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**The Synthesis - Structure Relationship in the ZnO-Cr<sub>2</sub>O<sub>3</sub> system****L.Mancić<sup>1\*</sup>, Z.Marinković<sup>2</sup>, P.Vulić<sup>3</sup>, O.Milosević<sup>1</sup>**<sup>1</sup>Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia and Montenegro.<sup>2</sup>Center for Multidisciplinary Studies, University of Belgrade, Kneza Višeslava 1a, 11 000 Belgrade, Serbia and Montenegro<sup>3</sup>Faculty of Mining and Geology, Department of Crystallography, Djušina 7, 11000 Belgrade, Serbia and Montenegro**Abstract:**

*In this work the development of the spinel phase in the ZnO-Cr<sub>2</sub>O<sub>3</sub> system was discussed from the viewpoint of the synthesis-structure relationship. The nanostructure evolution in particles obtained either via solution-based (spray pyrolysis) or solid-state (mechanical activation) synthesis procedures were investigated by XRD analysis. A detailed structural analysis of the spinel phase lattice parameters, average primary crystallite sizes and microstrains were performed in accordance with a procedure based on the Koalariet-Xfit program. Due to the importance of spinel-phase cation distribution for chemical and physical properties, a study of the site occupation factors, i.e. changes in the stoichiometry, of ZnCr<sub>2</sub>O<sub>4</sub> spinels was undertaken. The calculation based on atomistic methods for the description of both perfect and defect spinel ZnCr<sub>2</sub>O<sub>4</sub> crystal lattices has been applied and the presence of individual structural defects was determined.*

**Keywords:** *Spinel, ZnCr<sub>2</sub>O<sub>4</sub>, Spray pyrolysis, Mechanical activation, Structural analysis.*

**1. Introduction**

A growing number of different ceramic materials are used today for gas/humidity-sensing. The primary mechanism associated with their potential use involves several microstructure parameters that influence sensing behavior [1]. Among them, small grain size plays an important role since it was shown that decrease of the grain size to the nanometer level leads to many interesting and new properties [2,3]. Nanostructured materials are composed of discrete grains - crystallites and the spaces between them are microstructurally heterogeneous, and this heterogeneity enhances sensing properties in ceramics [4]. Additionally, when oxides with a spinel structure are considered the determination of the cation distribution and site occupancy, defect concentration and non-stoichiometry are of considerable relevance for understanding how a ceramic material interacts with its environment [5,6]. A spinel structure has oxygen anions in a face centered cubic (fcc) close packing. The unit cell contains 32 oxygen anions, 16 octahedral and 8 tetrahedral cations. In the case of the ZnCr<sub>2</sub>O<sub>4</sub> spinel phase, the zinc site is tetrahedrally coordinated with oxygen, while the chromium site is octahedrally coordinated by oxygen. The anionic array is described by the monovariant equivalent position  $32e''$ , point symmetry  $3m$ . For an ideal fcc anion

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arrangement, the value of the free parameter  $u$ , commonly known as the oxygen positional parameter that reflects the balance between tetrahedral Zn-O and octahedral Cr-O bond lengths, is  $\frac{1}{4}$ . If the unit cell is divided into octants then the origin is displaced and the  $u$  value shows slight deviation [7].

In this work, a comprehensive study of  $\text{ZnCr}_2\text{O}_4$  spinel structural features is performed utilizing two different approaches for both particle refinement and nanostructuring, i.e. build-up (spray pyrolysis) and break-down (mechanical grinding and activation using either a high-energy vibro-mill or planetary ball-mill). The preparation of nanocrystalline  $\text{ZnCr}_2\text{O}_4$  ceramics from a solution based chemical route during spray pyrolysis is expected to achieve high chemical homogeneity in as prepared particles, while mechanical activation will provide higher defect concentration in the spinel structure. As an extension to our earlier research [8,9], structural refinement of the  $\text{ZnCr}_2\text{O}_4$  spinel phase obtained through high-temperature solid-state reaction of as-prepared (spray-pyrolysed and mechanically activated) powders will be presented and discussed in relationship with the synthesis method applied.

