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APPLICATION OF MECHANOCHEMICAL PROCESSING TO SYNTHESIS OF YAG:Ce GARNET POWDER

ZASTOSOWANIE PROCESU AKTYWACJI MECHANOCHEMICZNEJ DO SYNTEZY ORANATU ITROWO-OLINOWEGO DOMIESZKOWANEGO CEREM

The paper presents the method of preparation YAG:Ce precursor powder with ability for synthesis at lower temperature. Mechanochemical processing of an initial powder mixture was used as a preliminary step for subsequent high-temperature treatment of the precursor. The specific surface area, phase composition and luminescence properties were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy. It has been shown that YAG structure formed at lower temperature by 300°C in comparison to the reference specimen but luminescence intensity was dependant on temperature of powder synthesis. The highest luminescence intensity was observed for powders synthesised at 1650°C.

Keywords: mechanochemical processing, phosphor, YAG:Ce garnet

W artykule przedstawiono otrzymywanie proszku granatu YAG:Ce z zastosowaniem zmodyfikowanej metody reakcji w stanie stałym. Mieszanina proszków wyjściowych została poddana procesowi aktywacji mechanochemicznej celem zwiększenia jego reaktywności podczas syntezy wysokotemperaturowej. Zbadano wpływ aktywacji na powierzchnię właściwą wyjściowej mieszaniny proszków. Proszek wygrzewany w różnych temperaturach został poddany analizie fazowej (XRD) oraz obserwacji na mikroskopie skaningowym (SEM). Zbadano niektóre właściwości optyczne: absorpcję i luminescencję przy wzbudzeniu $\lambda=450$ nm. Wykazano, że w wyniku aktywacji mechanochemicznej proszku wyjściowego YAG następuje obniżenie temperatury otrzymywania jednofazowego granatu itrowo-glinowego o 300°C, natomiast intensywność luminescencji zależała od temperatury syntezy; najwyższą uzyskano po syntezie w 1650°C.

1. Introduction

Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) monocrystals are commonly used as a material for laser host lattice, scintillation material or phosphor because of their good chemical and physical properties: the unique cubic structure of garnet and subsequent optically isotropic properties as well as excellent chemical stability at elevated temperature. More recently, it has been shown that YAG powders or polycrystalline ceramics are equivalent or better than single crystals made by the Czochralski method [1-4]. The former offer scalability in size, lower cost and simplicity of fabrication. YAG:Ce powders are of special interest since presently they are used for manufacturing a down converter in white light LEDs. Doped by cerium ions, YAG can convert blue light (460 nm) to yellow light (560 nm) as a result of f-d transition [5]. Presently, phosphor powders are em-

bedded in the resin or silicone matrix but this solution for white LEDs suffers from high thermal quenching of the phosphor itself and resin aging at elevated temperature since the resultant composite product shows very low thermal conductivity. Thus the latest reports on preparation transparent polycrystalline YAG:Ce ceramics [6-8] open a new interest in manufacturing YAG:Ce powders or YAG:Ce precursors with high densification ability.

A numerous synthesis techniques for preparation of YAG powders were reported: solid state reaction, precipitation, sol-gel, pyrolysis, combustion, freeze drying, spray pyrolysis and hydrothermal methods [9-15] but only the solid state reaction (SSR) is of interest for mass production. The latter, however, requires high temperature synthesis and the final product may contain other than YAG compounds.

In the $Y_2O_3 - Al_2O_3$ system three compounds with various Al:Y ratio are present. The SSR method used

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in this system produces a mixture of several phases in contrary to the equilibrium predicted ones: starting oxides and $Y_4Al_2O_9$ (YAM), $YAlO_3$ (YAP) and $Y_3Al_5O_{12}$ (YAG), independently of the initial composition. The several studies showed that the starting oxides are present up to the specific temperature: Al_2O_3 to 1600 °C and Y_2O_3 to 1300°C, if the molar ratio of alumina and yttria was set to 5:3 in the initial composition. Moreover, the specific phases are present in the given temperature range: YAM forms at 1100°C to 1400°C, YAP is present from 1200°C to 1600°C and YAG forms above 1300°C [16]. It is believed that YAG formation occurs via the solid state diffusion of smaller aluminium cations into the cubic structure of Y_2O_3 [17]. Consequently, application of high temperature (over 1600°C) is necessary to obtain the monophase YAG product since YAM and/or YAP residuals would destroy stoichiometry and related optical properties of the resultant polycrystalline powder. Thus the new SSR method of YAG:Ce powder preparation with ability for a large scale production would be interesting for both: phosphor powder for the resin-based down-converter and a source material/precursor for the subsequent ceramic manufacturing.

