OPTICAL PROPERTIES OF POWDER AND CERAMICS OF ALUMINIUM OXYNITRIDE OBTAINED BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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The synthesis method of aluminium oxynitride (AlON) powders by nitriding of Al/Al_2O_3 mixture under high-pressure nitrogen is proposed. The novelty of this method consists in adding $KClO_4$ or $Mg(ClO_4)_2$ and extra Al into the starting mixture ($Al+Al_2O_3$) to cause the exothermal aluminium oxidation reaction, which therefore initiates the aluminium nitriding reaction. The microstructure and phase composition of the AlON powders obtained by self-propagating high-temperature synthesis are demonstrated by means of SEM and XRD analysis. Diffuse reflection spectra of AlON powders have been measured and the values of band-gap energy have been calculated. Optical transmission and reflection characteristics of the AlON ceramic samples sintered from AlON powders at 1930°C have been studied. The influence of the technological parameters of ceramics production on their transparency is revealed – the most transparent sample is obtained from the powders synthesized with the $Mg(ClO_4)_2$ additive and sintered for 6 h.

Keywords: aluminium oxynitride, AlON, self-propagating high-temperature synthesis, combustion, optical properties, transparent ceramics

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1. Introduction

Aluminium oxynitride (AlON) is a well-known compound since 1959 when for the first time Yamaguchi and Yanagida reported the possibility of a spinel-type phase in the Al_2O_3–AlN system [1]. Nowadays, a high interest in AlON ceramic is caused by its excellent optical [2–4] and mechanical [5] properties. For instance, a combination of thermomechanical properties and transparency in UV, VIS, and IR of AlON is regarded as a challenge to tempered glass and sapphire single crystals in many applications [2]. Moreover, this material is also promising for high-temperature applications in aerospace engineering and power industry [6].

The classical methods of AlON synthesis are (i) the solid state reaction of AlN and Al_2O_3 [7], and (ii)

the carbothermal reduction of Al_2O_3 [8] at temperatures higher than 1700°C for a few hours. However, these methods have serious disadvantages such as a high cost of initial materials (for example, AlN), carbon impurities (which cause pores in sintered ceramics) and a low energy efficiency and complexity of the technology. In this study, we propose to utilize the self-propagating high-temperature synthesis (SHS) of AlON ceramics which is a highly efficient method to produce powders and ceramics, especially nitride ceramics [9]. This method is based on the combustion processes – the exothermic reaction of initial reagents and using only internal energy of the reacting systems without external heating. The SHS method allows one to synthesize a large number of high-temperature materials and ceramics based on individual nitrides or composite materials

useful for electronics, aerospace engineering, nuclear industry, metallurgy, etc. There are currently no reports about production of transparent AlON ceramics from SHS powders.

2. Experiment

2.1. AlON powder synthesis

Commercial powders of Al (ASD-4 brand, d_{50} = 7.5 μm), Al_2O_3 (α-Al_2O_3, 99.9% pure, d_{50} = 55 μm), $Mg(ClO_4)_2$ and $KClO_4$ (99.9% pure, reagent grade) were used as starting materials. Magnesium perchlorate $Mg(ClO_4)_2$ or potassium perchlorate $KClO_4$ were added to the mixture as an oxidizing agent. These powders taken in amounts to achieve single phase AlON powder (35.7 mol.% AlN/64.3 mol.% Al_2O_3) were dry-mixed in a ball mill for 4 h. The reactive mixture (40 g) was ignited by heating nichrome 80/20 wire at the top of the sample in a BN crucible under 20 MPa nitrogen pressure. The SHS reaction was completed in ~90 s. After cooling, the products were crushed and screened by using a 120 μm mesh. The combustion products were investigated using the X-ray phase analysis (Dron-3M), chemical analysis, scanning electron microscopy (SEM) for the material microstructure and particle morphology (a LEO-1450 scanning electron microscope with a built-in IN-CA ENERGY 350 (EDS) X-ray analyzer). These methods are traditionally used for the characterization of the phase content and structure parameters of ceramic samples [10–13]. Rietveld refinement was performed on XRD patterns t o calculate the lattice parameters of analysed phases. More information about combustion experiments is presented elsewhere [14, 15].

