

Structure studies on nanocrystalline powder of MgO xerogel prepared by the sol-gel method

G. DERCZ^{1,*}, K. PRUSIK¹, L. PAJĄK¹, R. PIELASZEK², J. J. MALINOWSKI³, W. PUDŁO⁴

¹University of Silesia, Institute of Materials Science, ul. Bankowa 12, 40-007 Katowice, Poland

²Polish Academy of Sciences, High Pressure Research Center, ul. Sokołowska 29/37, Warsaw, Poland

³Polish Academy of Sciences, Institute of Chemical Engineering, ul. Bałtycka 5, 41-100 Gliwice, Poland

⁴Silesian Technical University, Faculty of Chemistry, ul. M. Strzody 9, 41-100 Gliwice, Poland

Structure studies were performed on nanocrystalline powder of MgO xerogel prepared by the sol-gel technique, producing high purity, chemically homogeneous materials of relatively high specific surface area. Magnesium methoxide was used as an MgO precursor. The wet gel was dried under conventional conditions, yielding xerogel with periclase phase; the only crystalline form of magnesium oxide. The X-ray diffraction, scanning and transmission electron microcopies were used as the tools of structure analysis. The Toraya PRO-FIT procedure and the Rietveld refinement method were applied for X-ray data analysis. Both techniques apply the Pearson VII function for the description of line profiles. The gamma crystallite size distribution was determined using the FW(1/5)/(4/5)M method proposed by Pielaszek. The obtained values of $\langle R \rangle$ and σ (measure of polydispersity) of particle size parameters are equal to 7.1 nm and 2.1 nm, respectively, whereas the average crystallite size, estimated by the Williamson-Hall procedure, was equal to 7.5 nm. The R_{wp} , and S fitting parameters obtained from the Rietveld refinement were equal to 6.4% and 1.8, respectively. This would seem the most satisfactory result, when considering the nanosize of MgO crystallites and a very probable presence of amorphous phase.

Key words: MgO; xerogel; nanocrystalline material; Rietveld refinement; Toraya procedure; XRD; TEM; SEM

1. Introduction

There is currently a revolution in new materials that deals with the synthesis of nanoparticles of inorganic substances. Nanostructured materials with high surface area, high porosity, and particle sizes in the 1–10 nm range are becoming more available. These materials have shown great promise as adsorbents and catalysts [1].

*Corresponding author, e-mail: grzegorz.dercz@us.edu.pl

Magnesium oxide is an interesting basic oxide that has many applications in catalysis, adsorption and in the synthesis of refractory ceramics [2–5]. It is a unique solid because of its highly ionic character, simple stoichiometry and crystal structure, and it can be prepared in widely variable particle sizes and shapes [6]. It has been documented that the shape and size of nanocrystalline magnesium oxide particles endow them with high specific surface and reactivity, because of the high concentration of edge/corner sites and structural defects on their surface [7]. All these factors play a role in high efficiency of these materials in various heterogeneous reactions, e.g., with organophosphorous [8] and halogenated compounds [9].

The sol-gel synthetic route based on the use of magnesium alkoxide precursor, followed by drying under different conditions, has proved to be an efficient and successful approach to the production of nanocrystalline magnesium oxide particles [5, 7, 10].

The present work involves the structure analysis of nanocrystalline powder of MgO xerogel prepared by the sol-gel method with conventional drying procedure applied during synthesis. This analysis was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The above methods are standard ones used in studies of nanocrystalline materials [11–15].

2. Experimental

As the precursors, commercially available magnesium methoxide solution (Aldrich, 8.96 wt. % in methanol), methanol (POCH), and toluene (POCH) were used. The applied molar hydrolysis ratio was equal to 2 and the hydrolysis of magnesium methoxide solution was conducted in the presence of toluene. The volume ratio of toluene to methanol was 0.94. The gelling process was visually monitored by gently tilting the vials from time to time, to observe any change in the viscosity of the alcogel. Prior to drying, the wet gels were conventionally aged for 3 days. After ageing, the caps of vials containing alcogels were loosened for a few days to allow slow evaporation of the solvents. Next, the alcogels were vacuum-dried at room temperature for 12 h. Finally, the vials were transferred to an oven and heated at 60 °C for 48 h until constant weight was obtained. Heat treatment of magnesium hydroxide xerogel samples at 723 K under dynamic vacuum yielded the dehydrated magnesium oxide.