The course of YAG:Ce formation by SSR could be greatly enhanced if mechanochemical processing (MCP) of the initial powders mixture was applied. MCP involves the repeated collisions of powder particles with the milling media under the action of planetary milling with high energy. MCP can be operated at a large scale and was successfully employed in several reactive systems [18]. The MCP influence on YAG formation by the solid state reaction was previously checked by other authors [19-20], though they did not try to produce YAG:Ce phosphor material. Introduction of cerium oxide into the reaction system of Y_2O_3 - Al_2O_3 opens the questions of its susceptibility to deformation under MCP and subsequent behaviour during thermal treatment. This study examined the effect of the MCP into a sequence of phase formation in the Al_2O_3 - Y_2O_3 - CeO_2 system in the reducing atmosphere as well as some optical properties of the resultant YAG:Ce powder were studied.

2. Experimental

The samples with the general formula of $Y_{2.94}Ce_{0.06}Al_5O_{12}$ were prepared by a solid-state reaction with a high energy milling step using high purity commercial powder of η - Al_2O_3 (Sasol, 99.99 %), Y_2O_3 (Stark, 99.99%) and CeO_2 (AtomicChemicals, 99.99%). η - Al_2O_3 powder was chosen because of its high chemical activity and the high specific surface area. The stoichiometric amount of raw powders were grinded and mixed with anhydrous ethanol (99.8%) in a roller bench

with 10 mm Si_3N_4 balls for 24 hours, dried at room temperature for 24-48 hours. The planetary ball milling was performed in the Fritsch Premiumline 7 system with a rotation speed of 900 rpm for 30 min and followed by a break of 15 min for cooling. Such a cycle was repeated 8 times. The total time of milling was 4 hours. A 80 ml silicon nitride milling jar and 5 mm silicon nitride ball were used. A weight ratio between the milling balls and powder was 15:1. Prepared powders were annealed for 1 hour in an N_2/CO atmosphere in a graphite furnace (Thermal Technology) at temperatures varied from 900 to 1650°C.

An Rigaku MiniFlex II diffractometer was used for taking the powder diffraction patterns. The XRD patterns were collected in the 2 θ range of 10-60° with a step size of 0,02° and a scanning speed of 5° per minute using $Cu K\alpha_1$ radiation with $\lambda = 1.5406 \text{ \AA}$ with a nickel filter. Measurement of the phase weight fraction was done with the help of the Maud v2.22 software. XRD data after application of Rietveld refinement were used for calculation of YAG lattice parameters in powders after calcination at 1400-1600°C. Measurement of the optical properties was performed on the calcined powders and they were ground down in an agate mortar. Excitation and emission spectra were measured with an Edinburgh Instruments FS900 spectrometer equipped with a 450 W Xe arc lamp, mirror optics for powder samples and cooled single photon counting photomultiplier (Hamamatsu R2658). Excitation and emission spectra were recorded in the regions of 250 – 550 nm and 460 – 800 nm respectively. Philips powder U728 was used as a standard. Reflection spectra were recorded on ARC SpectraPro-300i (Acton Research Corporation) spectrometer equipped with 450 W Xe arc lamp, single photon counting photomultiplier and integration sphere. Reflection spectra were recorded in the region of 250 – 800 nm with the steps of 1 nm. Barium sulfate ($BaSO_4$, 99,998% purity, Alfa Aesar, Germany) was used as white standard. All measurements were carried out at room temperature. The grain size and morphologies of the samples were observed by a Hitachi 3400N scanning electron microscope (SEM) operated at 15kV.

