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MESOPOROUS MAGNESIUM OXIDE XEROGELS – SYNTHESIS AND STRUCTURAL CHARACTERISTICS

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The paper presents the results of a study on the synthesis of magnesium oxide xerogels. In the synthesis, the sol-gel method was used, in which magnesium methoxide was applied as a magnesium precursor. The obtained magnesium hydroxide was subjected to the thermal dehydration process to obtain magnesium oxide particles. The influence of xylene addition during magnesium methoxide hydrolysis on the structure of the magnesium hydroxide and oxide was investigated.

Keywords: *magnesium oxide, xerogel, sol-gel, nanomaterials, MgO crystallite*

W pracy przedstawiono wyniki badań nad syntezą cząstek kserożeli tlenku magnezu. W procesie syntezy zastosowano metodę zol-żel, w której wykorzystano metanolan magnezu jako prekursor tlenku magnezu. Otrzymany wodorotlenek magnezu poddano procesowi termicznej dehydratacji w celu otrzymania tlenku magnezu. Zbadano wpływ dodatku ksylenu na strukturę wodorotlenku i tlenku magnezu.

Słowa kluczowe: *tlenek magnezu, kserożel, zol-żel, nanomateriały, krystalit MgO*

1. INTRODUCTION

The rapid development of nanomaterial chemistry observed in recent years results in the synthesis of nanocrystalline metal oxides with unique sorption and catalytic properties [1-5]. These materials have enhanced surface area, high porosity, and crystallite sizes in the range of 1-10 nm. One such material is nanocrystalline magnesium oxide, which belongs to the group of basic oxides, that occurs naturally as periclase. The nanoparticles of magnesium oxide are used in catalysis, adsorption, and destructive adsorption or chemical adsorption with the simultaneous decomposition of the adsorbate

[6-14]. The unique properties of magnesium oxide nanoparticles are related to the parameters of the texture of the material, small crystallite size, and thus high reactivity [15].

The magnesium oxide is generally obtained in the process of thermal decomposition of magnesium hydroxide or magnesium carbonate [16-17]. An alternative approach to synthesize mesoporous magnesium oxide is a sol-gel method, which uses magnesium alkoxides as metal precursors [8, 18-20]. This process comprises hydrolysis of the magnesium alkoxide in an alcohol solution, removal of the solvent from the wet gel, and then thermal dehydration of the hydroxide to obtain magnesium oxide [21].

Herein, we have synthesized xerogels of highly crystalline magnesium oxide by sol-gel method, with xylene addition during hydrolysis of magnesium methoxide. The effect of the addition of xylene on the structure of magnesium hydroxide and magnesium oxide was investigated.

2. EXPERIMENTAL

2.1. SYNTHESIS OF MAGNESIUM HYDROXIDE XEROGELS

Xerogels of magnesium hydroxide, $Mg(OH)_2$ were prepared according to the procedure proposed in [21]. Magnesium methoxide, $Mg(OCH_3)_2$ was used as a precursor of magnesium. Two 0.4 M solutions of $Mg(OCH_3)_2$ in methanol and methanol with xylene (volume ratio 0.94) were prepared. Additionally, 0.8 M water solutions in methanol and methanol with xylene were prepared. The volume ratio of xylene to methanol was 0.32 and 0.94. In each experiment, 15 ml of the appropriate water solution was stirred in the flask with a magnetic stirrer, and then, 15 ml of a solution of magnesium methoxide was added by pipette. The samples were determined as follows x-KM-y, where x is the mole ratio of water to magnesium methoxide and y is the volume ratio of xylene to methanol. The composition of solutions used for the synthesis of xerogels of magnesium hydroxide is presented in Table 1.

Table 1. Composition of solutions used for the synthesis of magnesium hydroxide.
Tabela 1. Zestawienie składów roztworów zastosowanych w syntezie wodorotlenku magnezu.

