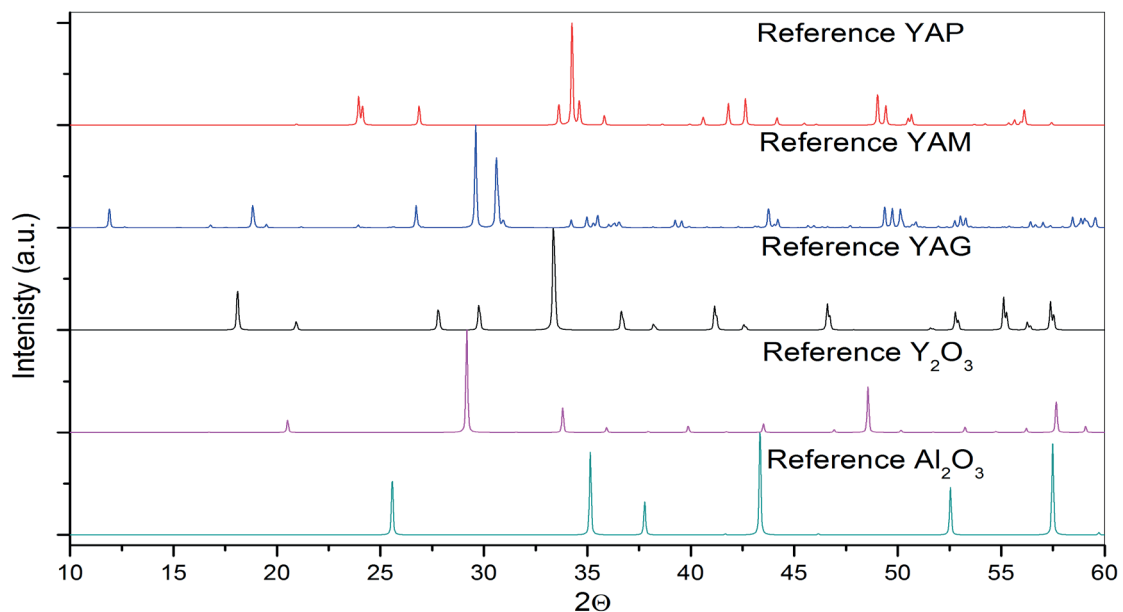


Fig. 1. X-ray reference diffraction patterns of the initial oxides and products in the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> system