3. Results and discussion

The study showed a specific surface area (SSA) of the starting powder of 25.6 m²/g. After the MCP the surface area increased to 42.4 m²/g. Estimation of particle size from the SSA measurement cannot be applied because of the specific surface properties of η - Al_2O_3 but doubling the SSA as a result of mechanochemical processing shows significant reconstruction of the existing agglomerates.

The mechanochemically processed powders were calcined at temperatures in the range of 900°C – 1300°C for 1 h. Fig. 1 shows the XRD patterns of powders after MCP and calcinations at different temperatures. JCSd card: YAM (No. 80039), YAP (No. 83027) and YAG were used for identification of the relevant phases. The calculated amount of the phase composition is given in Table 1. At temperature of 900°C all peaks are related to the YAM compound. After calcination at 1000°C next to the YAM phase the YAP phase was found and any traces of α -Al₂O₃ were not found. It means that Y₂O₃ involved reactions started before $\eta \rightarrow \alpha$ -Al₂O₃ transformation occurred. Instead, at temperature of 1100°C the YAG phase appears and the powder annealed at 1300°C contained only YAG phase. At this temperature all peaks of the samples match that one of YAG references (JCSd No. 280104). Accordingly, the formation of the pure YAG occurred at temperature lower by 300°C in comparison to the samples obtained by the solid state reaction without the MCP step. Similarly, H. Huang et al. [20] reported the mono-phase YAG composition after annealing at 1200°C if the milling time of MCP was increased to 20 hrs with the rotation rate of 200 rpm. The present results confirm ability of MCP for increasing reactivity in the Al₂O₃-Y₂O₃ system as alumina phase transformation was suppressed by formation of yttria bearing compounds.

It is interesting to note that temperature of YAG phase formation is close to the results of the wet method

precursor preparation and subsequent synthesis. However, it must be stressed that mechanochemical processing is much faster, easier and more effective in comparison to the wet chemical methods.

TABLE 1
Phase composition of the calcined samples at the given calcination temperature

Temperature of synthesis (°C)	Content of phases (%)		
	YAM	YAP	YAG
900	100	–	–
1000	47.2	52.8	–
1100	2.3	39.1	58.6
1200	–	1	99
1300	–	–	100

Fig. 2 shows the SEM images of the initial and the ball milled powders after calcination at different temperatures for 1 hour. Starting powder after MCP is presented in the Fig 2a and particles with sharp edges are visible as a result of MCP. Size of the particle size falls in the range of 2-6 μ m which is much higher that it could be expected from the specific surface area measurement and the average particle size of the initial powders. Thus agglomeration of the initial powder particles must have occurred to some extent.