## 2. Experimental work

$\text{ZnCr}_2\text{O}_4$  spinel synthesis *via* spray pyrolysis was done according to a previously described method [10]. Briefly, the common nitrates precursor solution ( $c=0.03\text{mol/dm}^3$ ) was atomized and the aerosol obtained was introduced in a tubular flow reactor heated up to  $900^\circ\text{C}$ . The droplet/particle residence time on the highest reaction temperature was only 3s, while hot air ( $700^\circ\text{C}$ ) was blown over the collected powder charge during the whole synthesis process (16h). The produced particles were thermally treated for additional 2 hours in a chamber furnace at a temperature of  $1000^\circ\text{C}$ .

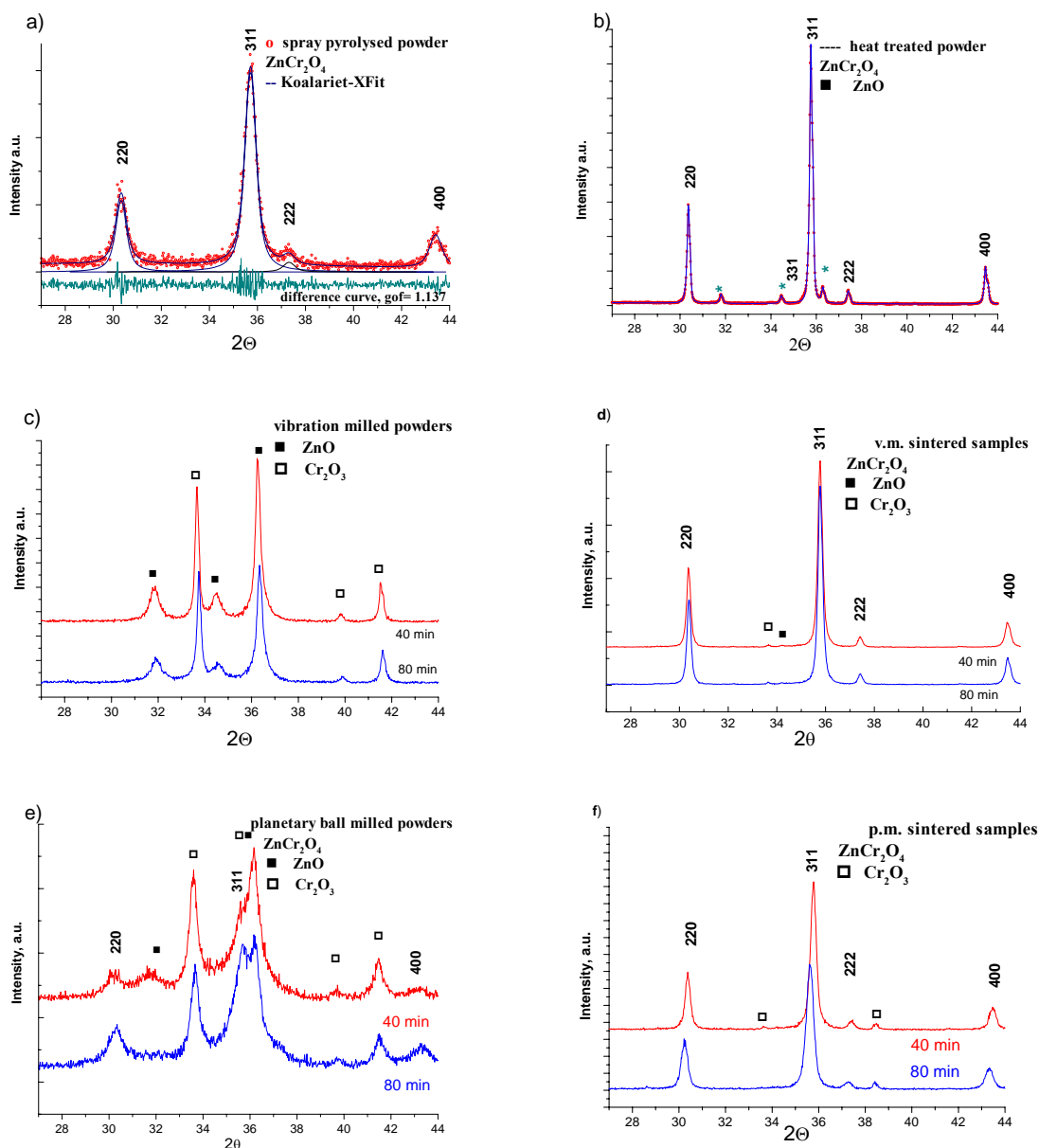
In order to obtain the  $\text{ZnCr}_2\text{O}_4$  spinel phase by mechanical activation mixtures of starting ZnO and  $\text{Cr}_2\text{O}_3$  powders in equimolar quantities were ground using either a high energy vibro-mill with steel rings or a planetary ball mill during 40 and 80 min. The vibro-mill with steel rings operated in a continual regime and the synthesis process was carried out in air. In the planetary ball mill a rotating disk carried vials that rotated in opposite directions. The rotation speed of the disk was 325 rpm and that of the vials was about 475 rpm. Zirconium oxide grinding balls (approx.10 mm in diameter) and bowls (volume  $500\text{ cm}^3$ ) were used with a ball to powder mixture mass ratio of 40:1. After milling, the powders were die pressed at 125MPa and sintered at  $900^\circ\text{C}$ , for 2 and 4 hours in the case of planetary and vibro-milling, respectively.

