

INTERACTION OF OXIDES IN THE ZnO-Nd₂O₃ SYSTEM

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Polycrystalline samples of ZnO + x mol.% Nd₂O₃ (x = 0 - 7.73) were prepared from the suspension of ZnO in Nd nitrate solution with following evaporation, drying and annealing at 1000 °C. The samples were characterized by X-ray diffraction analysis and ESR spectra measurement. The obtained samples have a two-phase structure with Nd₂O₃ covering ZnO grains. The addition of Nd₂O₃ to ZnO results in a decrease of the unit cell volume of ZnO, a decrease in the strength of the ESR band with g = 1.958 and a more pronounced asymmetry of this band. The experimental results are explained as due to the mutual interaction of both components of the mixture leading to a decrease in nonstoichiometry of both ZnO and Nd₂O₃. It is assumed that in the crystal structures of both oxides concentrations of native defects, i.e. Zn interstitials and oxygen vacancies in ZnO and Nd vacancies and oxygen interstitials in Nd₂O₃ are decreased.

INTRODUCTION

Studies of the systems of ZnO with rare earths (RE) oxides can be divided into 2 groups. The first group is devoted to the investigations of changes of luminescent properties of ZnO due to additions of earth metals, photo- and electroluminescence were studied as well [1-8]. The second group is devoted to the studies of varistor ceramics based on ZnO containing rare earth oxides as components [9-11].

The results of photo- and electroluminescent measurements were explained using two different models. According to Bhushan et al. [3] additions of RE oxides result in a shift of the position of luminescent bands of ZnO. According to the applied "donor-acceptor" model, RE ions in ZnO structure have a function of donors creating donor levels in the band model of ZnO. Nevertheless, they do not mention a type of defects associated with the considered donor levels.

Another ideas were given in [6-8]. Kassanyi et al. [6] from the comparison of photo- and electroluminescent spectra of pure ZnO sample and ZnO with additions of RE oxide came to the conclusion that a broad luminescent emission band of ZnO with RE oxides is composed of several subbands as a result of a partial absorption of the luminescent emission of pure ZnO by RE ions. They assumed that RE ions are incorporated in interstitial positions of the ZnO structure. As a support for this conclusion the authors [6] used the comparison of luminescent and diffusion-reflectance spectra of the studied samples.

The observed differences in the experimental results of studies [3] and [6] can be associated with a substantial difference in the contents of RE oxides in the studied samples. The concentrations of RE oxides in [3] did not

exceed 0.5 mol.%, whereas in the samples [6] the content of RE oxides was higher than 2 mol.%. In the above mentioned papers [3,6] no studies of phase homogeneity were carried out and thus it is not clear, whether the investigated samples were single-phase solid solutions or two-phase samples composed of ZnO and RE oxide.

The studies of ZnO-based ceramic materials for varistors with RE oxides [9-11] lead to the following conclusions: The samples are composed of two phases - one is ZnO grains and the other - an intergranular phase containing the RE oxide. The addition of RE oxides increases the concentration of interface states in ZnO. These states are created by a chemisorbed oxygen on the ZnO grains. An increased concentration of interface states lead to a higher non-linearity of ampere-voltage characteristics of the varistors. This effect is explained as due to the heat treatment of the ZnO-RE oxide mixture; when RE oxide with an oxygen overstoichiometry releases oxygen atoms, these are sorbed on the surface of ZnO crystallites, forming thus interface states determining varistor properties. RE oxides change as well, e.g. according to [10] Pr₆O₁₁ transforms into Pr₂O₃ or Tb₄O₇ changes into Tb₂O₃. Nevertheless, in [9-11] there is not any discussion of changes in ZnO lattice which can take place due to the heat treatment of the oxide mixture and their mutual interaction.

The presented paper deals with the investigation of changes in ZnO crystal structure caused by an addition of a rare earth oxide - in this case neodymium oxide Nd₂O₃. For the characterization study of the resulting product we have applied X-ray diffraction and ESR methods. The observed changes in the properties of ZnO - Nd₂O₃ powder samples are discussed in terms of changes in the real structure of both oxides.

EXPERIMENTAL PART

Preparation of ZnO samples

As a starting material for the preparation of "pure" ZnO we have used metallic zinc of 99.999 % purity, HNO₃ of semiconductor purity and ammonium solution prepared by absorption of NH₃ gas in redistilled water.

The metallic zinc was dissolved in a hot nitric acid. After cooling the obtained solution to room temperature, Zn(OH)₂ was precipitated by addition of ammonium solution. The obtained zinc hydroxide was separated by filtration and after drying it was decomposed to ZnO by heating in a platinum crucible at 1000 °C for 4 hours.