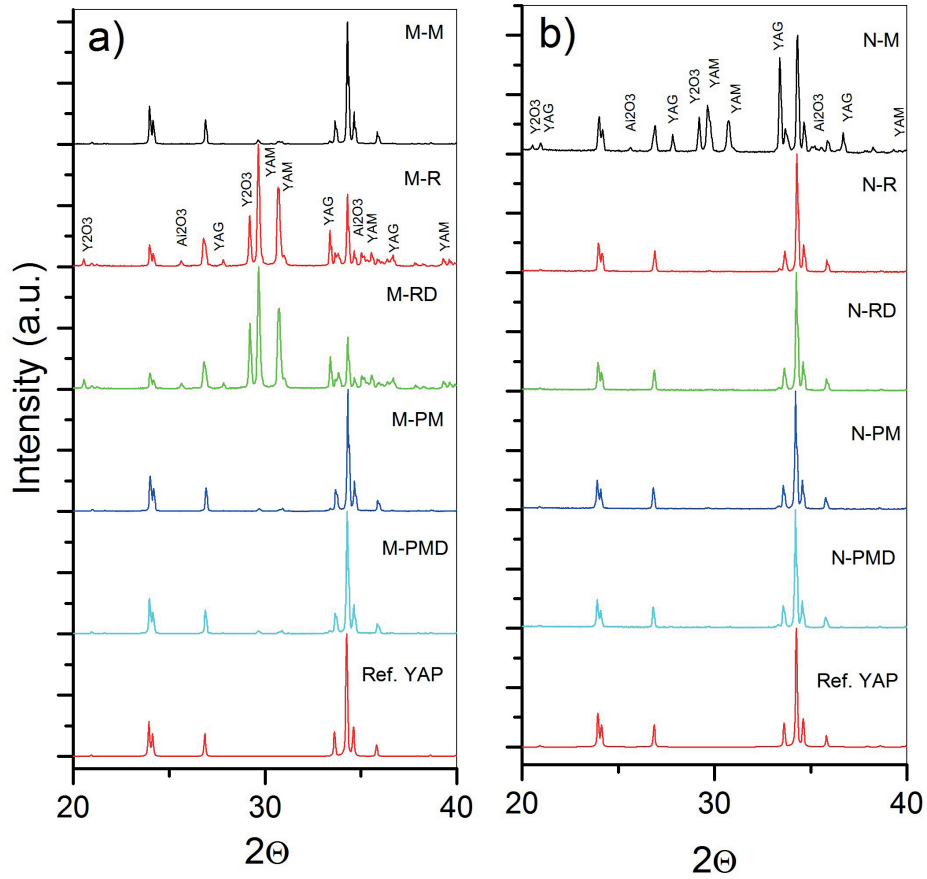


Fig. 2. X-ray diffraction patterns of specimens obtained via different homogenization ways of micro-powders (a) and nano-powders (b)

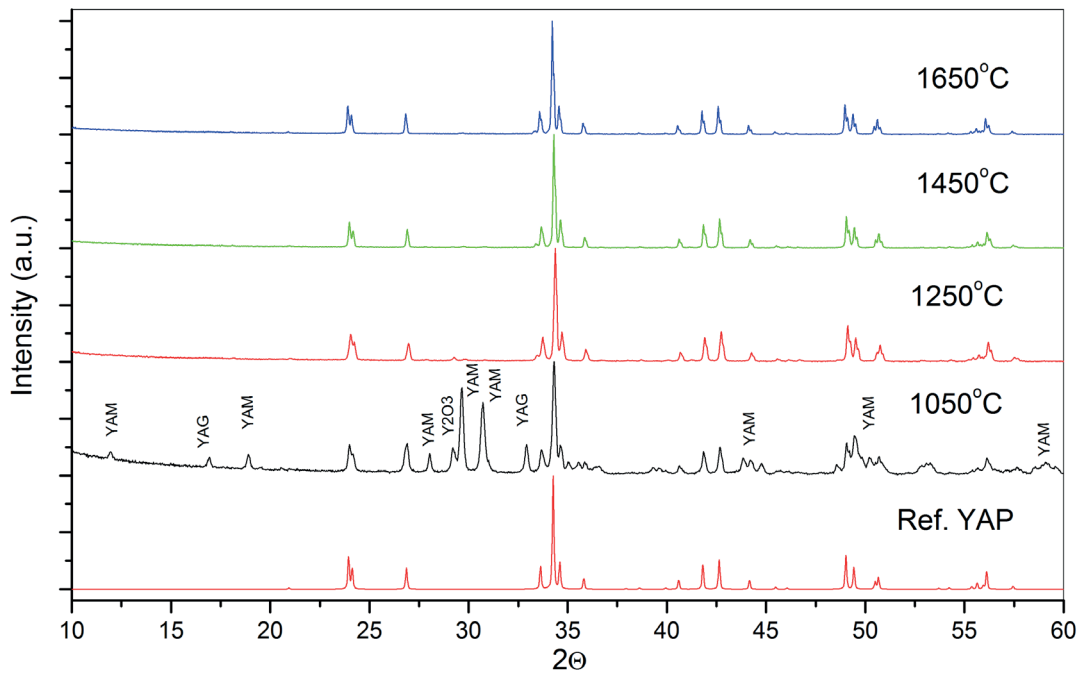


Fig. 3. X-ray diffraction patterns of specimen obtained from nano-powders by milling (N-PM), reacted at the temperature range of 1050 - 1650 °C