The X-ray powder diffraction (XRPD) data of the as-prepared and sintered samples was recorded using a Philips PW 1710 automated diffractometer with  $\text{CuK}_\alpha$  radiation and graphite monochromator. Scans were taken with a  $2\theta$  step size of  $0.02^\circ$  collected in the range of  $27-44^\circ$ , since this range covers the strongest detection lines of the oxides used as well as targeting the spinel phase. All diffraction peaks were used during structural refinements carried out by the Rietveld-based program Koalariet-Xfit [11]. The lattice parameters were deduced from XRD line positions using a least-squares refinement method. Peak profiles were fitted with a pseudo-Voigt function. Refinement continued till convergence reached the value of quality factor,  $\text{gof}$ , very close to 1 that confirms the goodness of refinement.

## 3. Results and discussion

According to XRD data (Fig.1), a substantial amount of the  $\text{ZnCr}_2\text{O}_4$  phase was formed in all investigated samples except in the powders activated in a vibro-mill (Fig.1c). As can be seen from the presented data, a well-crystallized cubic spinel phase  $\text{ZnCr}_2\text{O}_4$  (JCPDS

card no. 22-1107) was present both in heat treated (Fig.1b) and sintered (Figs.1d,f) powder samples.



**Fig. 1** XRD diffraction patterns of the as prepared spray-pyrolysed powder (a); heat-treated powder synthesized *via* spray pyrolysis (b); vibration-milled powders, 40 and 80min (c); sintered samples prepared from vibration-milled powders (d); planetary-milled powders, 40 and 80min (e); sintered samples prepared from planetary-milled powders (f).

The broadening of spinel phase reflections, evident in as prepared powders, gives an indication of nanostructure particle formation (Figs.1a,d). As an example of the performed structural refinement, the fitting curve and the difference curve between experimental and calculated diffraction profiles (gof=1.137) are presented together with the experimentally obtained data in Fig.1a. The program performed provides relevant information about the phase composition presented in Table I, as well as unit cell parameters, cation site occupancy, bond length, average crystallite size and crystal lattice microstrains of the targeting phase, Table II. Since it was shown that mechanical activation of the powder in a vibro-mill does not

promote the production of the spinel phase in a significant content, structural analysis of the initial oxides detected in investigated samples has been performed and the results obtained are given in Table III. All reflections visible on Fig.1c are very much broadened as well as partially or completely overlapped. Pure spinel phase formation is detected only in the spray-pyrolysed powder (Fig.1a) while different amounts of accompanying phase ZnO (JCPDS card no.36-1451), Cr<sub>2</sub>O<sub>3</sub> (JCPDS card no.38-1479), or both phases have been found in other samples (Figs.1b-f, Tab. I). However, a small amount (1.9%) of the ZnO phase appeared even in spray-pyrolysed powder after thermal treatment (Fig1b, Table I). For mechanically activated powders the content of accompanying ZnO phase decreased very rapidly, whereas the Cr<sub>2</sub>O<sub>3</sub> content decreased more slowly with increasing milling time. Differences exist among the amounts of oxides present, but the trends are the same. As already shown [12], the dominant process in the ZnO-Cr<sub>2</sub>O<sub>3</sub> powder system during milling is destruction of the ZnO crystal structure, since the other oxide component is much more stable. Based on the same study, a slight shift of the Cr<sub>2</sub>O<sub>3</sub> content in sintered samples (after 80 min of grinding) is attributed to the diminished mobility of the reacting Zn<sup>2+</sup> and Cr<sup>3+</sup> cations caused by particle agglomeration in the starting powdered mixtures.