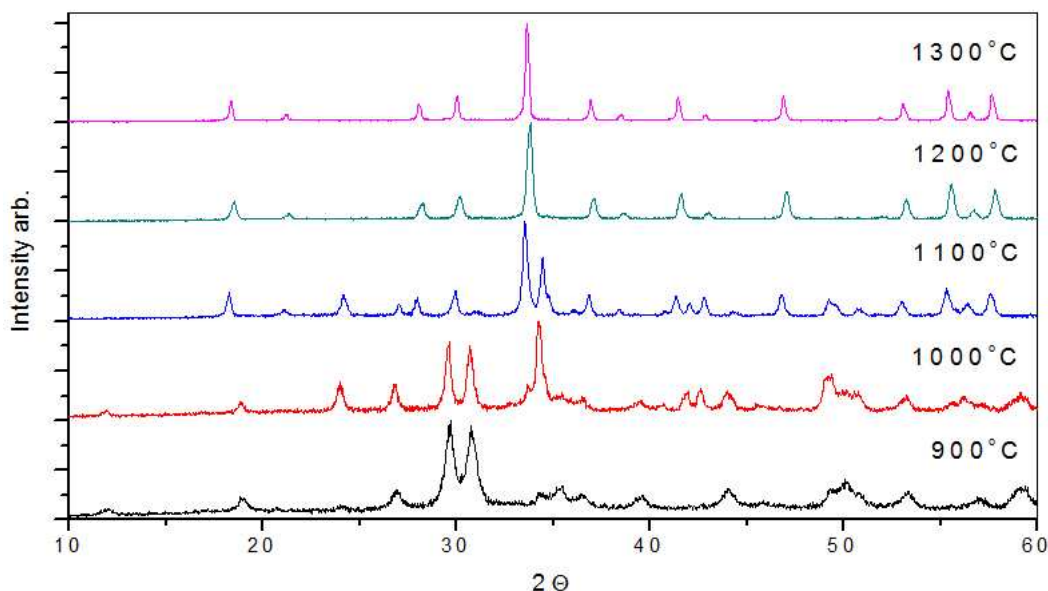
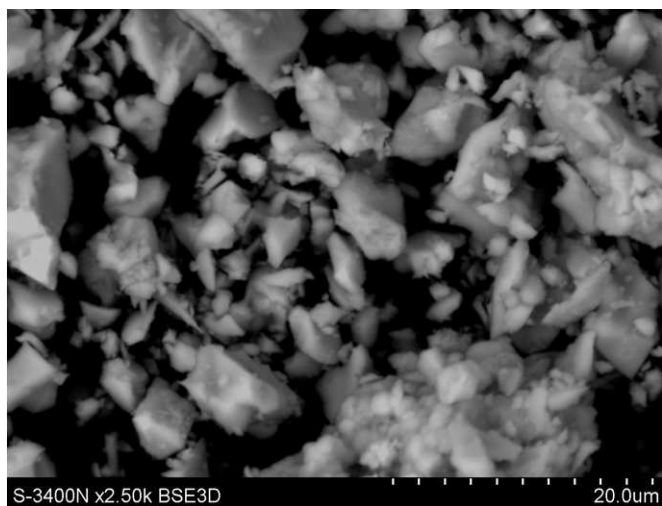
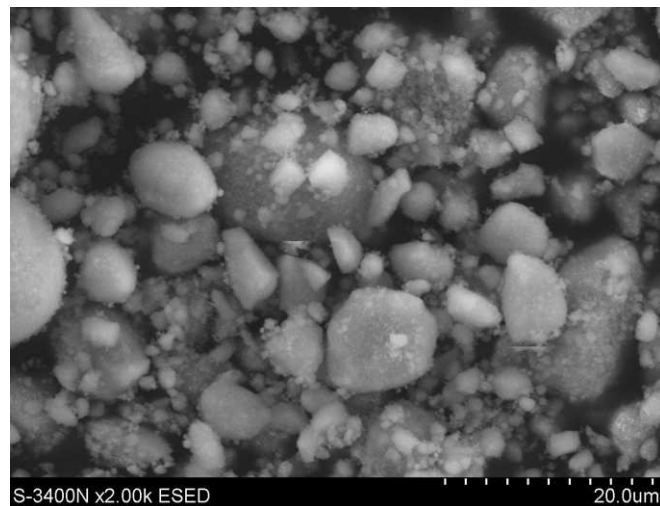


Fig. 1. XRD patterns of the YAG:Ce samples calcined at 900°C(a); 1000°C(b); 1100°C(c);1200°C(d); 1300°C(e) for 1h