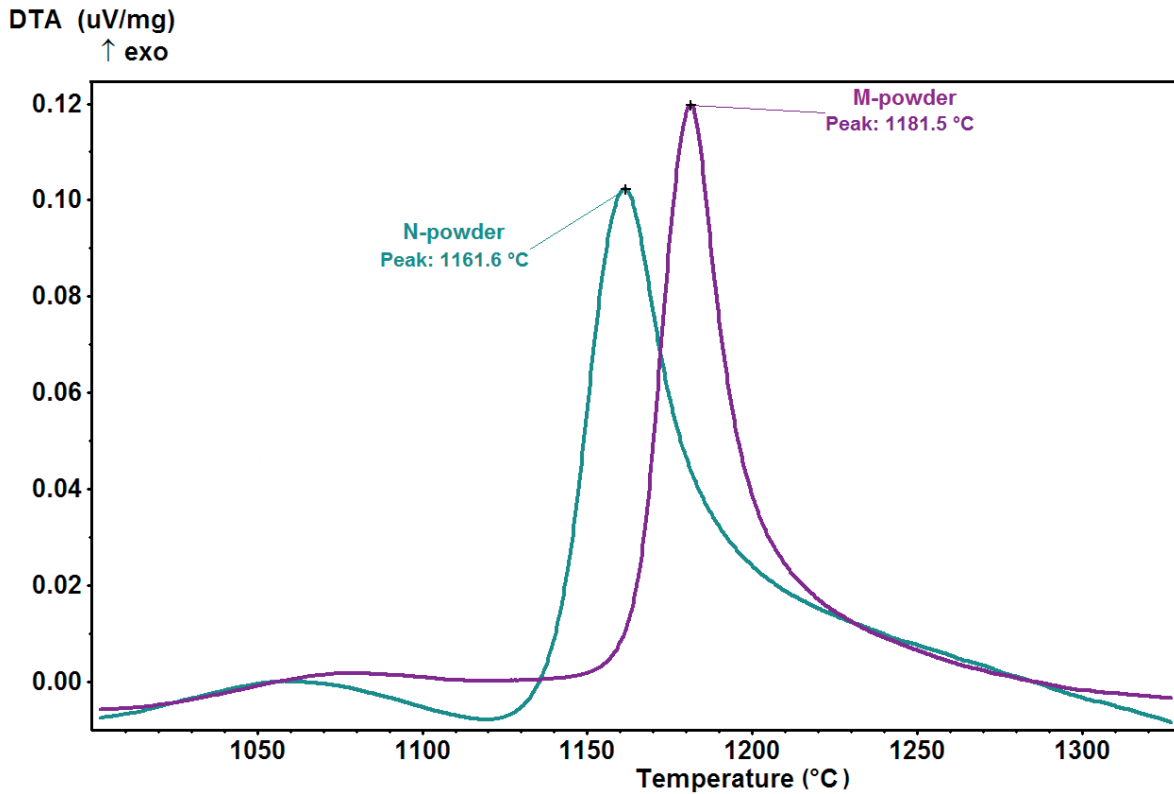


Fig. 4. Differential thermal analysis of micro- and nano-powder mixtures, M-PM and N-PM, respectively, from planetary milling preparation

A slightly different results were obtained if nano-substrates were homogenized with the methods used for micro-powders. First, the side phase-free YAP was obtained only if planetary milling of nano-substrate (N-PM) was applied. However, the roller mixing of nanopowders gave much better results in comparison to the micropowders since only a small amount of YAM ( $1.3 \text{ wt}\% \pm 0.41\%$ ) was present apart from YAP phase. On the other hand, hand-mixing in a mortar was not sufficient for homogenization of nanopowders since YAG contamination was visible in N-M specimen presented in Fig. 2b. Thus only planetary milling process guarantees the highest purity of the final product, but only for nano-substrates it was possible to obtain XRD-pure YAP phase. The smallest particle size and the effective mixing reduce the size of the local non-stoichiometry area. The impact of the deagglomeration step of milled micro- and nano-substrates was not visible on the X-ray patterns. This is due to the similar chemical character of both oxide substrates.