2.2. AlON ceramics sintering

AlON powder was ball-milled in isopropyl alcohol at 300 rpm for 6 h using Al_2O_3 balls of 2 mm diameter. 0.5 wt.% of Y_2O_3 was added to the milling process as a sintering additive. Dried powder was screened trough a 40 μm mesh. 6 g of the obtained AlON powder were pressed into a billet of 20 mm in diameter under 50 MPa. The samples were heated to 1930°C with a heating rate of 40°C/min and held for 2, 4 and 6 h. Then the sintered samples were ground and polished on both sides to 1.2 mm thickness for optical transmittance measurements.

2.3. Optical measurements

Optical parameters were measured using a UV–Vis–NIR spectrophotometer Cary-5000 with a UMA accessory (*Agilent Technologies*). The control of the optical transmittance and reflectance of AlON ceramics is essential for determining the quality of the final product as transparency material. The measurement of reflection spectra allows us to estimate the values of the refractive indices of these ceramics according to the spectrophotometric method of reflection at near-normal incidence angle (6 degrees in our case) [16].

We have measured the diffuse reflection spectra R of AlON powders and calculated the absorption coefficient using the method for the quantitative analysis of various powder substances based on the Kubelka–Munk theory [17]. The band-gap (E_g) was determined within the framework of the well-known formalism for the dependence of the absorption coefficient [18, 19].

3. Results and discussion

3.1. AlON powder synthesis

The XRD diagrams of powders synthesized using 14 wt.% $KClO_4$ (denoted as AlON K) and 11.4 wt.% $Mg(ClO_4)_2$ (denoted as AlON M) are presented in Fig. 1. As shown, this method allows one to produce aluminium oxynitride powder with the additive of $KClO_4$. One of the decomposition products of $KClO_4$ is KCl, and small traces of KCl are also detected in Fig. 1 (top). It should be noticed that potassium chloride is easily soluble in water. The lattice parameter of γ-AlON powder obtained using a mixture containing $KClO_4$ is 0.7945–0.7951 nm. This lattice parameter corresponds to γ-AlON with the following ratio $Al_{2.85}O_{3.45}N_{0.55}$.

The XRD diagram of powder synthesized using $Mg(ClO_4)_2$ (denoted as AlON M) is presented in Fig. 1 (bottom). This approach is capable to produce single phase aluminum oxynitride powder if the additive of $Mg(ClO_4)_2$ is 10–11.4 wt.%. The absence of magnesium chloride in experiments with magnesium perchlorate is explained by a lower boiling point than that of potassium chloride. The lattice parameter of AlON M powder is 0.7948–0.7953 nm. This lattice parameter also corresponds to γ-AlON having an atomic ratio $Al_{2.85}O_{3.45}N_{0.55}$. Taking into
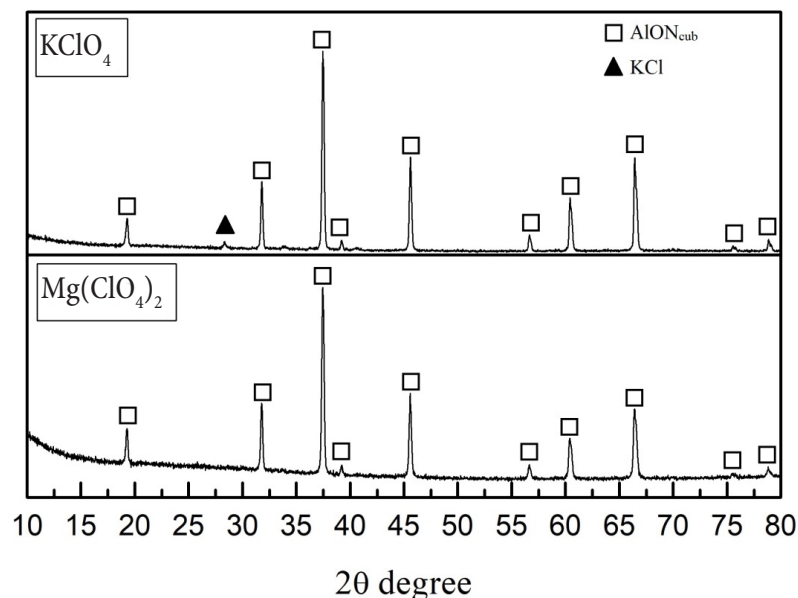
Fig. 1. The XRD pattern of combustion products of the mixture with $KClO_4$–AlON K (top) and with $Mg(ClO_4)_2$–AlON M (bottom): □ is $AlON_{cub}$, ▲ is KCl.

account that AlON compound is a solid solution of AlN and Al_2O_3, significant differences in the lattice parameters observed in AlON M and AlON K can be explained by a wide homogeneity zone of γ-AlON.