COMPOSITION OF SOLUTIONS	2-KM-0	2-KM-0.32	2-KM-0.63
$Mg(OCH_3)_2$ in methanol/xylene	0.4 M; 15 mL	0.4 M;15 mL	0.4 M; 15 mL
H_2O in methanol/ xylene	0.8 M; 15 mL	0.8 M;15 mL	0.8 M; 15 mL
xylene/methanol (vol.) in H_2O solution	0	0	0.32
xylene/methanol(vol.) in $Mg(OCH_3)_2$ solution	0	0.94	0.94
xylene/methanol (vol.) for mixture	0	0.32	0.63

The mixture was vigorously stirred until the start of the gelation process was observed. The resulting gels were subjected to aging in sealed tubes for three days. After that time, the gels were dried in the following manner: at ambient in the open flask for three days, under vacuum at ambient temperature for ca.14 hours, and finally in an oven at 333 K for two days.

2.2. SYNTHESIS OF MAGNESIUM OXIDE XEROGELS

The synthesized samples of magnesium hydroxide were dehydrated to obtain a magnesium oxide. For this purpose, the sample was placed in a quartz crucible and it was heated (under vacuum) in the furnace equipped with the PID temperature controller. The ramp and soak heating condition was the following: ramp from room temperature to 323 K; soak at 323 K for 1 h; ramp from 323 to 723 K at 0.5 K/min; soak at 723 K for 5 h. Next, the furnace was cooled down to ambient, and the sample was placed in the desiccator.

2.3. SAMPLE CHARACTERIZATION

The textural characteristics of the samples were determined from nitrogen adsorption-desorption isotherms measured at 77 K with a Micromeritics ASAP 2000 instrument. The specific surface area S_{BET} was determined using a standard method proposed by Braunauer, Emmett, and Teller [22]. The pore size distribution was determined from the desorption branch of the isotherm using the BJH model [23].

X'Pert Philips diffractometer with Cu–K_{α} radiation (λ=l.5418 Å) equipped with curved graphite monochromator on diffracted beam was applied for the collection of X-ray diffraction patterns at room temperature. X-rays were generated from a Cu anode supplied with 40 kV and a current of 30 mA. The scanning rate of 0.04°/s was used. Crystallites size was calculated employing the Scherrer equation [24].

3. RESULTS AND DISCUSSION

The structural properties of xerogels obtained were determined by measuring the low-temperature nitrogen adsorption and X-ray diffraction. Adsorption/desorption isotherms and the pore size distribution for samples of hydroxide and magnesium oxide xerogels are shown in Fig.1- 4. X-ray diffraction patterns of selected samples are presented in Fig. 5 and 6.

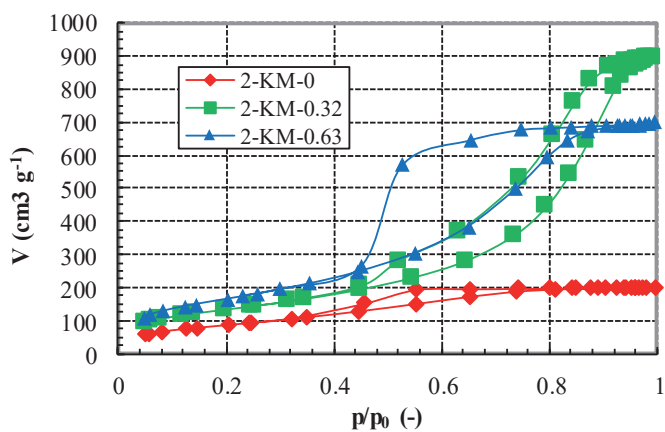The texture and structure parameters of the synthesized materials are presented in Table 2.

Fig. 1. Nitrogen adsorption/desorption isotherms of 2-KM-0 and 2-KM-0.63 before dehydration
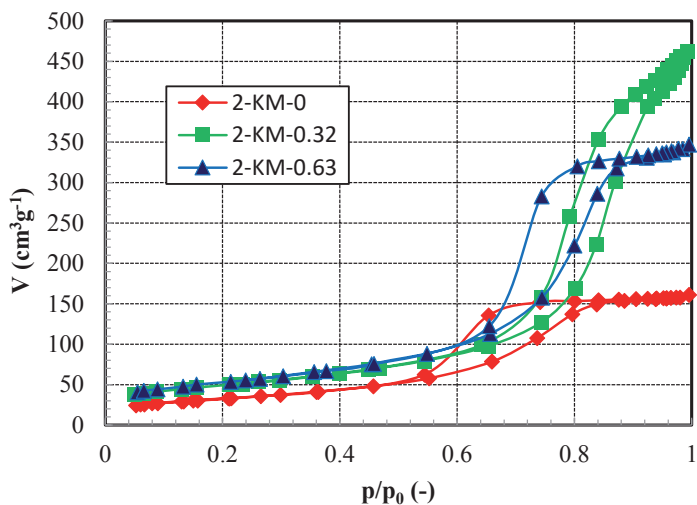Rys. 1. Izotermy adsorpcji/desorpcji azotu próbek 2-KM-0 i 2-KM-0.63 przed dehydratacją