The XRD patterns for planetary milled nano-substrates after calcination at the temperature range of 1050 - 1650 °C are shown in Fig. 3. Multi phase composition with YAM and YAP dominant phases was obtained after heat treatment at 1050 °C. This shows the start of the formation of YAP phase from YAM and  $\text{Al}_2\text{O}_3$ . The single YAP phase is observed above calcination temperature of 1250 °C.

Differential thermal analysis of milled micro and nano-substrates are shown in Fig. 4. Strong YAP phase formation peak at 1182 °C was recorded for the micro-powder. For the nano-specimen the same peak is shifted to 1162 °C, lower

temperature by 20 °C. No other strong peaks that could indicate the secondary phases formation, were registered.

Morphology of the fractured pellets prepared by different methods of homogenization are shown in the Fig. 5 and 6. If comparing the morphology of micro-powder derived specimens then the impact of homogenization methods on the occurrence of two types of fractures: intergranular and transgranular, can be seen. The estimated grain size increases from 4  $\mu\text{m}$  for powder mixed in mortar (Fig. 5a) to 6 - 8  $\mu\text{m}$  if the mill was used (Fig. 6c). In a case of the roller homogenization it should be noted that a multi-phase composition was obtained thus it has effect on morphology of the grains, which is shown in Fig. 5b, c, and e. Morphology of milled nano-powders derived pellets shows the well-crystallized grains with the average size of 14  $\mu\text{m}$ . There is no sign of transgranular fracture in the SEM picture of N-PM specimen.

A significant share of the transgranular fracture may indicate the presence of a smaller and straighter grain boundary or ongoing of sintering grains during high temperature process.

In nano-powder specimens, nano-particles have a large surface energy and they can rapidly grow. Thus, the larger and well crystallized grains were occurred. Surface energy of the micro-powder is lower and grain growth during the sintering is also slower. Partial sintering between particles takes place which leads to the formation of hard/semi-sintered grains. This process may cause cracking of grains. Different phase composition and mechanical properties between grain and grain boundary also lead to transgranular cracking, if the phase with better mechanical properties is formed.