3.2. AlON ceramics sintering

This is our first attempt of the sintering of AlON ceramics from the powder obtained by the SHS method. The SEM images of the microstructure of AlON K and AlON M powders before the milling process are presented in Fig. 2(a, b). The particle size of as-synthesized AlON M powder is about 1–3 μm, while the microstructure of AlON K powder represented by significantly bigger agglomerates seems like melted/sintered. After ball milling with 0.5 wt.% of Y_2O_3 the average particle size of

AlON K and AlON M powders was $d_{50} = 1.8$ μm. Then the powders were uniaxially pressed under 50 MPa and the obtained green bodies were sintered at 1930°C in a graphite furnace under 0.1 MPa nitrogen pressure for 2, 4 and 6 h. After the sintering process all ceramic samples were grounded/polished on both sides to 1.2 mm thickness for further optical measurements.

3.3. Optical measurements of AlON ceramic samples

Keeping in mind practical applications of this material, it is important to measure the transmission of ceramics. Figure 3 exhibits the transmission spectra of AlON M and AlON K ceramics which were sintered for 2 and 6 h in each case. It
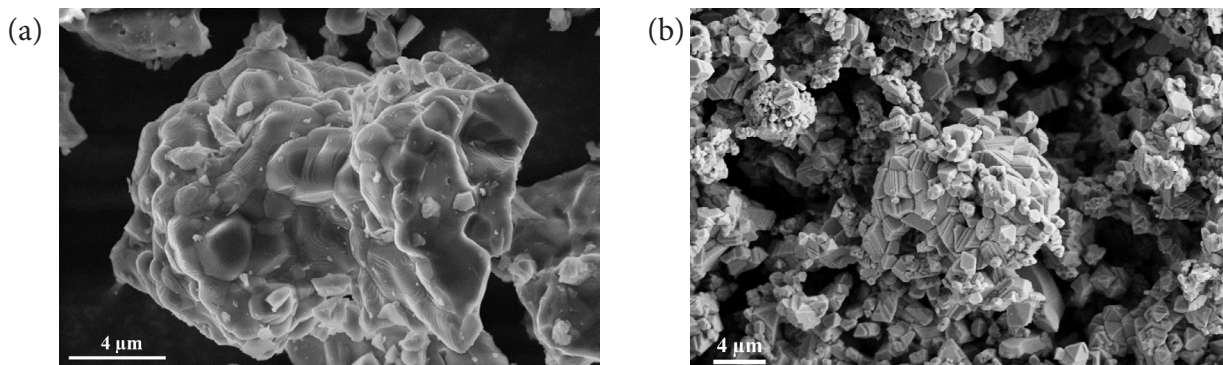

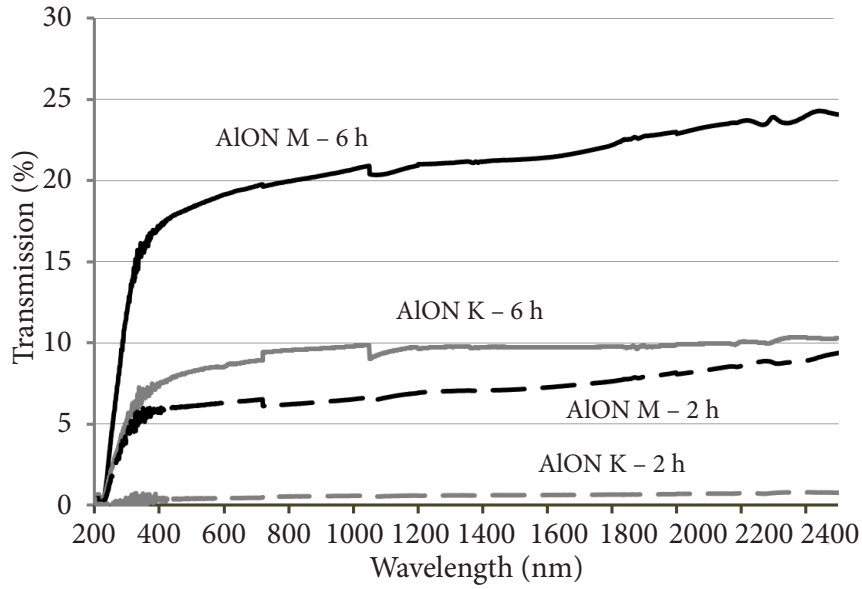Fig. 2. SEM images of AlON K (a) and AlON M (b) powders.