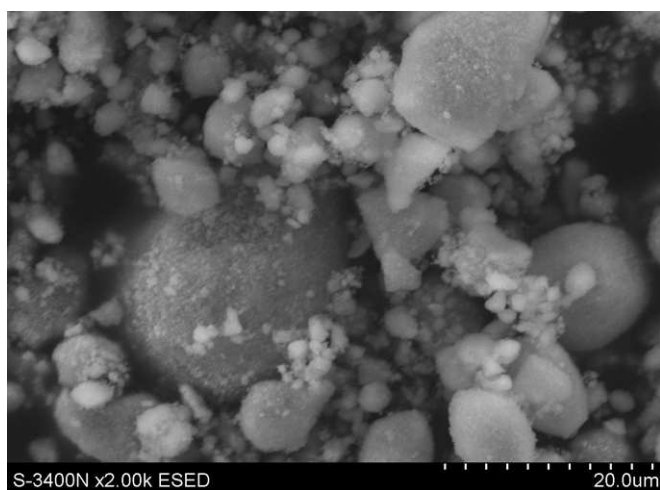
a) Mixture of the powders after MCP



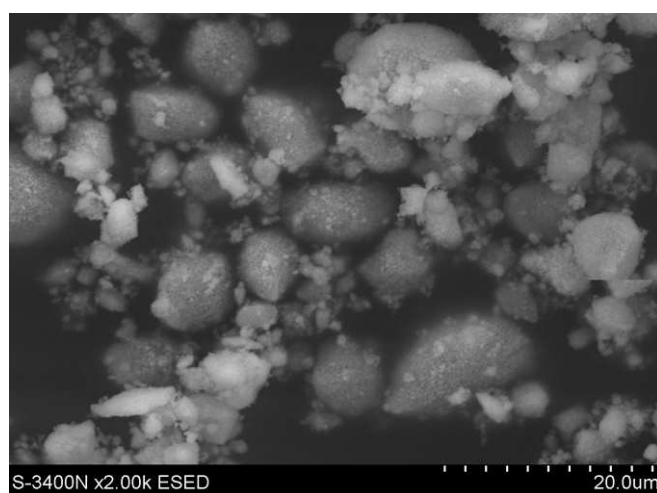
b) 1100°C



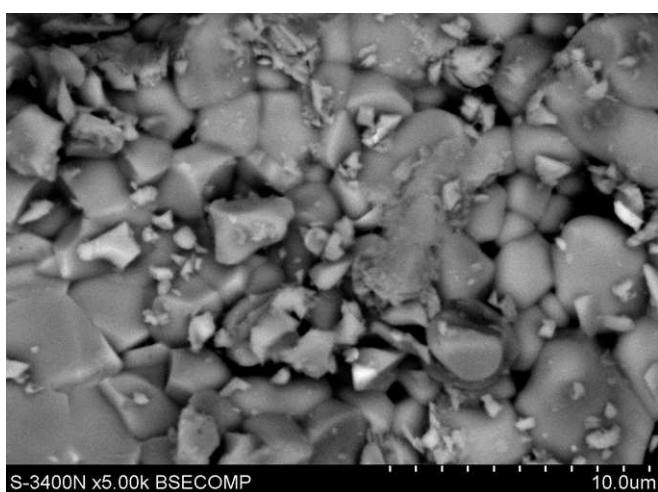
c) 1200°C



d) 1300°C



e) 1400°C



f) 1500°C

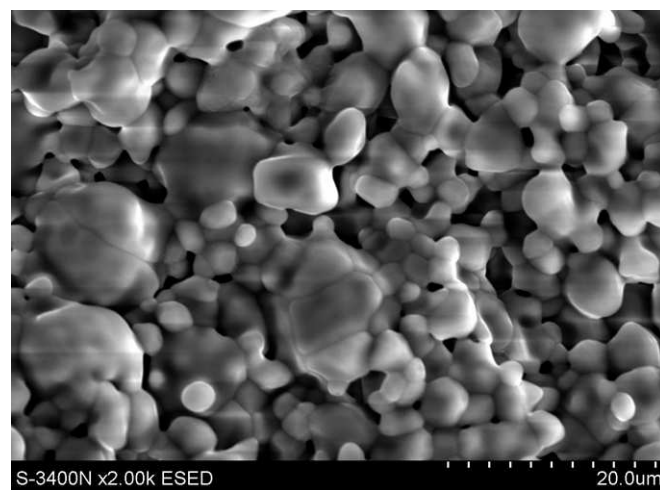


Fig. 2. SEM micrographs of the starting powders after MCP (a) and resultant powders after calcinations at 1100-1500°C (b-f) for 1h

Increase of calcination temperature led to the change of the particle shape and size (Fig. 2b – d). Significant changes of the particle shape were observed after annealing at 1100°C and were related to the formation of a considerable amount of YAG particles. Increase of temperature up to 1400°C (Fig. 2e) showed the substantial change of particle shapes followed by the extensive sintering after annealing at temperature of 1500°C Fig. 2f). This development of the particle morphology shows their potential for densification and possibilities for dense ceramics formation.