**Tab. I** Semi-quantitative XRD phase analysis of powdered and pressed samples (w/w)

Synthesis process	Spray-pyrolysed powder		Vibration-milled powder				Planetary-milled powder			
	as-prepared	calcinated	as-prepared		sintered 4h		as-prepared		sintered 2h	
Time	3s+16h	2h	40min	80min	40min	80min	40min	80min	40min	80min
ZnCr <sub>2</sub> O <sub>4</sub>	100	98.1	0.2	0.3	97.9	97.6	24.9	47.2	96.6	97.0
ZnO	-	1.9	34.6	34.4	-	-	23.0	10.3	0.6	0.6
Cr <sub>2</sub> O <sub>3</sub>	-	-	65.2	65.3	2.1	2.4	52.1	42.5	2.8	2.4

**Tab. II** ZnCr<sub>2</sub>O<sub>4</sub> spinel phase structural data (Koalariet-Xfit)

Synthesis process applied	Spray-pyrolysed powder		Vibration-milled powder*		Planetary-milled powder			
	as-prepared	heat treated	sintered 4h		as-prepared		sintered 2h	
Time	3s+16h	2h	40min	80min	40min	80min	40min	80min
<i>a</i> (Å)	8.332	8.330	8.336	8.339	8.369	8.380	8.344	8.352
Zn <sup>2+</sup> occ.	0.976	0.967	1.063	1.072	0.968	0.938	1.009	0.951
Cr <sup>3+</sup> occ.	0.984	0.962	1.049	1.047	0.946	1.032	1.081	1.048
<i>u</i>	0.260	0.259	0.261	0.262	0.258	0.258	0.255	0.258
Zn-O (Å)	1.953	1.932	1.959	1.974	1.928	1.934	1.876	1.918
Cr-O (Å)	2.001	2.011	1.999	1.992	2.031	2.028	2.047	2.20
cr.size (Å)	333.5	3377.4	897.2	905.8	105.0	109.3	534.5	536.5
microstrain	0.552	0.065	0.231	0.215	0.001	0.001	0.344	0.662
defect type**	Cr <sup>4+</sup> clustered Defects		Cr <sup>4+</sup> clustered defects		Zinc interstitial or oxygen vacancy defects, isolated		Oxygen vacancy clusters	

\* in vibration milled powder (as-prepared), a low content of the spinel phase has been determined and structural refinement was not performed

\*\* estimated by model developed by D.J.Grimes et al. [18]

A comparison of the data presented in Tab. I shows that mechanical activation in the planetary ball mill results in the formation of the  $\text{ZnCr}_2\text{O}_4$  phase in the powdered mixtures. The spinel phase content increases from 24.9 to 47.2 in the course of milling. Due to the high-energy impact during synthesis the particles of individual oxide phases come into contact with each other at the time of ball-to-ball and/or ball-to vial wall collision, decrease in size to the nanometric level and result in nucleation of  $\text{ZnCr}_2\text{O}_4$  particles by solid-state diffusion [13]. Accordingly, a spinel phase with a smallest crystallite size is formed in these powders (10.5 and 10.93 nm, Tab. II). After sintering the nanocrystalline structure persisted, but an increase of microstrain is observed indicating that certain amounts of new lattice imperfections are created inside the spinel lattice. Evidence of the formation of non-stoichiometric material in all samples is additionally confirmed through a survey of the following parameters: the variation degree of spinel lattice parameter,  $a$ ;  $\text{Zn}^{2+}$  and  $\text{Cr}^{3+}$  site occupancy; oxygen positional parameter  $u$ , all given in Tab. II.

