

## Structural Changes of ZnO – Cr<sub>2</sub>O<sub>3</sub> System during Mechanical Activation and Their Influence on the Spinel Synthesis

ZORICA V. MARINKOVIĆ<sup>1</sup>, TATJANA V. SREČKOVIĆ<sup>2</sup>, IREANA PETROVIĆ-PRELEVIĆ<sup>2</sup> and MOMČILO M. RISTIĆ<sup>3</sup>

<sup>1</sup>Center for Multidisciplinary Studies, University of Belgrade, Kneza Višeslava 1a, Belgrade 11000 (Yugoslavia)

<sup>2</sup>Faculty of Mining and Geology, University of Belgrade, Kneza Višeslava 1a, Belgrade 11000 (Yugoslavia)

<sup>3</sup>Serbian Academy of Sciences and Arts, Kneza Višeslava 1a, Belgrade 11000 (Yugoslavia)

E-mail: mzorica@mi.sanu.ac.yu

### Abstract

An equimolar ZnO and Cr<sub>2</sub>O<sub>3</sub> powder mixture was mechanically activated by grinding using a high-energy vibrational mill for 0–180 min. Structural changes of the material that occur during mechanical treatment were analyzed using the surface characterization method (specific surface area, and based on the latter the calculated mean particle size) and X-ray diffraction line broadening theory. The characteristic temperatures within in the temperature range of 20–1100 °C that is the consequence of a solid state reaction were determined using differential thermal analysis. Evolution of the phase composition of the solid state reaction between zinc oxide and chromium oxide was followed using X-ray analysis of samples isothermally sintered at 900 °C for 15, 60, 120 and 240 min.

### INTRODUCTION

Mechanical activation is used a lot as a method for the modification of physicochemical properties of dispersed systems in technologies for obtaining powders and ceramics [1, 2]. Among other things, the influence of the mechanical activation on starting compounds is manifested by an important increase of crystal lattice microstrain values [3].

It is already established that some spinels have advanced gas sensing and catalytic properties [4, 5]. There is also a number of ceramic materials with spinel crystal structure used for humidity sensing. Spinel, such as ZnCr<sub>2</sub>O<sub>4</sub>, are very suitable for aggressive environments [6].

The present work reports an investigation concerned with the influence of mechanical activation on microstructural changes of the ZnO – Cr<sub>2</sub>O<sub>3</sub> system and their influences on the spinel synthesis.

### EXPERIMENTAL

Mixtures of starting ZnO (Merck, p. a. 99 %) and Cr<sub>2</sub>O<sub>3</sub> (Fluka, p. a. 99 %) powders in equimolar quantities were used in experimental procedures. Mechanical activation was performed by grinding (dry), of conventionally prepared mixture of powders, in a continual regime in a vibrational mill with steel rings (CUP Mill Type MN 954/3 KHD HUMBOLDT WED-AG AG) in air. Grinding times were varied from 5 to 180 min. Specific surface area determinations of starting powders and mechanically activated mixtures were carried out using the BET method with N<sub>2</sub> adsorbate (Gilas-Alcetel XR 850 instrument). The particle size was calculated from the specific surface area with the presumption of spherical shape.

Zinc oxide and chromium oxide powder mixtures activated for 0, 40 and 80 min were chosen for further characterization. In order to clarify the obtained results, the following de-

TABLE 1

Specific surface area and particle size of the examined powders

Sample	$S_p$ , $m^2/g$	$d$ (spherical shape), $mm$
ZnO	3.85	0.278
$Cr_2O_3$	4.26	0.270
ZC-00	4.89	0.229
ZC-05	5.46	0.206
ZC-10	7.13	0.158
ZC-20	7.67	0.146
ZC-40	8.09	0.139
ZC-80	5.50	0.204
ZC-120	6.78	0.187
ZC-180	7.37	0.152

notation will be used for activated mixtures: ZC- $t$ , where number  $t$  represents the time of activation.

The behaviour of powders during thermal treatment between 20 and 1100 °C in air was monitored by differential thermal analysis with constant heating rate of 10 °C/min, using Netzch Sta 409 instrument.

Heating under isothermal conditions was carried out in furnace (Lenton Tube furnace LTF) at temperature of 900 °C for 15, 60, 120 and 240 min in air.