Reflection spectra of the powders after annealing at 1400°C – 1600°C are presented in Fig. 3. The ground state of Ce^{3+} is split into $^2F_{7/2}$ and $^2F_{5/2}$ with an energy difference of about 2200 cm^{-1} . The next higher state is split by crystal field and hence there are more than one Ce^{3+} absorption bands in the region between 200 and 500 nm. Consequently, there are two absorption bands in Fig.3 centred at 460 and 340 nm, both of them related to $4f^1 \rightarrow 5d^1$ transitions of Ce^{3+} , resulting from Ce^{3+} sites in a distorted cube of garnet. The spectrum of YAG:Ce calcined at 1400°C is typical for that material, however it is seen that the intensity of the reflection spectra decreases with the temperature of synthesis. (Fig. 3). Such behaviour could be ascribed to the shape and the surface state of powder particles prepared for the optical properties measurements. The higher temperature of annealing was applied the higher sintering of loosely packed particles was observed (Fig.2f). Therefore, they required grinding in an agate mortar before reflection spectra measurement.

Fig. 4 shows the emission spectra of the YAG:Ce powders due to the electron transitions from the lowest crystal-splitting component of 5d level to the ground state of Ce^{3+} . The emission spectra present one broad emission band located from 400 to 750 nm. Intensity of the emission is changed as a result of annealing temperature: with increase of calcination temperature the intensity of emission increases as well. Since emission is related only to Ce^{3+} ions with $4f^1$ electronic configuration inside the garnet crystal structure (site positions), as they can take part in the $4f \rightarrow 5d$ transition resulting in the yellow light emission, two explanations of the observed phenomenon are possible. First, the YAG:Ce powdered specimens were calcined in the reducing at-

mosphere of the graphite furnace, the $Ce^{4+} \rightarrow Ce^{3+}$ transition was not completed at 1550°C and was continued at higher temperature. Thus increase of calcination temperature in the reducing atmosphere is expected to enhance $Ce^{4+} \rightarrow Ce^{3+}$ reaction and to raise a number of Ce^{3+} ions present in the garnet host lattice. Kaczmarek et al. [21] observed the $Ce^{4+} \leftrightarrow Ce^{3+}$ transitions in YAG:Ce monocrystal determined by annealing temperature, environment and level of Ce doping. Correspondingly, Y. Pan et al [14] reported that the highest emission intensity of YAG:Ce phosphor powder was noted for the specimen calcined at 1500°C in CO flow.

Second possible explanation involves the actual position of Ce^{3+} ions in the synthesised product if we assume that reducing environment of the graphite furnace was sufficient for the $Ce^{4+} \rightarrow Ce^{3+}$ transition at 1500°C. Large cerium ions do not enter YAG structure easily, there are evidences of increased cerium ions concentration at grain boundaries [22] although authors do not reveal details of YAG:Ce ceramics manufacturing. At lower temperature, only part of the total cerium ions may enter the host lattice of YAG whereas the remaining Ce^{3+} ions can be present on the surface or at grain boundaries in the as-sintered YAG particles. Higher temperature of synthesis increases solubility of cerium ions in the YAG crystal lattice and a greater number of ions is active in the luminescence process. The explanation could be supported by measurement of YAG:Ce crystal lattice parameters. Substitution of Ce^{3+} ions (128.3 pm) for dodecahedral Y^{3+} ions (115.9 pm) must increase YAG:Ce lattice constant. The measured value of a parameter of the garnet unit cell changed from $a=1200.9\text{ pm}$ for powders calcined at 1400°C to $a=1201.6\text{ pm}$ if the powder was calcined at 1650°C. The latter is close to the value of 1201.2 pm reported for YAG:Ce phosphor with $Ce=0.3\text{ at.}\%$ [23].

The opposite effect of calcination temperature on the absorption and emission intensity of the resultant phosphor powders is not clear. Both, absorption and emission, are related to a number of Ce^{3+} in site positions. Nevertheless, emission takes place only in the excited ions while absorption could be reduced by surface effects of powder particles. It seems, that scattering effects are less important if compared to the emission yield of the phosphor.