Fig. 2. Nitrogen adsorption/desorption isotherms of 2-KM-0 and 2-KM-0.63 after dehydration
Rys. 2. Izotermy adsorpcji/desorpcji azotu próbek 2-KM-0 i 2-KM-0.63 po dehydratacji
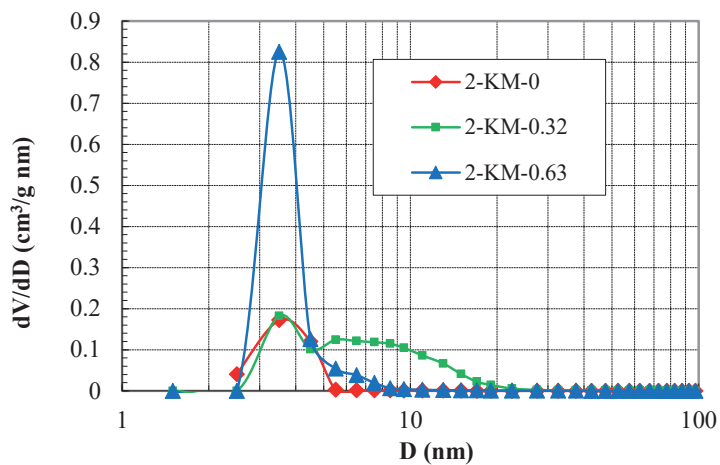
Fig. 3. Pore size distribution of 2-KM-0, 2-KM-0.32 and 2-KM-0.63 samples before dehydration
Rys. 3. Rozkład objętości porów próbek 2-KM-0 2-KM-0.32 i 2-KM-0.63 przed dehydratacją
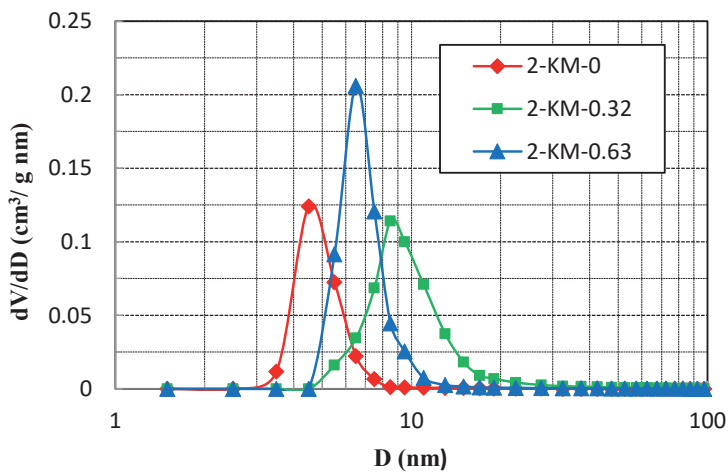