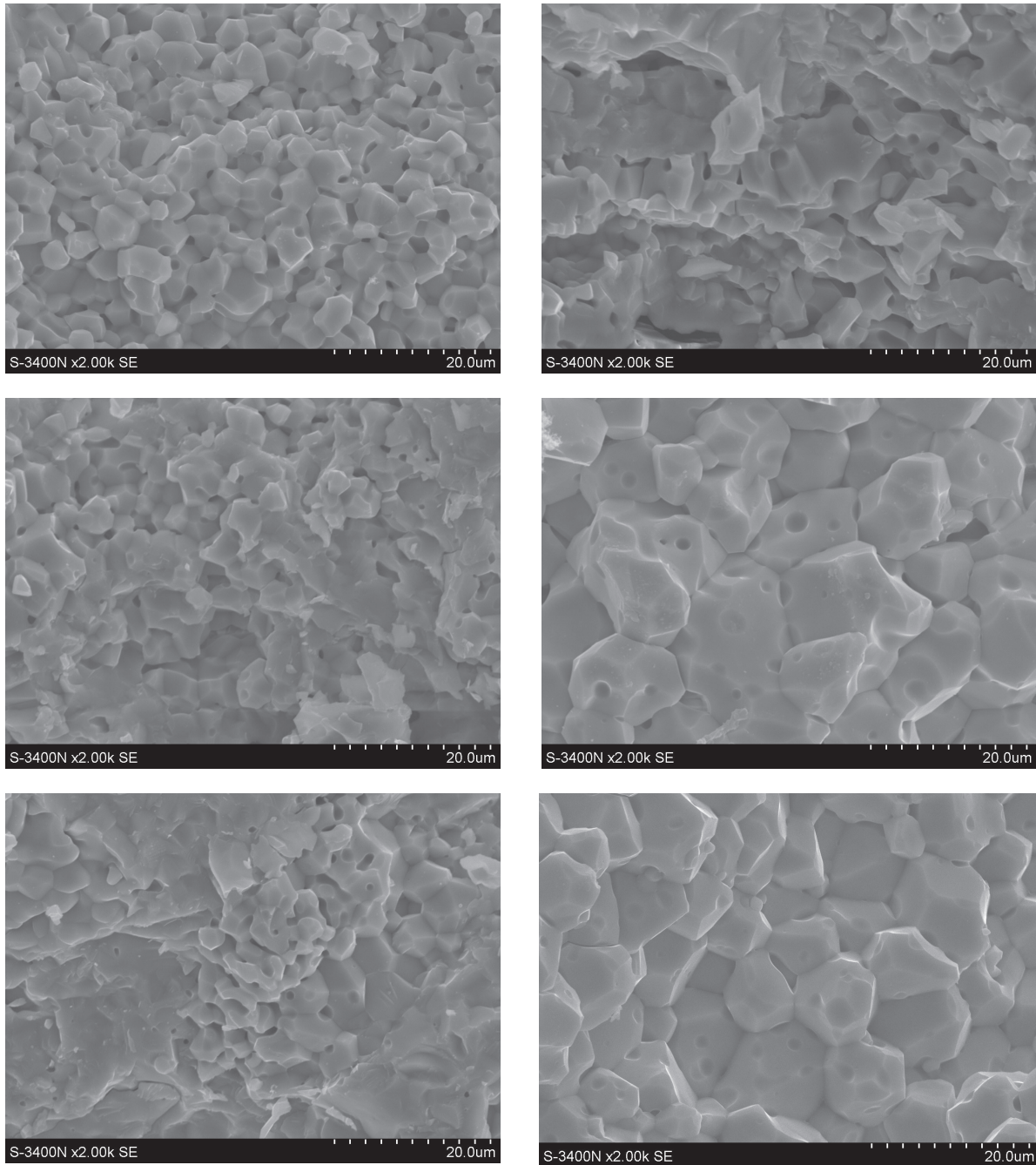


Fig. 5. Morphology of pellets (fracture) from micro-powders (left) and nano-powders (right) reaction sintered at temperature of 1650 °C for 8 h: M-M (a), N-M (b) M-R (c), N-R (d), M-RD (e), N-RD (f) (SEM, secondary electron mode)

Morphology of milled nano-specimens with and without deagglomeration step of starting powders is presented in Fig. 6b and Fig. 6d. Beneficial effects of deagglomeration can be observed. Wider grain size distribution was observed in milled N-PM specimen in comparison with deagglomerated N-PMD specimen.

Specimen without deagglomeration has a grain size from 2 to 18  $\mu\text{m}$ . Lack of 2-6  $\mu\text{m}$  grains and thereby similar size of all grains in deagglomerated specimen is depicted. Pores around 2  $\mu\text{m}$  diameter are occurred on the surface of grains which are larger than 10  $\mu\text{m}$ . Their presence is related to the excessive/rapid growth/merger grains and have a negative effect on the density of the material.

Morphology of N-PM powders after synthesis at various

temperatures is presented in Fig. 7. After synthesis at 1250 °C the average grain size of YAP is about 0.5  $\mu\text{m}$ . The calcination at the 1450 °C leads to grain growth up to 2  $\mu\text{m}$  and finally, after the calcination at 1650 °C they reach the size of 10  $\mu\text{m}$ .

Obviously, the grain growth occurs with increasing of calcination temperature. Since the pure YAP phase is completed after synthesis at 1250 °C thus the increase of the calcination temperature gives an opportunity to tune the expected size of grains. Porosity on the surface of particles is shown in the highest synthesis temperature, what was also observed on the fracture of this specimen. That kind of pores is formed by diffusion process during sintering. It can be assumed that the lower temperature of sintering should be more suitable for YAP polycrystalline ceramics.