The non-stoichiometry of the spinel compound, caused by the dissolution of excess oxide, is already known and such containing three valent ions is more typical [14]. In this case, it should be related to  $\text{Cr}_2\text{O}_3$ , however considering  $\text{Zn}^{2+}$  and  $\text{Cr}^{3+}$  cation radii in the spinel phase, the higher value for unit-cell parameter,  $a$ , obtained, indicates the spinel cell was richer in zinc. The presence of  $\text{ZnO}$  as an accompanying phase in the process of  $\text{ZnCr}_2\text{O}_4$  spinel synthesis is indicative from several X-ray diffraction studies [15-19]. As mentioned before, stoichiometric  $\text{ZnCr}_2\text{O}_4$  has a face-centered cubic arrangement of oxygen ions space group  $\text{Fd}3\text{m}$ , in which  $\text{Cr}^{3+}$  ions occupy half of the octahedral and the  $\text{Zn}^{2+}$  ions fill one-eighth of the tetrahedral sites enclosed within the anion sublattice. There is also the possibility for the formation of Schottky defects and three kinds of Frenkel defects at high temperatures. Due to the very strong crystal field stabilization energy in octahedral coordination of low-spin  $\text{Cr}^{3+}$ , it was assumed that all  $\text{Cr}^{3+}$  were present on octahedral sites, so all chromate spinels containing octahedral  $\text{Cr}^{3+}$  are normal. With this distribution, the theoretical calculated lattice parameter of the crystal is  $8.340\text{\AA}$  [19]. So, the variation in the reported lattice parameter in the range  $8.321\text{-}8.359\text{\AA}$  [13-18] should be related to the formation of non-stoichiometric and defective material. Their fundamental interpretation is based on the model developed by Grimes et al. [19]. This model represents a set of atomistic methods for simulation and description of the perfect and defect spinel  $\text{ZnCr}_2\text{O}_4$  crystal lattice based on the calculation of the formation energies of an ideal crystal, as well as a set of isolated defects and also defect cluster formation. According to this model the different defect reactions associated with  $\text{ZnO}$  dissolution give rise to different combinations of defects. Two of them, isolated and clustered  $\text{Cr}^{4+}$  defects presence, lead to a decrease of the lattice parameter, while others result in an increase of the spinel unit cell.

According to the values of parameter,  $a$ , obtained in this study ( $8.330\text{-}8.380\text{\AA}$ , Table II), different types of defects are accommodated in the spinel lattice as the consequence of different synthesis methods applied. In the spray pyrolysed- and vibration milled- powders after sintering, the excess of  $\text{Zn}^{2+}$  present in the spinel lattice is compensated by  $\text{Cr}^{4+}$  ions, i.e. clustered  $\text{Cr}^{4+}$  defects. Having in mind our previous results and literature data [8-10, 15-19], this type of defect is the most favorable manner in which excess  $\text{ZnO}$  can be accommodated in the spinel lattice. For the powders obtained *via* planetary ball milling, the significant increase of the parameter,  $a$  indicates that either zinc interstitial or oxygen vacancy could be present, both as isolated defects. Namely, these types of defects result in a similar cell increase, so without additional quantitative analysis and precise zinc content determination it could not be concluded which of them is dominant. However, sintering of the powder leads to a slight decrease of the parameter  $a$ , suggesting either defect clustering or reduction. According to the proposed model, the nearest cell parameter calculation assumes oxide vacancy clustering, so summarizing all of the data presented in Table II, it could be postulated that oxide vacancy is the dominant defect created during planetary ball milling. Along with

this, accommodation of defects in the spinel lattice is also indicative by the changes observed in Zn-O and Cr-O bond lengths. Namely, a number of excess  $Zn^{2+}$  ions present in the spinel cell have moved in tetrahedral interstitial sites resulting in an increases of the interstitial volume.

**Tab. III** ZnO and  $Cr_2O_3$  phases structural data (Koalariet-Xfit)

Synthesis process: Vibration-milled powder			
Milling time:		40min	80min
<i>ZnO phase</i>			
<i>a</i> (Å)		3.257	3.257
<i>c</i> (Å)		5.220	5.220
$Zn^{2+}$ occ.		0.987	0.896
Zn-O (Å)		1.956	1.962
O-Zn (Å)		2.072	2.050
cr.size (Å)		200	164
<i>Cr<sub>2</sub>O<sub>3</sub> phase</i>			
<i>a</i> (Å)		4.972	4.972
<i>c</i> (Å)		13.631	13.630
$Cr^{3+}$ occ.		0.936	0.917
cr.size (Å)		890	770