Fig. 4. Pore size distribution of 2-KM-0, 2-KM-0.32 and 2-KM-0.63 samples after dehydration
Rys. 4. Rozkład objętości porów próbek 2-KM-0 2-KM-0.32 i 2-KM-0.63 po dehydratacji
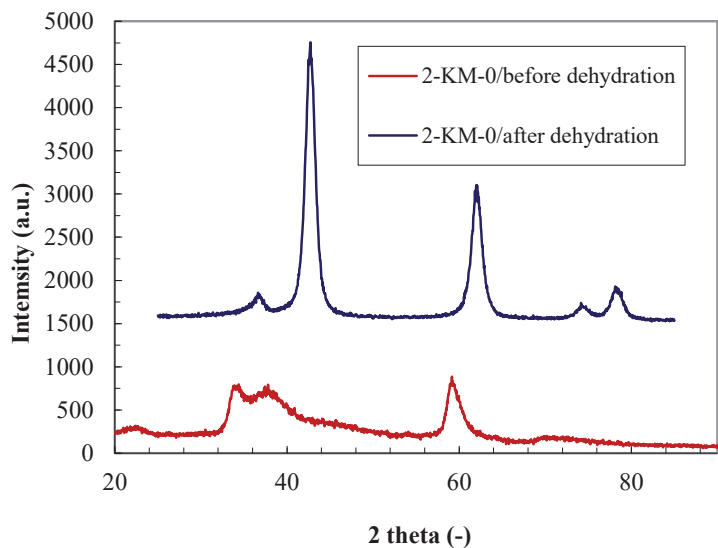
Fig. 5. XRD patterns of 2-KM-0 sample before and after dehydration.
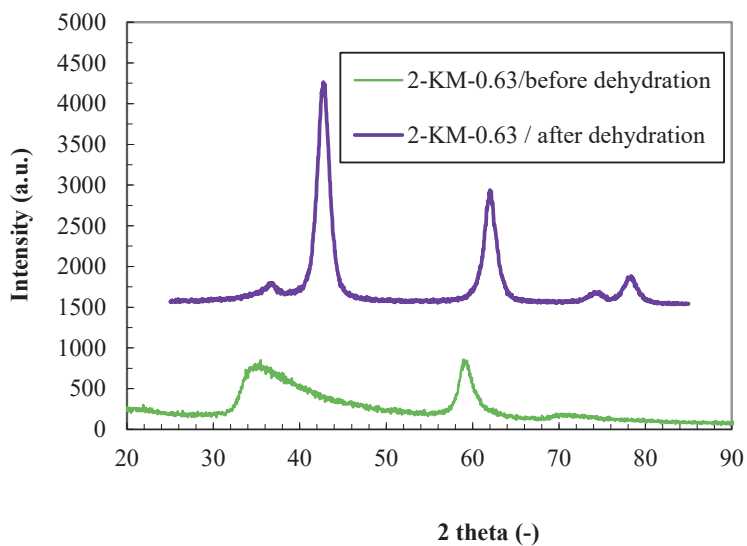Rys. 5. Widma XRD próbki 2-KM-0 przed i po procesie dehydratacji.

Fig. 6. XRD patterns of 2-KM-0.63 sample before and after dehydration.
Rys. 6. Widma XRD próbki 2-KM-0.63 przed i po procesie dehydratacji.

Table 2. Structural parameters of xerogels of Mg(OH)$_2$ and MgO.
Tabela 2. Parametry strukturalne kserożeli wodorotlenku magnezu i tlenku magnezu.

Sample name	S_{BET}, m^2 g^{-1}		V_p, cm^3 g^{-1}		$L_{59(2\theta)}$, nm	$L_{62(2\theta)}$, nm
	Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO	Mg(OH)$_2$	MgO
2-KM-0	321	118	0.34	0.25	5.8	7.8
2-KM-0.32	488	176	1.40	0.71	4.9	6.9
2-KM-0.63	614	189	1.10	0.53	5.4	6.5

All the isotherms exhibit broad capillary condensation hysteresis loops typical for materials possessing mesopores. However, the shapes of the hysteresis loop are different for each sample. The hysteresis loop for the 2-KM-0 sample can be classified as type H3 type according to IUPAC nomenclature. Such behaviour is characteristic for solid consisting of aggregates/agglomerates of particles forming slit-shaped pores. Sample 2-KM-0.32 is characterized by a hysteresis loop of H1 type typical for solids with cylindrical pores. On the other hand, for sample 2-KM-0.63, H2 hysteresis loop is observed. This is typically seen for materials with small openings pores (ink bottle pores).

The specific surface area of magnesium hydroxide and, in consequence, of magnesium oxide samples increased with an increase in the xylene to methanol volume ratio. At the same time, the dehydration process leads to the significant reduction of the specific surface area S_{BET} of magnesium oxide nanoparticles.

The great improvement in the structural parameters of MgO xerogels could result mainly due to the application of hydrophobic solvent (xylene) during the sol-gel process. An excess of xylene affects the hydrolysis-condensation process contributing to the protection of the structure of the gel during the drying process. The incorporation of xylene reduces the surface tension at the gas-liquid-pore wall, which is one of the major causes of stress formation [25].