Fig. 3. Optical transmission spectra of the AlON M ceramic samples sintered for 2 and 6 h (AlON M for 2 h and AlON M for 6 h) and AlON K ceramic samples sintered for 2 and 6 h (AlON K for 2 h and AlON K for 6 h).

is clearly shown that the most transparent sample is obtained from AlON M powder sintered for 6 h and its transparency is higher than 20% in the visible spectral range.

The reflection spectra (Fig. 4) of ceramic samples allowed us to estimate the values of refractive indices using the spectrophotometric method of reflection at a near-normal incidence angle (6 degrees in our case), and this method is described thoroughly in [16]. The dispersion of refractive indices is summarized in Table 1.

Due to the fact that the reflection spectra of ceramics have differences, possibly due to the difference in the surface quality, it was decided to measure the diffuse reflection of AlON M and AlON K powders (Fig. 5).
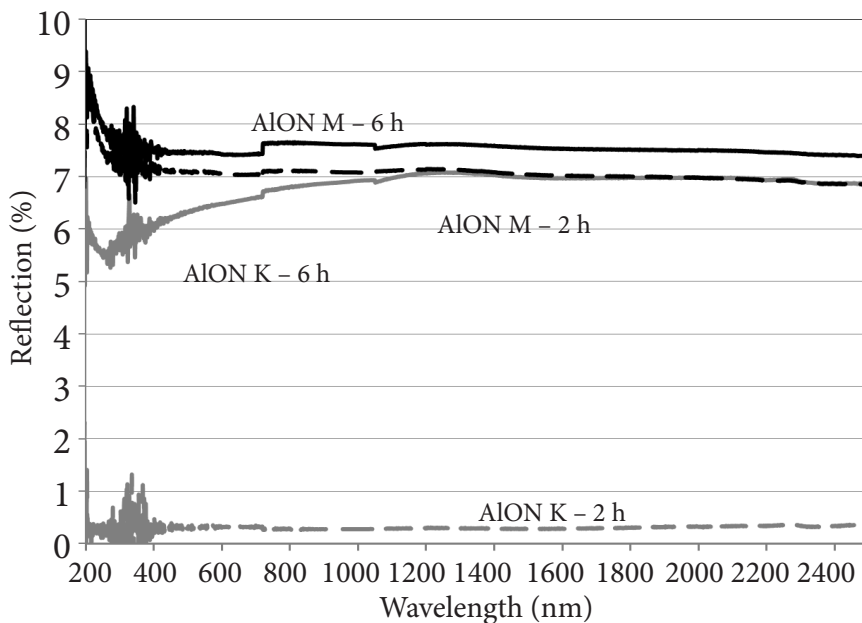

Fig. 4. Optical reflection spectra of the AlON M ceramic samples sintered for 2 and 6 h (AlON M for 2 h and AlON M for 6 h) and AlON K ceramic samples sintered for 2 and 6 h (AlON K for 2 h and AlON K for 6 h).

Table 1. The dispersion of the refractive indices of AlON ceramic samples.

λ, nm	n
200	1.85
400	1.75
600	1.72
800	1.72

Based on the Kubelka–Munk theory, methods for the quantitative analysis of powder materials are successfully developed in [17]. This theory is based on the possibility of analysing the absorption spectra using the diffuse reflection spectra. The spectral dependences of the absorption coefficient k_{Abs} were calculated from the measured diffuse reflection spectra R using the Kubelka–Munk formula (Eq. 1)

$$F(R) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k_{Abs}}{s} \approx \alpha, \qquad (1)$$

where R is the normalized measured diffuse reflection coefficient, and s is the scattering coefficient taken in this case as 1.