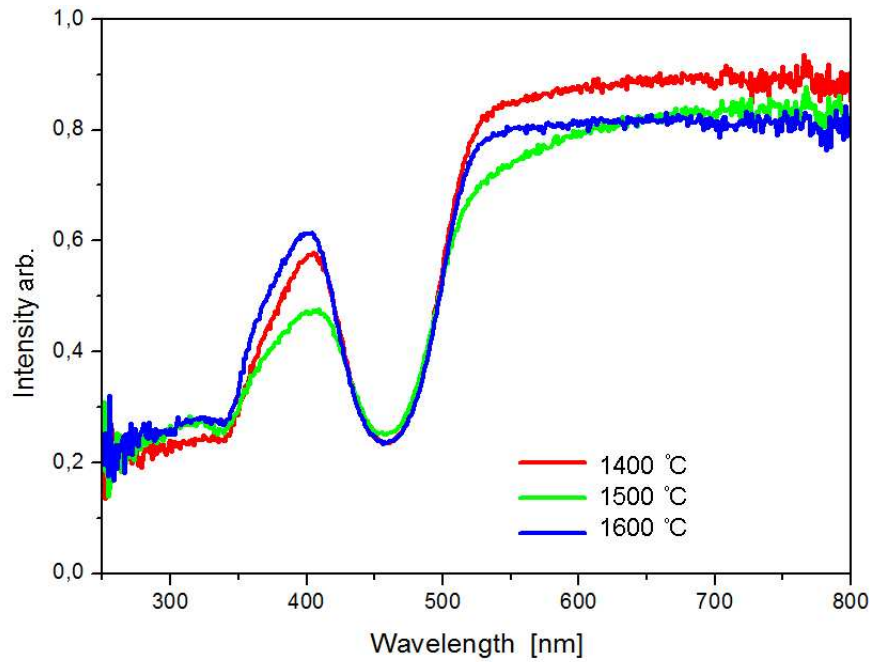


Fig. 3. Influence of annealing temperature on reflection spectra of the samples $Y_{2.94}Ce_{0.06}Al_5O_{12}$ after MCP

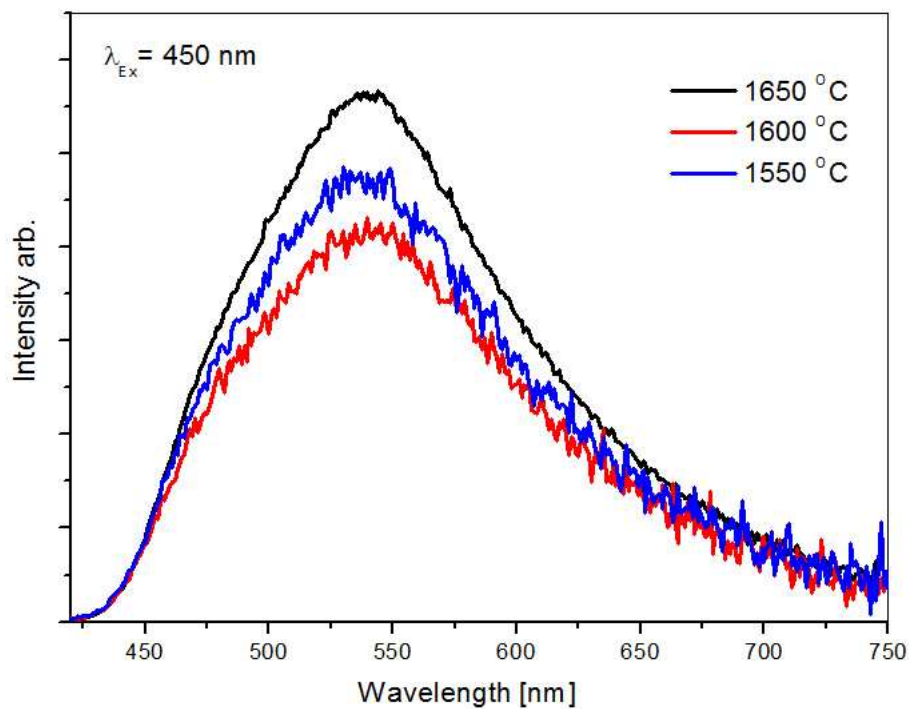


Fig. 4. Influence of the annealing temperature on the emission spectra of samples $Y_{2.94}Ce_{0.06}Al_5O_{12}$ after MCP

Extensive sintering of YAG particles at temperature over $1400^{\circ}C$ required the relevant grinding prior to measurement and changed particle shapes and the surface state as it was observed in the microscopic studies (Fig. 5). The higher calcination temperature the more in-

tensive grinding was involved and it resulted in a greater number of the broken particles with a damaged surface. The surface state of the particles controls the light reflection as an intensive scattering could happen on the damaged surface.