The Toraya PRO-FIT procedure and Rietveld refinement method were applied in X-ray data analysis. The PRO-FIT procedure enables the determination of parameters of individual diffraction lines, and applies the Pearson VII function for the description of line profiles [16]. This function appeared to be the most useful also in the Rietveld refinement procedure. The Rietveld analysis was performed using the DBWS-9807 program, which is an updated version of the DBWS programs for the Rietveld refinement with PC and mainframe computers [17]. The crystallite sizes and lattice distortions were analyzed using the Williamson-Hall method [18]. The crystallite size distribution was determined using the Pielaszek procedure [19].

X-ray diffraction patterns were collected by an X-Pert Philips diffractometer equipped with a curved graphite monochromator on diffracted beam, and with the following slits (in the sequence from copper tube to proportional counter): Soller (2°), divergence ($1/2^\circ$), antiscatter ($1/2^\circ$), Soller (2°) and receiving (0.15 mm). The powder morphology was analyzed using the SEM (JEOL JSM-6480) and TEM (JEOL 3010) techniques. A nitrogen adsorption-desorption isotherm measured at 77 K with a Micromeritics ASAP 2000 instrument was used to obtain the value of the specific surface area, S_{BET} .

3. Results and discussion

The X-ray diffraction pattern presented in Fig. 1 clearly shows that in the studied powder sample periclase is present, the only crystalline form of magnesium oxide. The broadening of diffraction lines is clearly seen.

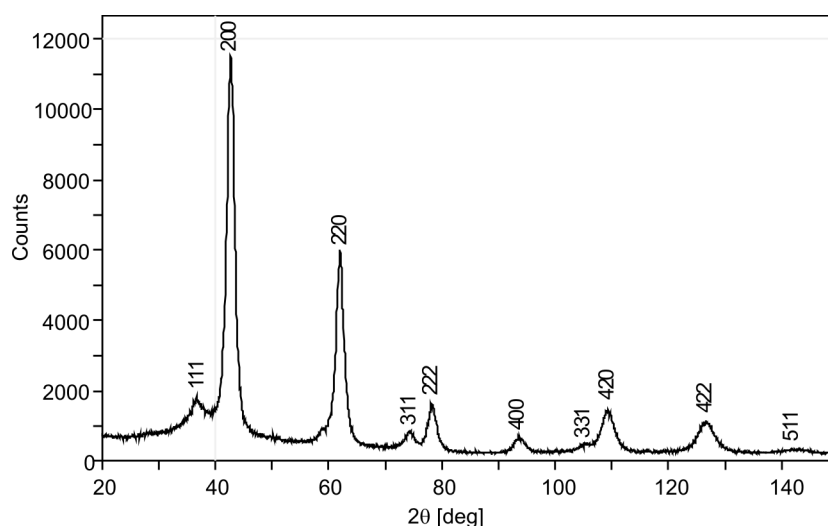


Fig. 1. X-ray diffraction pattern of MgO powder

From the analysis of the Williamson-Hall plot (not presented here) it can be concluded that the size-broadening is the main component of physical line broadening. The estimated average size of MgO crystallites is equal to 7.5 nm, whereas the lattice distortion is negligible (0.11%). The Pielaszek procedure [19] was applied to determine the size distribution of MgO nanocrystallites. The measurement of two widths of the same diffraction line at $1/5$ and $4/5$ of the peak maximum ($\text{FW}1/5\text{M}$ and $\text{FW}4/5\text{M}$, respectively) allows the determination of the average crystallite size $\langle R \rangle$ and the dispersion of sizes σ , which is more informative. From these parameters the gamma crystallite size distribution [19] can be drawn. The dispersion parameter σ , a measure of the crystallite size polydispersity, is as