The estimation of the band-gap E_g was carried out within the framework of the well-known formalism for the dependence of the absorption coefficient in the fundamental edge region for the direct allowed transitions (Eq. 2)

$$\alpha = \alpha_0 \frac{(h\upsilon - E_g)^{r/2}}{h\upsilon}, \qquad (2)$$

where $h\upsilon$ is the photon energy, eV.

To estimate the band-gap E_g of our samples, the values of $F(R)$ were calculated and plotted in the Tauc coordinates $h\upsilon$-$(\alpha h\upsilon)^2$ [18, 19]. The coefficient r differs for direct-gap ($r = 1$) or indirect-gap ($r = 4$) materials. According to [18], the coefficient for aluminium oxynitride powders AlON is $r = 1$ and Eq. (2) is transformed into Eq. (3), taking into account the Kubelka–Munk function in Eq. (4):

$$\alpha h\upsilon = (h\upsilon - E_g)^2, \qquad (3)$$

$$F(R_{\infty})h\upsilon = (h\upsilon - E_g)^2. \qquad (4)$$

To the inflection point on the curve $h\upsilon$-$(h\upsilon F(R_{\infty}))^2$ a tangent line is drawn, and the intersection point of the tangent line and the horizontal axis is the value of the band-gap E_g (Fig. 6). The values of the band-gap E_g for aluminium oxynitride powder AlON K are about 5.7 eV, while for the AlON M powder they are about 5.85 eV.

The values of band-gap energies demonstrate that the quality of AlON M samples is better than that of AlON K. One of the reasons why the AlON K band-gap value obtained from optical measurements is smaller than the AlON M band-gap value is a high concentration of intrinsic defects (shallow traps) in the material. It means that the AlON M powder, in addition to a better crystallinity and a more refined microstructure, reveals a lower concentration of the intrinsic defects. All these facts clearly demonstrate
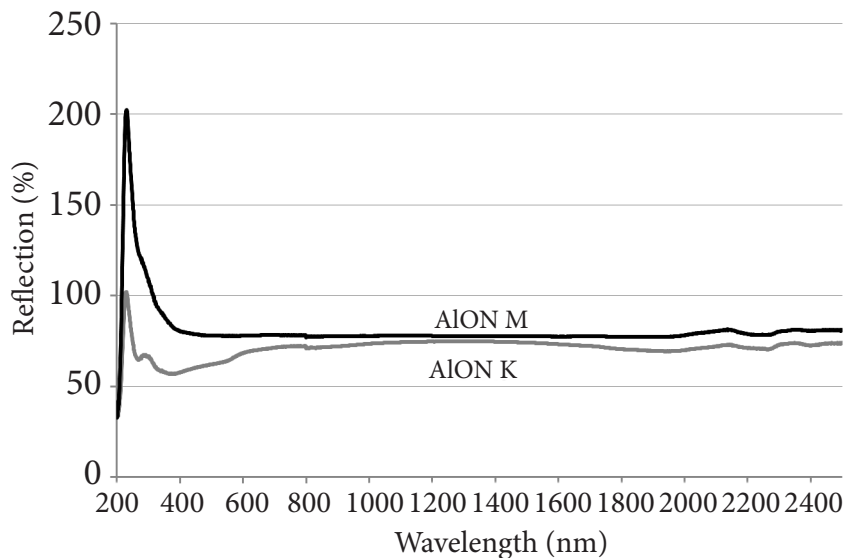