A significant, more than two-fold increase in the pore volume V_p of the magnesium oxide samples was observed after the addition of xylene. At the same time, based on the presented results, it is difficult to correlate the increase in the pore volume of the samples with the increase in the volume fraction of xylene used for the synthesis. An almost 50% decrease in the pore volume was observed compared to the pristine samples. Pore size distributions for samples 2-KM-0 and 2-KM-0.63 reveal that the samples before dehydration (Fig. 3) contain small mesopores in the range 2.5-5.5 nm and 2.5-9 nm respectively, with a maximum of pore sizes distribution at ca. 3.5 nm. It was observed that sample 2-KM-0.32 had a very broad pore size distribution in the range of 2.5-20 nm. The synthesized magnesium oxide xerogels were characterized by larger mesopores in the range of 3-8.5 nm (sample 2-KM-0), 4.5-20 nm (sample 2-KM-0.32), and 4.5-10

nm (sample 2-KM-0.63). The peak positions are at 4.5 nm, 8.5 nm, and 6.5 nm for samples 2-KM-0, 2-KM-0.32, and 2-KM-0.63, respectively.

XRD patterns of samples before dehydration (Fig. 5 and 6) indicates the presence of $Mg(OH)(OCH_3)$ (decaying peak at 2θ of 33,5°) and peak at 2θ of 59° proves that $Mg(OH)_2$ is present in the large amount [19]. Crystalline structure cannot be well defined for samples before dehydration due to the strong influence of scattering. The rough estimation of magnesium hydroxide crystallites sizes L was made using the Scherrer equation for reflex at 2θ=59°. The results are presented in Table 2.

On the other hand, the XRD spectra of the samples after dehydration reveals the presence of broadened diffraction peak from periclase, the crystalline form of magnesium oxide. No peaks of other impurities were observed, which indicated that the MgO is of high purity. An average MgO crystallite size L calculated from Scherrer equation for reflex at 2θ=62° is between 6.5-7.8 nm, wherein smaller size crystallites characterized xerogels which were synthesized with xylene added.

CONCLUSIONS

- Nanosized magnesium oxide xerogels were obtained in the process of vacuum dehydration of magnesium hydroxide synthesized by the sol-gel method.
- The addition of xylene has a significant effect on the morphology of magnesium oxide and led to the preparation of magnesium oxide xerogels with a higher specific surface area.
- The process of dehydration of magnesium hydroxide results in obtaining MgO nanoparticles characterized by larger crystallites, a smaller specific surface area, and pore volume, as well as a larger pore diameter than the pristine hydroxide.
- MgO crystallite sizes calculated from Scherrer equation for reflex at 2θ=62° is in the range of 6.5-7.8 nm.

OZNACZENIA - SYMBOLS

S_{BET} – specific surface area, $m^2 g^{-1}$
        powierzchnia właściwa BET, $m^2 g^{-1}$
V_p – total pore volume, $cm^3 g^{-1}$
        całkowita objętość zaadsorbowana, $cm^3 g^{-1}$
D – pore diameter, nm
        średnica porów, nm
$L_{59(2\theta)}$, $L_{62(2\theta)}$ – crystallite size (Scherrer equation) for $Mg(OH)_2$ and MgO, respectively, nm
        rozmiar krystalitu (wg równania Scherrera) odpowiednio, dla $Mg(OH)_2$ i MgO, nm

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MEZOPOROWATE KSEROŻELE TLENKU MAGNEZU – SYNTEZA I WŁAŚCIWOŚCI STRUKTURALNE

Obserwowany w ostatnich latach burzliwy rozwój chemii nanomateriałów skutkuje między innymi syntezą nanokrystalicznych tlenków metali o unikalnych właściwościach sorpcyjnych i katalitycznych Materiały te charakteryzują się rozwiniętą powierzchnią właściwą, wysoką porowatością oraz rozmiarami krystalitów w zakresie 1-10 nm. Jedną z takich substancji jest nanokrystaliczny tlenek magnezu, MgO należący do grupy tlenków zasadowych, występujący w przyrodzie jako minerał peryklaz. Nanocząstki tlenku magnezu znajdują zastosowanie w katalizie, adsorpcji oraz destrukcyjnej adsorpcji, czyli adsorpcji z jednoczesnym chemicznym rozkładem adsorbatu. Unikalne właściwości nanocząstek tlenku magnezu związane są z parametrami tekstury materiału, małym rozmiarem krystalitów oraz wysoką reaktywnością powierzchniowych atomów.