X-ray diffraction data for mechanically activated mixtures and thermally treated samples were collected in the range 0–80° (2 $\theta$ ), using Phillips PW-1820 diffractometer with  $CuK_\alpha$

radiation and graphite monochromator, in step-scanning mode (0.02 °/2 s).

## RESULTS AND DISCUSSION

Investigations of kinetics of mechanical activation, regardless of the type of mill, proved that the change of particle size during this process is usually performed through three stages [1, 3]. The first stage is characterized by the reduction of particle size *vs* time, the second is the agglomeration process and the third one is an equilibrium process during which the particle size is practically the same. Specific surface area changes in an analogous way, but in the opposite direction.

Analysis of results given in Table 1 showed that grinding process regarding the ZnO –  $Cr_2O_3$  system could be described as a three-stage process mentioned above. The dominant process during the first stage of grinding (0–40 min) is materials comminution, during which the amount of finely dispersed material is increased, as well as the concentration of structure defects and surface charge, *etc.* Generally, this leads to a raising trend of agglomeration thus contributing to the decrease of specific surface area [1], which was noticed during the second stage of grinding (40–80 min).

Further activation, for more than 80 min, being the third stage of grinding, is charac-

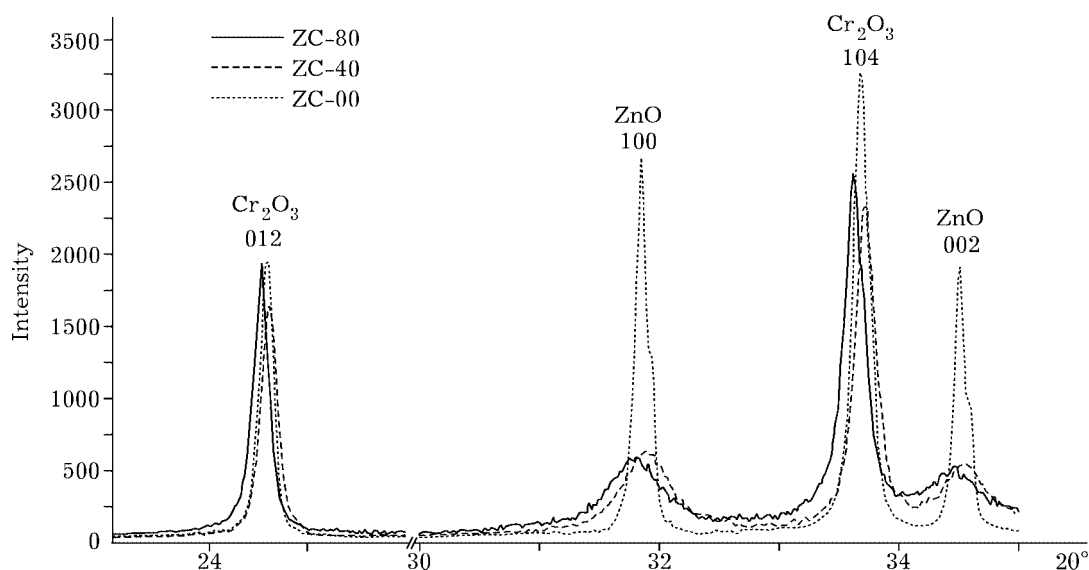


Fig. 1. X-ray diffraction patterns of the examined ZnO –  $Cr_2O_3$  mixtures.

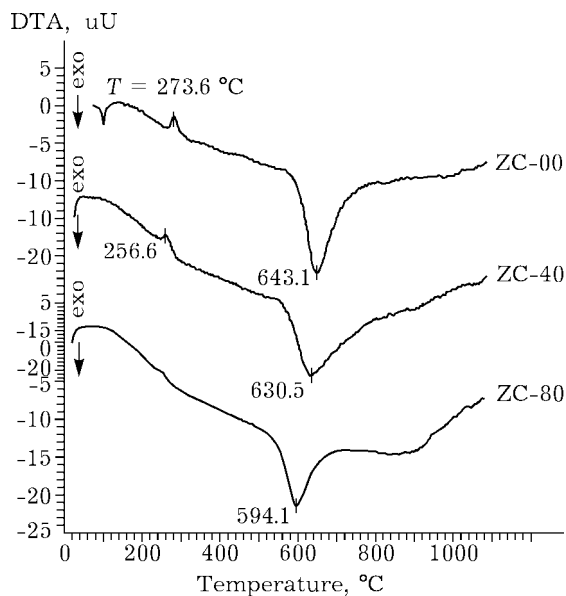


Fig. 2. Curves obtained by differential thermal analysis from mechanically activated mixtures.