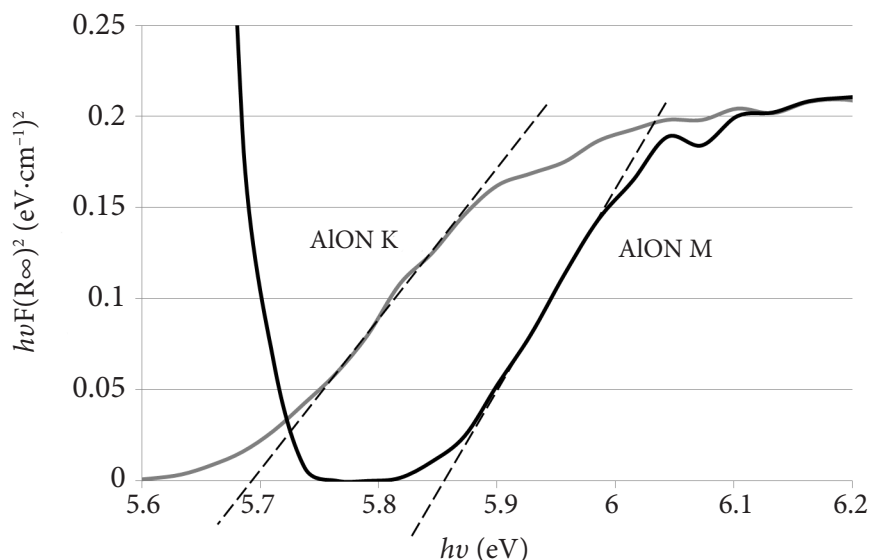Fig. 5. Diffuse reflection spectra of the AlON M and AlON K powders.

Fig. 6. F(R) plotted in the Tauc coordinates hv-$(\alpha hv)^2$ of the AlON M and AlON K powders with the tangent lines and estimation of the band-gap E_g.

the advantage of the $Mg(ClO_4)_2$ additive over the $KClO_4$ additive in the AlON synthesis using the SHS method. However, it is worth noting that the differences in crystallinity and microstructures between the AlON M and the AlON K series are not crucial for the significantly distinguished transparency of ceramics observed for the corresponding samples. Therefore, we suggest that the intrinsic defects play the main negative role in the transparency of the AlON ceramics. During the sintering process, the intrinsic defects usually migrate to the grain boundaries forming defect interfaces among them that cause the light scattering and obviously the decrease of ceramics transparency. The smaller concentration of intrinsic defects in AlON M powder is one of the reasons of the significantly better AlON M ceramics transparency compared to that of the AlON K ceramic sample.

4. Conclusions

We have developed the synthesis method of aluminium oxynitride powder based on the self-propagation high-temperature synthesis technique. Using the $Mg(ClO_4)_2$ additive, single phase AlON powder was obtained, while the $KClO_4$ additive leads to small traces of KCl in the final AlON powder. Using the Kubelka–Munk function we have obtained the band-gap values for aluminium oxynitride powders synthesized with the dif-

ferent additives. Our results show that the AlON powder synthesized with the $Mg(ClO_4)_2$ additive has a bigger band-gap energy value than the AlON powder produced with the $KClO_4$ additive (5.85 versus 5.7 eV, respectively). This fact can indicate that the AlON M powder has a smaller amount of defects (shallow traps). We suggest that these defects play a negative role in the transparency of sintered AlON ceramics. The best optical transmission was obtained with AlON M ceramics and it is transparent up to 20% in the visible spectral range.

Acknowledgements

References

[1] G. Yamaguchi and H. Yanagida, Study on the reductive spinel – a new spinel formula AlN–Al_2O_3

instead of the previous one Al_3O_4, Bull. Chem. Soc. Jpn. **32**, 1264–1265 (1959).

[2] J.W. McCauley, A simple model for aluminum oxynitride spinels, J. Am. Ceram. Soc. **61**, 372–373 (1978).

[3] N.D. Corbin, Aluminum oxynitride spinel: A review, J. Eur. Ceram. Soc. **5**(3), 143–154 (1989).

[4] F.Y.C. Boey, X.L. Song, Z.Y. Gu, and A. Tok, AlON phase formation in a tape-cast Al_2O_3/AlN composite, J. Mater. Process. Technol. **89–90**, 478–480 (1999).

[5] C.T. Warner, T.M. Hartnett, D. Fisher, and W. Sunne, in: *Ceramic Armor and Armor Systems II*, Ceramic Transactions Volume 178, ed. E. Medvedovski (The American Ceramic Society, Westerville, Ohio, 2006) pp. 19–35.

[6] J.W. McCauley, P. Patel, M. Chen, G. Gilde, E. Straßburger, B. Paliwal, K.T. Ramesh, and D.P. Dandekar, AlON: A brief history of its emergence and evolution, J. Eur. Ceram. Soc. **29**, 223–236 (2009).