W pracy przedstawiono wyniki badań dotyczące otrzymywania kserożeli tlenku magnezu. W procesie syntezy zastosowano metodę zol-żel, w której wykorzystano metanolan magnezu jako prekursor magnezu. Zsyntetyzowane próbki wodorotlenku magnezu poddano procesowi dehydratacji w celu otrzymania tlenku magnezu. Dehydratację przeprowadzono w komorze pieca, w warunkach dynamicznej próżni podnosząc temperaturę do 723 K wg zadanego programu temperaturowego.

Zbadano wpływ wpływu dodatku ksylenu, na etapie hydrolizy metanolanu magnezu, na strukturę wodorotlenku i tlenku magnezu. Parametry tekstury otrzymanych materiałów określono w oparciu o pomiary metodą niskotemperaturowej adsorpcji azotu. Określono powierzchnię właściwą S_{BET}, a z desorpcyjnej gałęzi izotermy rozkład objętości porów metodą BJH. Analiza widm dyfrakcji rentgenowskiej (XRD) umożliwiła określenie wielkości krystalitów zsyntetyzowanych materiałów przy wykorzystaniu równania Scherrera. Proces dehydratacji prowadził do znacznego zmniejszenia powierzchni właściwej S_{BET} otrzymanych cząstek tlenku magnezu (z 320-600 m^2g^{-1} do 120-190 m^2g^{-1}). Jednocześnie dodatek ksylenu na etapie syntezy powoduje, że powierzchnia właściwa kserożeli tlenku magnezu zwiększa się z ok. 120 do 190 m^2g^{-1}. Obecność hydrofobowego rozpuszczalnika jakim jest ksylen, wpływa na proces hydrolizy-kondensacji, obniżając powstające naprężenia w efekcie zmniejszenia napięcia powierzchniowego na granicy gaz-ciecz-por przyczyniając się do ochrony struktury żelu podczas procesu suszenia. Zaobserwowano prawie 50% zmniejszenie objętości porów w stosunku do próbek przed procesem dehydratacji. Objętość porów kserożeli tlenku magnezu wynosiła 0.25-0.71 cm^3g^{-1}. Próbki 2-KM-0 i 2-KM-0.63 przed dehydratacją zawierały małe mezopory w zakresie odpowiednio 2.5-5.5 nm i 2.5-9 nm, z maksimum rozkładu przy ok.

3.5 nm. Próbka 2-KM-0,32 posiadała bardzo szeroki rozkład wielkości porów w zakresie 2.5-20 nm. Kserożele tlenku magnezu charakteryzowały się mezoporami w zakresie 3-8.5 nm (2-KM-0), 4.5-20 nm (2-KM-0.32) and 4.5-10 nm (2-KM-0.63). Maksimum rozkładu wielkości porów występowało przy 4.5 nm, 8.5 nm i 6.5 nm odpowiednio dla próbek 2-KM-0, 2-KM-0.32 oraz 2-KM-0.63.

Widma XRD próbek przed dehydratacją wskazują na obecność $Mg(OH)(OCH_3)$, a pik przy $2\theta=59°$ dowodzi, że wodorotlenek magnezu występuje w dużej ilości. Wielkości krystalitów wodorotlenku magnezu określone dla $2\theta=59°$ wyniosły 4.9-5.8 nm. Z kolei, widma XRD próbek po dehydratacji wskazują na obecność krystalicznej postaci tlenku magnezu, peryklazu. Średnia wielkość krystalitów MgO obliczona dla refleksu przy $2\theta=62°$ mieści się w zakresie 6.5-7.8 nm, przy czym kserożele zsyntetyzowane z dodatkiem ksylenu charakteryzowały się mniejszymi rozmiarami krystalitów.

Dodatek ksylenu na etapie syntezy kserożeli mezoporowatego tlenku magnezu metodą zol- żel, pozwala na otrzymanie cząstek o większej powierzchni właściwej i mniejszym rozmiarze krystalitów, co jest istotne z punktu widzenia potencjalnego zastosowania tego rodzaju materiałów w praktyce.