terized by the increase of specific surface area due to the process of breaking and grinding of previously formed particle assemblages – granules, agglomerates and aggregates. Most probably, comminution and deformation of the residual initial particles also occur. There are many systems where the secondary agglomeration structure is destroyed during grinding. This process may not have a significant influence on the increase of dispersivity, but rearrangement disorder of atomic bonds could change the material behavior essentially [7].

Qualitative XRPD analysis of mechanically treated powders showed the presence of two phases, ZnO and Cr<sub>2</sub>O<sub>3</sub>, in all three different mixtures (Fig. 1). Furthermore, no new (spinel) phase was detected, and thus we conclude that mechanochemical reactions did not occur during milling.

TABLE 2

Microstructural parameters of ZnO at diffraction lines (100) and Cr<sub>2</sub>O<sub>3</sub> at diffraction lines (012) obtained by double-Voight method

Sample	ZnO		Cr <sub>2</sub> O <sub>3</sub>	
	$D_v$ , Å	$\langle e^2(D_v/2) \rangle^{1/2}$	$D_v$ , Å	$\langle e^2(D_v/2) \rangle^{1/2}$
ZC-00	985(30)	7.0(1)	419(14)	–
ZC-40	90(7)	–	373(33)	9(8)
ZC-80	40(20)	–	405(49)	10(6)

Note.  $D_v$  – volume weighted crystallite size;  $\langle e^2(D_v/2) \rangle^{1/2}$  – root mean square strain.

Mechanical energy introduced in the system by activation is used for the comminution of the constituent phases and mainly for disordering of the ZnO crystal lattice. Big crystallites and crystal grains of ZnO in non-activated powder mixture (ZC-00) give sharp characteristic reflections as noticed in the X-ray pattern, while the reduction of crystallite degree of ZnO in activated powder mixtures (ZC-40 and ZC-80) causes broadening of diffraction lines (see Fig. 1).

Simultaneously, with the change of particle size during materials dispersion, other consequences of profound changes that occur in a material such as the reduction of mean crystallite size, defect of the crystal lattice and residual microstrains, should be analyzed.

Microstructural changes in the constituent powders as a consequence of grinding were investigated by X-ray diffraction line broadening theory [8]. Sharp ZnO peaks of non-activated powder become considerably broadened after 80 min of grinding. Broadening of ZnO peaks indicates that reduction of crystallite size occurs due to intensive milling.

Analysis of microstructural parameters calculated from the diffraction data obtained from differently activated ZnO and Cr<sub>2</sub>O<sub>3</sub> powder mixtures shows that basic microstructural changes occur with zinc oxide particles within the examined time period of mechanical activation. Results presented in Table 2 and Fig. 1 show that after 40 min of activation ZnO crystallite size decreases nearly 10 times, and slightly decreases during 40 min of activation. In the examined grinding range Cr<sub>2</sub>O<sub>3</sub> crystallite size changes very little, practically within the standard deviation. Different behavior could be explained by the great difference of the crystal lattice energy of ZnO and