[7] H.X. Willems, M.M.R.M. Hendrix, R. Metselaar, and G. de With, Thermodynamics of Alon I: Stability at lower temperatures, J. Eur. Ceram. Soc. **10**, 327–337 (1992).

[8] J. Zheng and B. Forslund, Carbothermal synthesis of Aluminium Oxynitride (ALON) powder: Influence of starting materials and synthesis parameters, J. Eur. Ceram. Soc. **15**, 1087–1100 (1995).

[9] I.P. Borovinskaya, V.E. Loryan, and V.V. Zakorzhevsky, in: *Nitride Ceramics: Combustion Synthesis, Properties, and Applications* (Wiley-VCH Verlag, Weinheim, 2015).

[10] E.D. Politova, G.M. Kaleva, A.V. Mosunov, N.V. Sadovskaya, D.A. Kiselev, A.M. Kislyuk, T.S. Ilina, and S.Yu. Stefanovich, Dielectric and local piezoelectric properties of lead-free KNN-based perovskite ceramics, Ferroelectrics **569**(1), 201–208 (2020), https://doi.org/10.1080/0015019 3.2020.1822677

[11] E.D. Politova, G.M. Kaleva, A.V. Mosunov, N.V. Sadovskaya, D.A. Kiselev, A.M. Kislyuk, T.S. Ilina, and S. Yu. Stefanovich, in: *Proceedings of 2019 IEEE International Symposium on Applications of Ferroelectrics* (IEEE, 2020), https://doi.org/10.1109/ISAF43169.2019.9034969

[12] E.D. Politova, N.V. Golubko, G.M. Kaleva, A.V. Mosunov, N.V. Sadovskaya, E.A. Fortalnova, D.A. Kiselev, T.S. Ilina, A.M. Kislyuk, S.Yu. Stefanovich, and P.K. Panda, Ferroelectric and local piezoelectric properties of modified KNN ceramics, Integr. Ferroelectr. **196**(1), 52–59 (2019), https://doi.org/10.1080/10584587.2019.1591955

[13] A. Pille, *Development of Optically Transparent Alumina and Spinel Ceramics with Fine Microstructure.* Mechanics of Materials [physics.class-ph], Thesis (Université Sorbonne Paris Cité, 2018).

[14] T.G. Akopdzhanyan and I.P. Borovinskaya, AlON powders by SHS under nitrogen pressure with $KClO_4$ as a booster, Int. J. Self-Propag. High-Temp. Synth. **26**, 244–247 (2017), https://doi.org/10.3103/S1061386217040021

[15] T.G. Akopdzhanyan, I.P. Borovinskaya, and E.A. Chemagina, Aluminum oxynitride by SHS under high pressure of nitrogen gas, Int. J. Self-Propag. High-Temp. Synth. **26**, 110–114 (2017), https://doi.org/10.3103/S1061386217020029

[16] N.S. Kozlova, A.P. Kozlova, E.V. Zabelina, Zh.A. Goreeva, I.S. Didenko, and T. Burt, *Spectrophotometric Methods of Refractive Indices Measurement. Measuring the Refractive Index of Single Crystal Optical Materials Using Two Methods*, Agilent Application Note (2019), https://www.agilent.com/cs/library/applications/application-refractive-index-cary-5000-uv-vis-5994-0052en-us-agilent.pdf

[17] V.M. Zolotarev, *Photonics Materials Research Methods* (ITMO, Saint-Petersburg, 2008) [in Russian].

[18] M.R. Loghman-Estarki, F. Davar, S. Ghorbani, M. Zendehdel, and M.H. Taherian, Synthesis and characterization of aluminum Oxy nitride (AlON) from the nanosized gel precursor, Ceram. Int. **42**, 16861–16866 (2016), https://doi.org/10.1016/j.ceramint.2016.07.180

[19] M.M. Mikhailov and A.C. Verevkin, The variation of band gap width in zirconium oxide powders on grinding, Russ. Phys. J. **47**(6), 600–604 (2004), https://doi.org/10.1023/B:RUPJ.0000047840.56967.3d

SAVAIME SKLINDANČIOS AUKŠTATEMPERATŪRINĖS SINTEZĖS BŪDU GAUTŲ ALIUMINIO OKSINITRIDO MILTELIŲ IR JŲ KERAMIKŲ OPTINĖS SAVYBĖS

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