$$\sigma = \sqrt{\langle R^2 \rangle - \langle R \rangle^2} \quad (1)$$

The procedure proposed by Pielaszek bears the same limitations as the Scherrer method. This means that only size-broadening of diffraction lines appears, whereas stacking fault, twinning probabilities and lattice strains are negligible. The applied sol-gel preparation procedure, high symmetry of crystal structure (diffraction lines do not overlap) and ionic binding of MgO are very convenient in fulfilling the above limitations. The crystallite size distribution, as calculated by the Pielaszek procedure, is presented in Fig. 2. A 200 diffraction line profile was applied in calculations; relatively large polydispersity of crystallite sizes was observed.

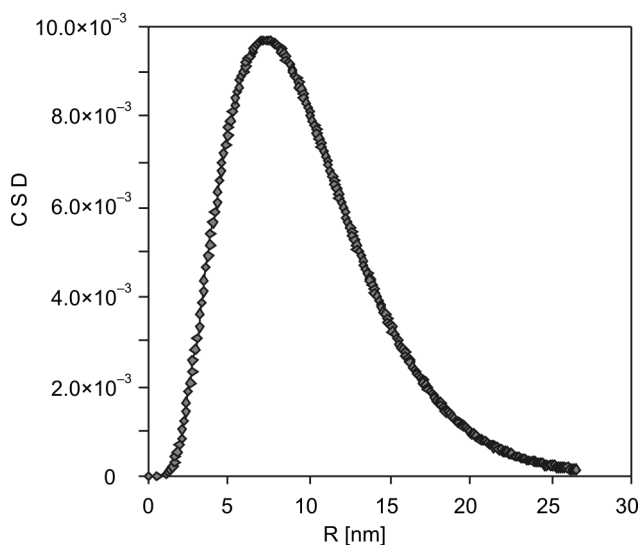


Fig. 2. Gamma crystallite size distribution (CSD) with average crystallite size $\langle R \rangle = 7.1 \text{ nm} \pm 0.6 \text{ nm}$ and dispersion $\sigma = 2.1 \text{ nm} \pm 0.2 \text{ nm}$

The Rietveld refinement method was used for the determination of the lattice parameter of MgO nanocrystalline phase (Table 1).

Table 1. Lattice (a_0), crystallite size (D , $\langle R \rangle$, σ) and lattice distortion ($\langle \Delta a/a \rangle$) parameters for studied MgO powder

Space group	a_0 , lattice parameter		Williamson - Hall		FW(1/5)/(4/5)M	
	Rietveld [nm]	ICDD [nm]	D [nm]	$\langle \Delta a/a \rangle$ [%]	$\langle R \rangle$ [nm]	Σ [nm]
$Fm\bar{3}m$	0.4226(1)	0.4213	7.5(9)	0.11(2)	7.1(6)	2.1(2)