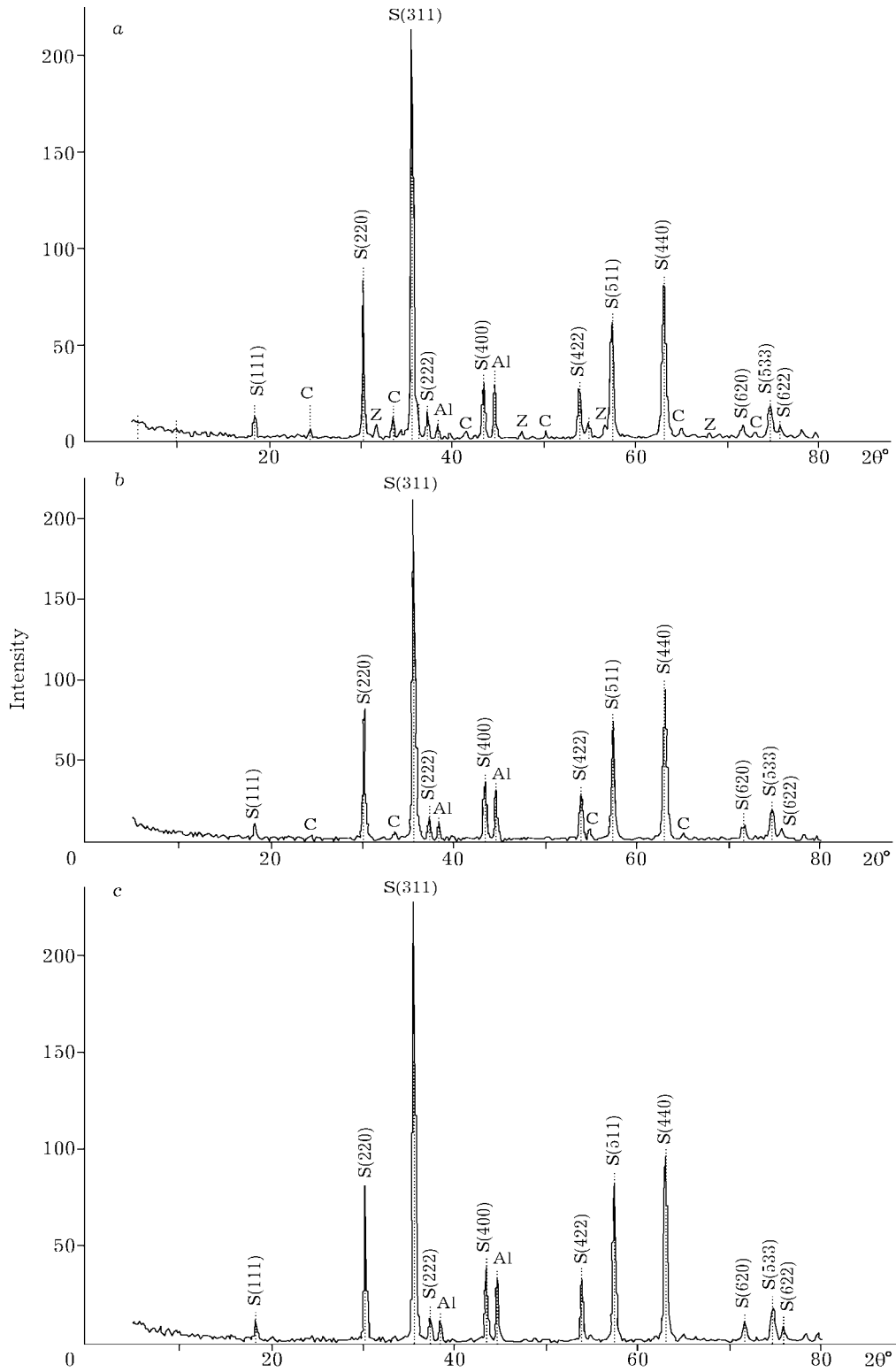


Fig. 3. X-ray diffraction patterns for the isothermal heating,  $T = 900^\circ\text{C}$  and  $t = 60$  min, of samples ZC-00 (a), ZC-40 (b) and ZC-80 (c). Here and in Fig. 4: S - ZnCr<sub>2</sub>O<sub>4</sub> (spinel), Al - Al holder, C - Cr<sub>2</sub>O<sub>3</sub>; Z - ZnO.