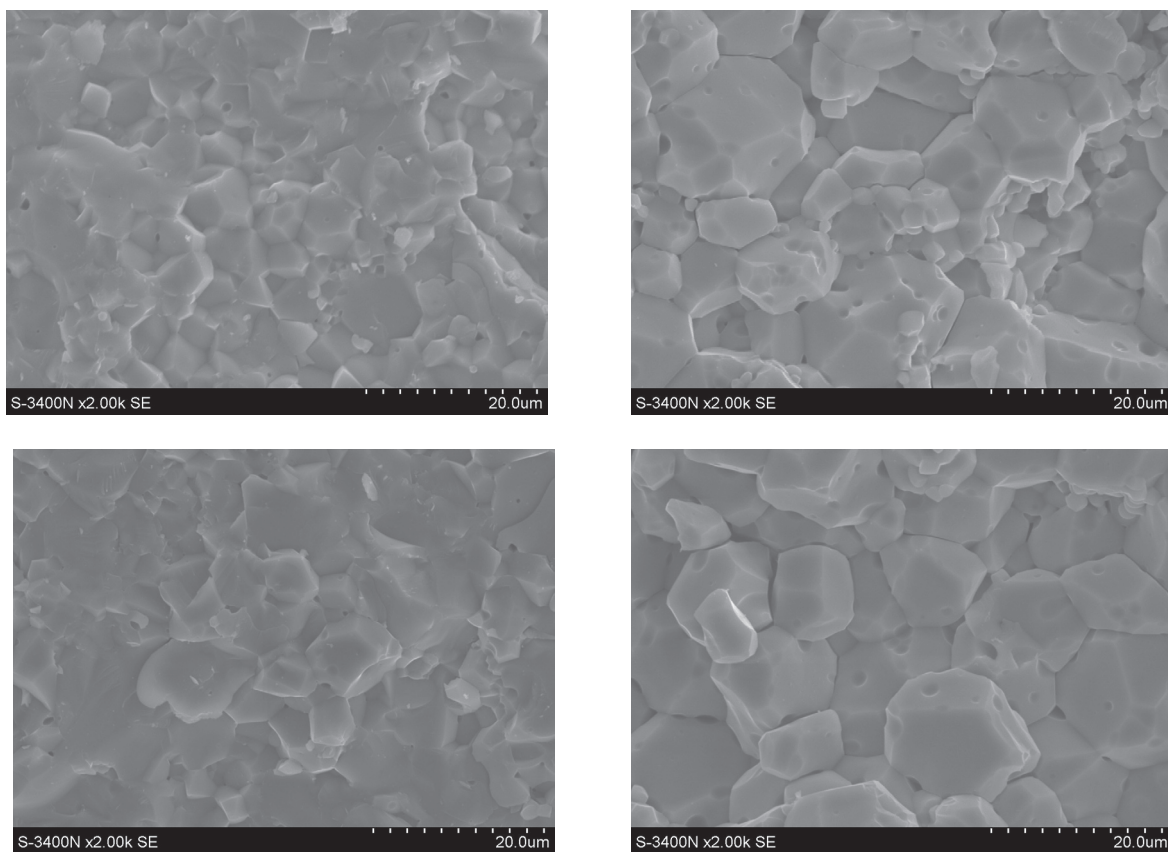


Fig. 6. Morphology of the pellet fracture from micro-powders (left) and nano-powders (right) sintered at temperature of 1650 °C for 8 h: M-PM (a), M-PMD (b) N-PM (c), N-PMD (d) (SEM, secondary electron mode)