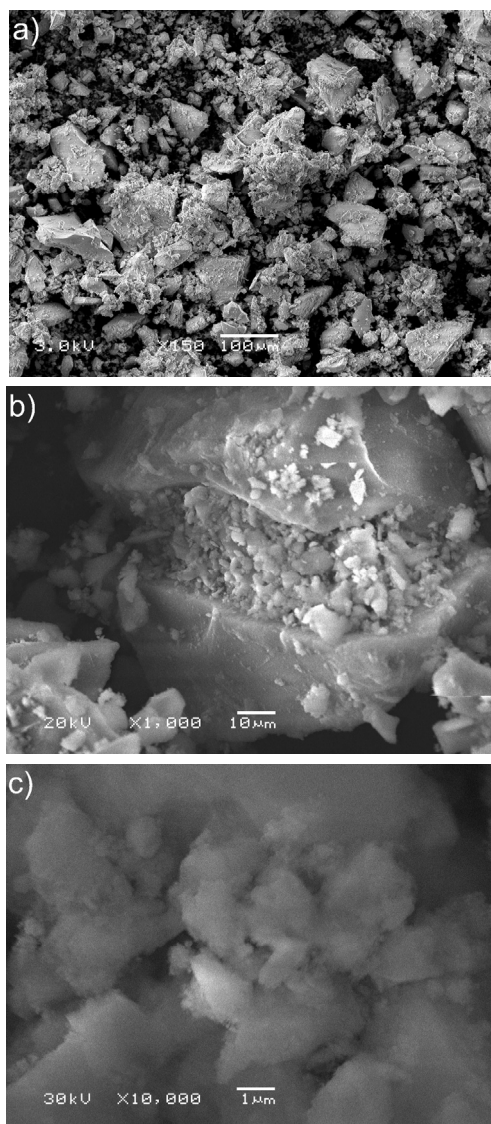


Fig. 3. SEM images of the MgO powder

Scanning and transmission electron microscopy images are presented in Figs. 3 and 4, respectively. These images indicate that the powder sample is an agglomerate of particles. From the analysis of TEM images and the X-ray diffraction pattern, it can be concluded that the amorphous phase is also present. Thus the values of R_{wp} and the S fitting parameters obtained from the Rietveld refinement, equal to 6.41% and 1.81, respectively, seem to be satisfactory. The electron microscopy images indicate an extended surface of powder particles. The specific surface area, as determined by the BET method, is equal to 138 m²/g.

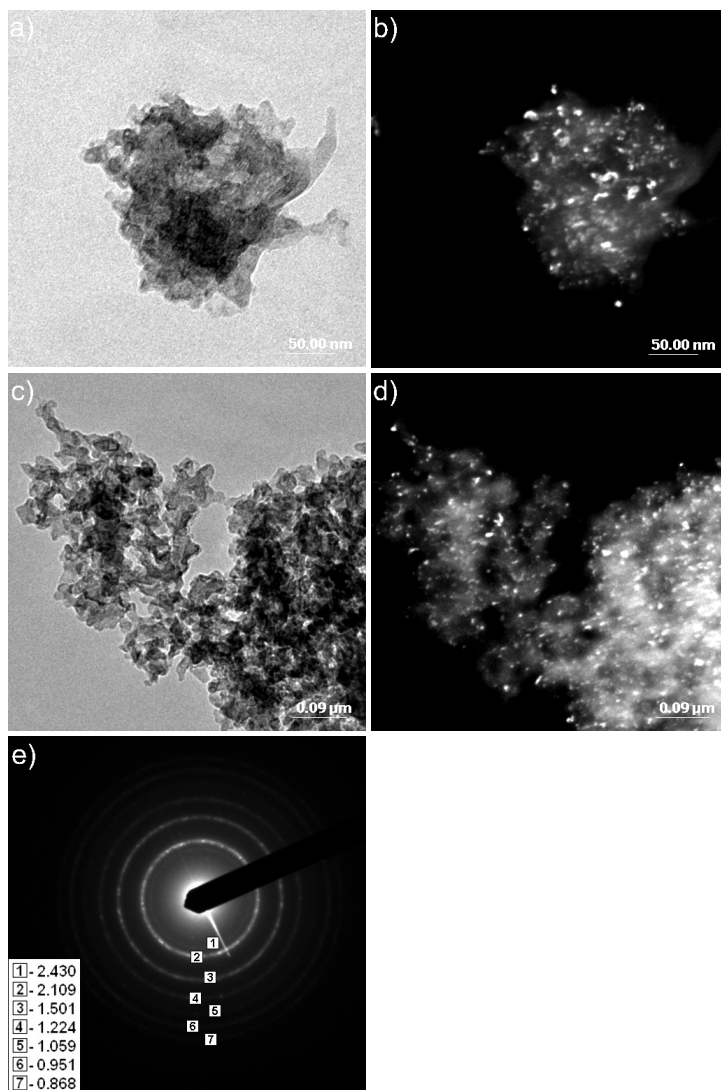


Fig. 4. TEM images of the MgO sample:
a, c) bright field, b, d) dark-field and e) electron diffraction pattern

4. Conclusions

The observed diffraction line broadening from MgO phase can be attributed to fine crystallite size. Good agreement between the average crystallite sizes, as determined by the Williamson–Hall analysis and by the Pielaszek procedure, was obtained. From the Williamson–Hall analysis, the lattice distortion ($\langle \Delta a/a \rangle$) is relatively low and equal to 0.11 %, whereas the average crystallite size is estimated to be 7.5 nm.