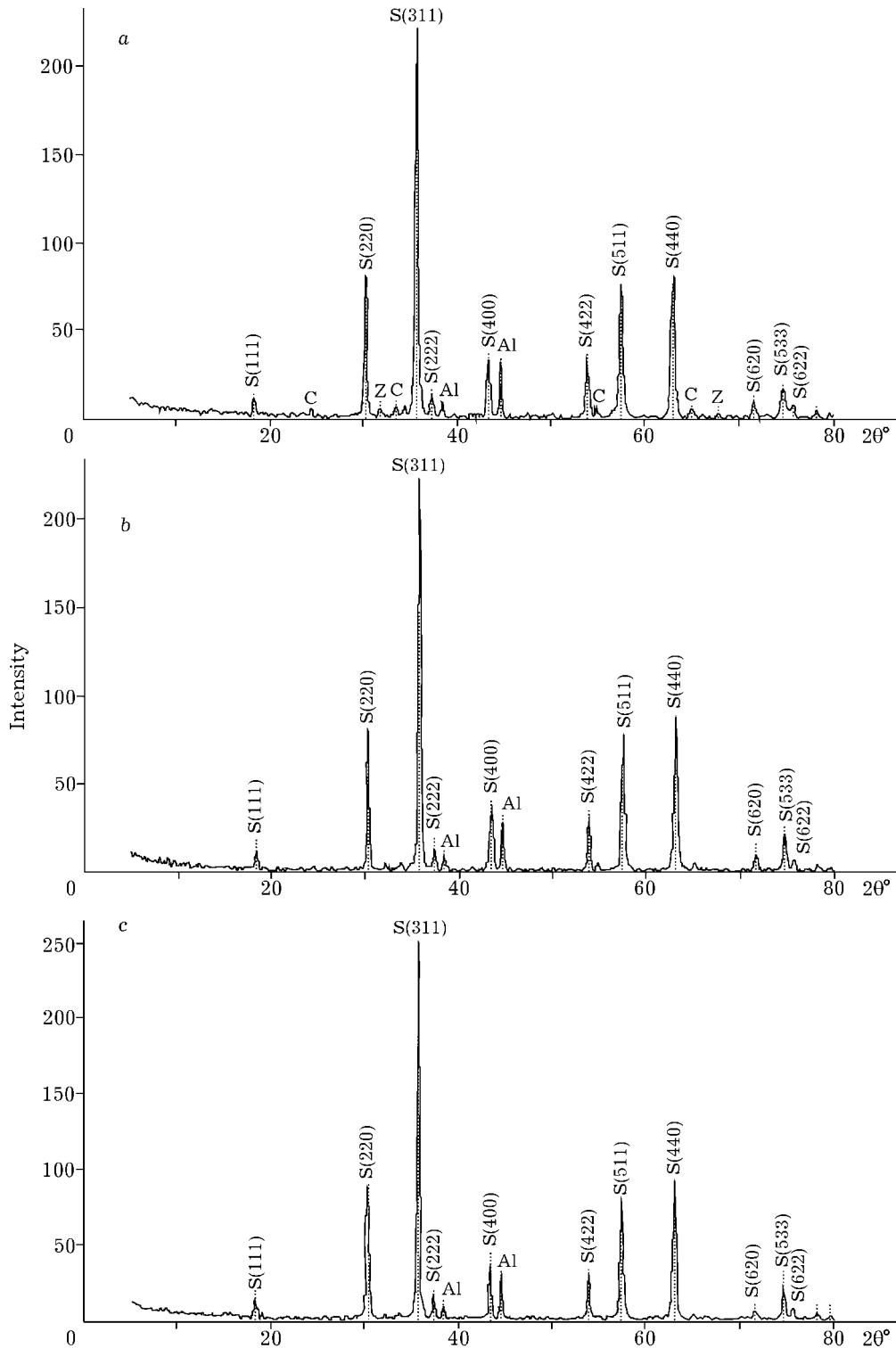


Fig. 4. X-ray diffraction patterns for the isothermal heating,  $T = 900$  °C and  $t = 120$  min, of samples ZC-00 (a), ZC-40 (b) and ZC-80 (c).

Cr<sub>2</sub>O<sub>3</sub> being 4107.25 and 15 186 kJ/mol, respectively [9]. One could say that the dominant process in the ZnO–Cr<sub>2</sub>O<sub>3</sub> system is the destruction of ZnO crystal structure due to high microhardness of Cr<sub>2</sub>O<sub>3</sub> [10].

It can be concluded that the residual microstrains of crystallites are present in insignificant amount because their values are low with extremely high standard deviation, or are impossible to detect.

The next question is whether agglomerated powders formed during the second stage of activation are more or less active. The results obtained using DTA analysis undoubtedly show that powders activity is raising with the grinding time regardless of the process of agglomeration.