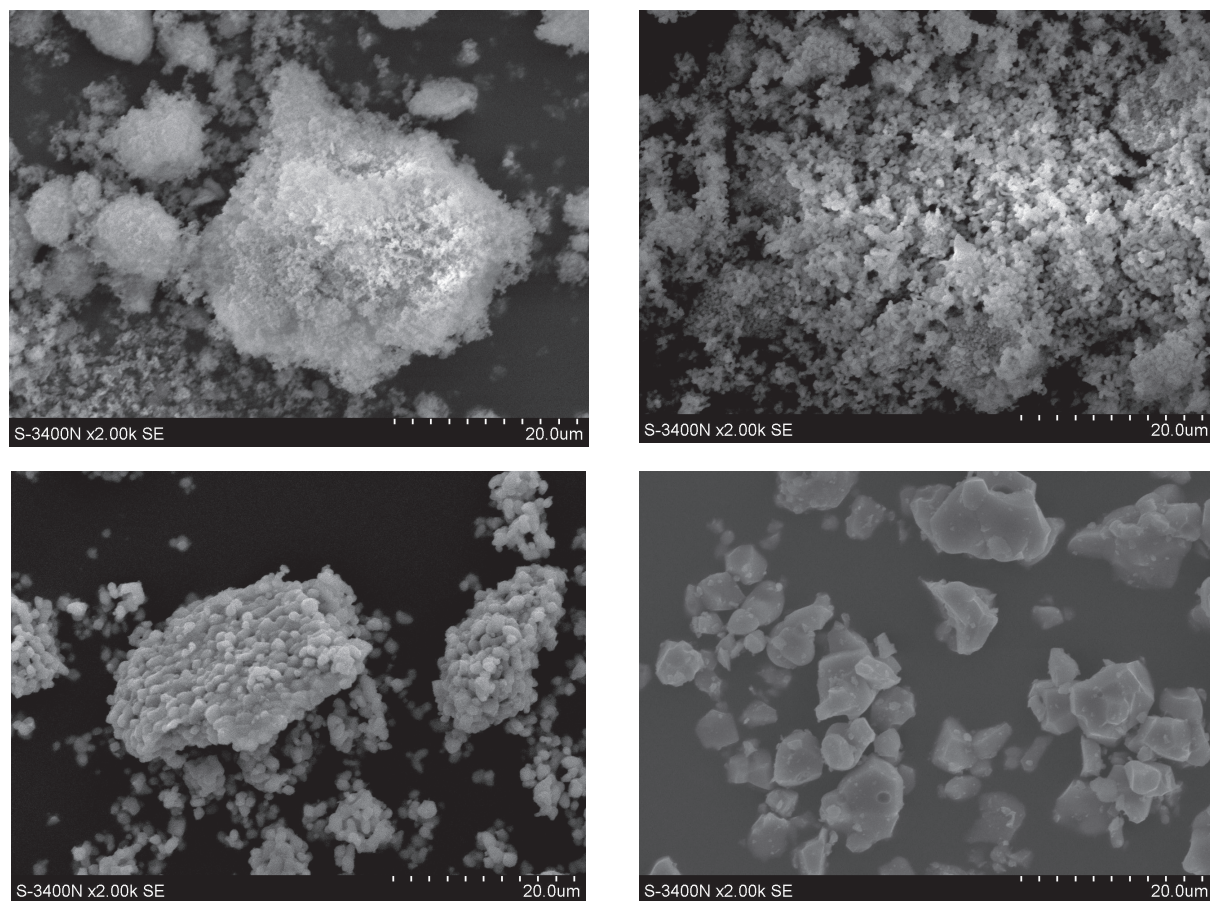


Fig. 7. Morphology of N-PM specimens synthesized at 1050 °C (a), 1250 °C (b), 1450 °C (c) and 1650 °C (d), (SEM, secondary electron mode)

#### 4. Conclusions

The pure, single phase of YAP was obtained through the use of powder substrates with a nanometer particle size. The improvement of the homogeneity and reduction of the local non-stoichiometric areas is also affected by planetary mill as a mixed medium. The particle size of substrates has slight effect on the temperature of formation of the YAP phase, which is only 20 °C lower if nano-powders are used. A significant effect of particle size of substrate on morphology of synthesized specimens was noticed. Larger and well crystallized grains were obtained from nano-substrates. The ultrasound deagglomeration reduced particle size distribution in final specimens. The grain size can be controlled by parameters of the high temperature heat treatment.

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