The average crystallite size determined by the Pielaszek procedure is equal to 7.1 nm, with dispersion σ (measure of crystallite size polydispersity) equal to 2.1 nm. Despite the nanosize of MgO crystallites and the presence of amorphous phase, a good fit was found between the calculated X-ray pattern and the experimental one from the Rietveld refinement. Scanning and transmission electron microscopy images show the agglomerate nature of the powder sample, and an unfolded surface. The specific surface area, determined by the BET method, is equal to 138 m²/g.

References

- [1] LUCAS E., DECKER S., KHALEEL A., SEITZ A., FULTZ S., PONCE A., LI W., CARNES C., KLABUNDE K.J., *Chem. Eur. J.*, 7 (2001), 2505.
- [2] CHOUDHARY V.R., RANE V.H., GADRE R.V., *J. Catal.*, 145 (1994), 300.
- [3] RAJAGOPALAN S., KOPER S., DECKER S., KLABUNDE K.J., *Chem. Eur. J.*, 8 (2002), 2602.
- [4] XU B.Q., WEI J.H., WANG H.Y., SUN K.Q., ZHU Q.M., *Cat. Today*, 68 (2001), 217.
- [5] UTAMAPANYA S., KLABUNDE K.J., SCHLUP J.R., *Chem. Mater.*, 3 (1991), 175.
- [6] MORRIS R.M., KLABUNDE K.J., *Inorg. Chem.*, 22 (1983), 682.
- [7] KLABUNDE K.J., STARK J., KOPER O., MOHS C., PARK D.G., DECKER S., JIANG Y., LAGADIC I., ZHANG D., *J. Phys. Chem.*, 100 (1996), 12142.
- [8] LI Y.X., SCHLUP J.R., KLABUNDE K.J., *Langmuir*, 7 (1991), 1394.
- [9] HOOKER P.D., KLABUNDE K.J., *Environ. Sci. Technol.*, 28 (1994), 1248.
- [10] ŠTENGL V., BAKARDJEVA S., MAŘIKOVÁ M., BEZDIČKA P., ŠUBRT J., *J. Mater. Sci.*, 57 (2003), 3998.
- [11] JUNG H.S., LEE J.K., KIM J.Y., HONG K.S., *J. Sol. State Chem.*, 175 (2003), 278
- [12] WANG J.A., NOVARO O., BOKHIMI X., LÓPEZ T., GÓMEZ R., NAVARRETE J., LLANOS M.E., LÓPEZ-SALINAS E., *Mater. Lett.*, 35 (1998), 317.
- [13] NAKAMURA Y., OGURO K., UEHARA I., AKIBA E., *J. Alloys Compd.*, 298 (2000), 138.
- [14] DERCZ G., PRUSIK K., PAJĄK L., GORYCZKA T., FORMANEK B., *J. Alloys Compd.*, 423 (2006), 112.
- [15] DERCZ G., FORMANEK B., PRUSIK K., PAJĄK L., *J. Mater. Proc. Tech.*, 162–163 (2005), 15.
- [16] TORAYA H., *J. Appl. Cryst.*, 19 (1986), 440.
- [17] YOUNG R.A., SAKHIVEL A., MOSS T.S., PAIVA-SANTOS C.O., *J. Appl. Cryst.*, 28 (1995), 366.
- [18] WILLIAMSON G.K., HALL W.H., *Acta Metall.*, 1 (1953), 22.
- [19] PIELASZEK R., *J. Alloys Compd.*, 382 (2004), 128.

Received 18 February 2008

Revised 2 June 2008