The results of structural refinement performed in vibration-milled powders, Tab. III, suggest that a highly disordered zinc oxide structure is present in powder mixtures together with chromium (III) oxide crystallites, which changed structurally to a significantly lower degree. Different oxide behavior could be explained by the great difference of the crystal lattice energy of ZnO and  $Cr_2O_3$  being 4107.25 and 15186 kJ/mol, respectively. Consequently, the zinc oxide structure is much more prone to destruction, its crystallites are smaller in size in comparison to chromium oxide and its unit cell parameters are higher than in the ideal zinc oxide crystal. Namely, perfect ZnO has a hexagonal close packed (hcp) ion arrangement with  $a=3.250$  and  $c=5.205$ . The unit cell contains only two ions, one at the origin (and hence at all corners) and one inside the cell at positions  $\frac{1}{3}$ ,  $\frac{2}{3}$ , and  $\frac{1}{2}$ . Closely packed layers occur only in one orientation of hcp structures for which only T+ fully occupied interstitial sites exist [7]. However, the extremely low  $Zn^{2+}$  site occupation value of 0.896 obtained after 80 minutes of mixture milling together with increased lengths of both Zn-O and O-Zn implies zinc introduction into the octahedral interstitial environment. Distribution of the zinc ions over both octahedral and tetrahedral interstitial sites in ZnO, as well as  $Cr^{3+}$  ion displacement from its original position in  $Cr_2O_3$  ( $Cr^{3+}$  occ: 0.936 and 0.917, Table III) during the synthesis process enhance  $ZnCr_2O_4$  formation in significant quantity after 4 hours of sintering.

#### 4. Conclusion

A detailed structural analysis of the  $ZnCr_2O_4$  phase obtained *via* various synthesis methods clearly showed that the lattice parameters of cubic spinel depended on the preparation conditions. These changes are associated with non-stoichiometry and defect structure establishment. The unit cell is divided into octants and the origin is displaced. This deviation increases the volume ratio between the occupied tetrahedral and octahedral sites, and results in different defect accommodation. Using an atomistic model for the description of a defect crystal lattice in the interpretation of experimental results obtained, an excess of  $Zn^{2+}$  ions is determined in the spinel phase. It was shown that in the spray pyrolysed and vibration milled powders after sintering, this excess of  $Zn^{2+}$  ions is compensated by clustered  $Cr^{4+}$

defects. The creation of oxide vacancy, either in isolated or clustered form, is typical for the planetary-ball milled powders. Since zinc oxide dissolution in the spinel lattice is more likely through distributing the divalent zinc ions over both octahedral and tetrahedral sites with charge compensation provided by chromium ion clustering, the stabilization of the thermodynamically less favored defects, oxygen vacancies, is probably a consequence of the materials nanostructuring.

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**Резюме:** Получение функциональных нанофазных порошков на основе ZnO и CrO<sub>3</sub> исследовано с точки зрения влияния выбора процесса синтеза на структуру частиц

образованной шпинели. На самом деле, ультразвуковое реакционное распыление обуславливает протекание реакции в дисперсной системе на уровне капли, в то время как механическая активация порошков, при помощи твердофазных реакций приводит к образованию шпинели  $ZnCr_2O_4$ . Структурные изменения наблюдались методом Rietveld (программа Coalariet-Xfit) с целью определения размера кристаллитов, микронапряжений коэффициента заполнения атомов, длины связей в кристаллической решетке и весовой доли присутствующих фаз. Показано, что определенная функциональная микроструктура нанофазных частиц шпинельной фазы образуется *in situ* в процессе нуклеации и роста кристаллитов. Это приводит к поддержанию определенного механизма перераспределения катионов и образования нестехиометрической шпинели.

**Ключевые слова:** Шпинель,  $ZnCr_2O_4$ , пиролиз распылением, механическая активация, структурный анализ.

**Садржај:** Добијање функционалних нанофазних прахова на бази  $ZnO$  и  $Cr_2O_3$  проучено је са становишта утицаја избора процеса синтезе на структуру честица образованог спинела. Наиме, ултразвучно реакционо распршивање условљава одвијање реакције у дисперзном систему на нивоу капи, док поступци механичке активације прахова доводе до настајања спинела  $ZnCr_2O_4$  реакцијама у чврстој фази. Структурне промене праћене су коришћењем Rietveld методе (програм Koalariet-Xfit) са циљем одређивања величине кристалита, микронапрезања, фактора окупираности положаја атома, дужине веза у кристалној решетки и тежинског удела присутних фаза. Показано је да се одређена функционална микроструктура нанофазних честица спинелне фазе формира *in situ* у процесу нуклеације и раста кристалита (то доводи до фаворизовања одређеног механизма прерасподеле катјона и образовања нестехиометријског спинела).

**Кључне речи:** Спинел,  $ZnCr_2O_4$ , спрејпиролиза, механичка активација, структурна анализа.