The exothermic peak observed at DTA thermograms (Fig. 2) corresponds to a solid state reaction between ZnO and Cr<sub>2</sub>O<sub>3</sub>. This is the result of a nucleation process and the initial stage of reaction product formation, the spinel phase of ZnCr<sub>2</sub>O<sub>4</sub>. It is quite clear that the position of exothermal peak moves towards lower temperatures for activated mixtures ZC-40 and ZC-80 (630.5 and 594.1 °C, respectively) with respect to the non-activated mixture ZC-00 (643.1 °C). Hence, systems activity is increasing due to the increase of total specific surface area (internal + external) regardless of the decrease of the free specific surface area. This phenomenon could be explained in the following way.

During the first stage of grinding an increase of specific surface area occurs, and therefore the total system's energy is rising mainly on the account of the increase of surface energy of the system. Due to the high increase of systems surface energy, agglomeration of particles, *e. g.* the reduction of systems surface energy occurs during the second stage of grinding. However, the existence of newly built internal surfaces has a significant influence on the increase of internal system's energy, which contributes to further increase of system's activity [11].

The influence of mechanical activation on the solid state reaction in the ZnO – Cr<sub>2</sub>O<sub>3</sub> system was examined in details during isothermal heating at 900 °C for 15, 60, 120 and 240 min. Detailed quantitative analysis of X-ray diffractograms of sintered samples point to the existence of all three phases – the initial ZnO and Cr<sub>2</sub>O<sub>3</sub>, and ZnCr<sub>2</sub>O<sub>4</sub> as a reaction product in samples ZC-00 sintered for 15, 60 and 120 min. The appearance of only one, spinel phase was noticed just in samples sintered for 240 min [12]. The existence of only zinc chromate was also noticed in samples ZC-40 after sintering for 120 min and samples ZC-80 after sintering for 60 min. X-ray patterns pre-

sented in Figs. 3 and 4 show the influence of mechanical activation and time of activation on the acceleration of the solid state reaction.

## CONCLUSION

It was established that the kinetics of mechanical activation of ZnO and Cr<sub>2</sub>O<sub>3</sub> powder mixture occurs in three stages (I – grinding, II – agglomeration, III – fine grinding of previously formed agglomerates and further grinding of the starting structures). Activity of powders increases with the increase of the grinding time, regardless of the agglomeration process.

Analysis of microstructural parameters revealed that essential microstructural changes occur mainly in the crystal structure of ZnO. Mechanical activation caused significant reduction of zinc oxide crystallite size. These phenomena were not observed for chromium oxide.

The influence of mechanical activation of the starting mixture on the solid state reaction between ZnO and Cr<sub>2</sub>O<sub>3</sub> was studied under isothermal conditions. It was established that the increase of activation time lowers the temperature of the beginning of sintering reaction, and accelerates the formation of spinel (zinc chromate), thus enabling the reduction of the temperature range for performing the reaction.

## REFERENCES

- 1 G. Heinicke, *Tribochemistry*, Akademie-Verl., Berlin, 1984.
- 2 Ye. G. Avvakumov, *Mechanical Methods of the Activation of Chemical Processes*, Nauka, Novosibirsk, 1986 (in Russian).
- 3 K. Tkačova, *Mechanical Activation of Minerals*, Elsevier, Amsterdam, 1989.
- 4 Y. Shimizu and S. Kusano, *J. Am. Ceram. Soc.*, 73 (1990) 818.
- 5 L. C. Honeybourne and R. K. Rasheed, *J. Mater. Chem.*, 6, 3 (1996) 277.
- 6 J. Fagan and V. Amarakoon, *Am. Ceram. Soc. Bull.*, 72, 3 (1993) 119.
- 7 G. S. Khodakov, *Uspekhi khimii*, TXXXII (1963) 860.
- 8 B. E. Warren, *X-Ray Diffraction*, Addison-Wesley, Reading, 1969.
- 9 *Fiziko-khimicheskie svoystva okislov: Spravochnik*, Moscow, 1978.
- 10 T. F. Grigoryeva, I. A. Vorsina, A. P. Barinova, N. Z. Lyakhov, *Neorgan. materialy*, 33, 8 (1997) 993.
- 11 G. R. Karagedov, N. Z. Lyakhov, *Ibid.*, 33, 7 (1997) 817.
- 12 B. A. Marinković, Z. V. Zakula, T. V. Srećković *et al.*, *Cryst. Res. Technol.*, 34, 7 (1999) 881.