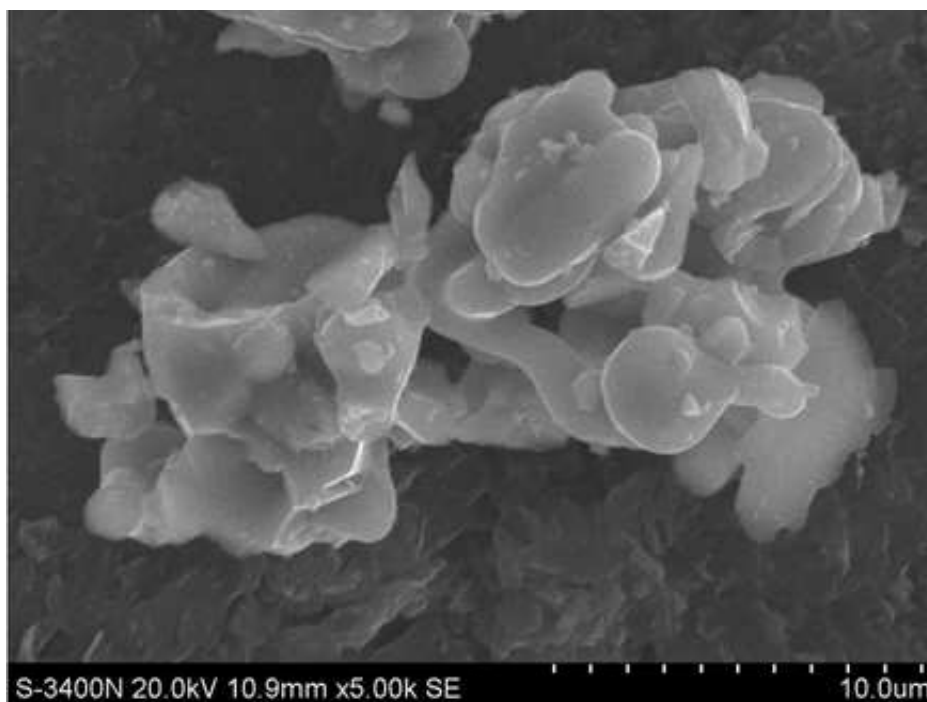


Fig. 5. YAG:Ce particles after synthesis at 1600°C followed by grinding in the agate mortar

4. Conclusions

The presented results show the dual effect of mechanochemical processing on reactions/sintering in the examined Al_2O_3 - Y_2O_3 - CeO_2 system. The applied parameters of MCP were sufficient for increase of chemical reactivity between alumina and yttria particles as $\eta \rightarrow \alpha$ - Al_2O_3 transition was suppressed by preceding formation of yttria bearing phases. Consequently, pure YAG was obtained at 1300°C as a result of the high temperature synthesis, which is about 300°C lower than in traditional solid-state reaction and slightly higher than for the wet-chemical methods derived precursor. On the other hand, application of MCP was not satisfactory in terms of Ce^{3+} ions placement on the dodecahedral site in the garnet structure after completed synthesis of YAG at 1300°C. Both, increase of emission intensity and increase of the unit cell parameters suggest formation of a greater number of Ce^{3+} ions in the site position if higher temperature of YAG:Ce synthesis was applied. If we combine the last conclusion with the high sinterability of powders at 1600°C and the resultant requirement for powder pulverization, we conclude that application of mechanochemical processing to manufacturing YAG:Ce powders for the blue-light conversion purpose in white LEDs is of limited significance. On the other hand, the present findings open the new way for preparation of transparent YAG:Ce ceramics.

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