Preparation of ZnO - Nd₂O₃ samples

For the preparation of homogeneous ZnO - Nd₂O₃ samples the following procedure was used: The stoichiometric amount of Nd(NO₃)₃ · 6 H₂O corresponding to the given formula ZnO + *x* mol.% Nd₂O₃ was dissolved in redistilled water. The necessary amount of ZnO was dispersed into this solution and thoroughly homogenized by mixing. The suspension was carefully evaporated and the solid product after drying was heated in a Pt crucible in air up to 1000 °C holding this temperature for 4 hours. In such a way ZnO + *x* mol.% Nd₂O₃ samples with *x* = 0.08; 0.23; 0.38; 0.76; 3.81 and 7.73 were prepared.

X-ray diffraction analysis

X-ray powder diffractograms of the samples were collected on a vertical X-ray diffractometer HZG-4B

(VEB Freiburger Präzisionsmechanik, Freiberg, Germany), equipped with a goniometer of 25 cm diameter and a proportional detector. Cu-K_α radiation was used with K_β radiation eliminated by a nickel filter; in the range 2 Θ = 10 - 35 °, the interplanar spacing was calculated using λ = 0.154178 nm and in the range 2 Θ = 35 - 90 ° Cu-K_{α1} radiation (λ = 0.154051 nm) was used.

Powdered silicon (*a* = 0.543055 nm) served as an internal standard. The lattice parameters were computed using the least-squares technique to increase the accuracy, the minimized quantity being (2 Θ_{exp} - 2 Θ_{calc})².

Measurement of ESR spectra

The ESR spectra of polycrystalline samples were measured using the ESR 221 apparatus (Akademie der Wissenschaften der Zentrum Wissenschaftlichen Gerätebau, Berlin) in the X-band (γ = 9.5 GHz) at liquid nitrogen temperature.

RESULTS

The results of X-ray diffraction analysis of the prepared ZnO - Nd₂O₃ samples are summarized in Tables 1 and 2. In Table 1 there are the values of lattice parameters *a* and *c*, and unit cell volume of ZnO crystallites at the doped samples with *x* in the range 0 - 7.73 mol.%. Nd₂O₃. In table 2 there are similar data for Nd₂O₃ crystallites obtained from the samples with the highest Nd₂O₃ content (*x* = 3.81 and 7.73 mol.%) and for pure Nd₂O₃ obtained by thermal decomposition of Nd(NO₃)₃·6H₂O by the same way as the other ZnO - Nd₂O₃ samples.

Table 1. Lattice parameters of zinc oxide in ZnO - Nd₂O₃ polycrystalline samples.

sample no.	<i>c</i> _{Nd₂O₃} (mol.%)	<i>a</i> (nm)	<i>c</i> (nm)	<i>cla</i>	<i>V</i> (nm ³)	Δ*
1	0.00	0.32505 (1)	0.52043 (3)	1.6011 (2)	0.047619 (4)	0.0029
2	0.08	0.32504 (1)	0.52037 (2)	1.6010 (1)	0.047612 (2)	0.0024
3	0.23	0.32504 (1)	0.52036 (2)	1.6009 (1)	0.047611 (2)	0.0021
4	0.38	0.32504 (1)	0.52034 (1)	1.6008 (1)	0.047609 (2)	0.0019
5	0.76	0.32504 (1)	0.52031 (1)	1.6008 (1)	0.047606 (1)	0.0015
6	3.81	0.32503 (1)	0.52024 (1)	1.6006 (1)	0.047598 (2)	0.0017
7	7.73	0.32502 (1)	0.52019 (3)	1.6005 (2)	0.047591 (4)	0.0043

Table 2. Lattice parameters of neodymium oxide in ZnO - Nd₂O₃ polycrystalline samples.

sample	<i>a</i> (nm)	<i>c</i> (nm)	<i>cla</i>	<i>V</i> (nm ³)	Δ*
ZnO + 3.81 mol.% Nd ₂ O ₃	0.3826 (1)	0.6005 (1)	1.570 (1)	0.07612 (3)	0.0052
ZnO + 7.73 mol.% Nd ₂ O ₃	0.3826 (1)	0.6004 (1)	1.569 (1)	0.07612 (3)	0.0035
Nd ₂ O ₃	0.3830 (1)	0.5990 (1)	1.566 (1)	0.07620 (3)	0.0026

* Δ = $\frac{1}{N} \sum_{i=1}^N |2 \Theta_{\text{exp}} - 2 \Theta_{\text{calc}}|$, where 2 Θ_{exp} is the experimental diffraction angle, 2 Θ_{calc} is the angle calculated from lattice parameters and *N* is the number of investigated diffraction lines.

The obtained ESR spectra are shown in figures 1 and 2. The changes in the volume of unit cell of ZnO and the strength of the ESR band with changes in the Nd₂O₃ content are given in figure 3.

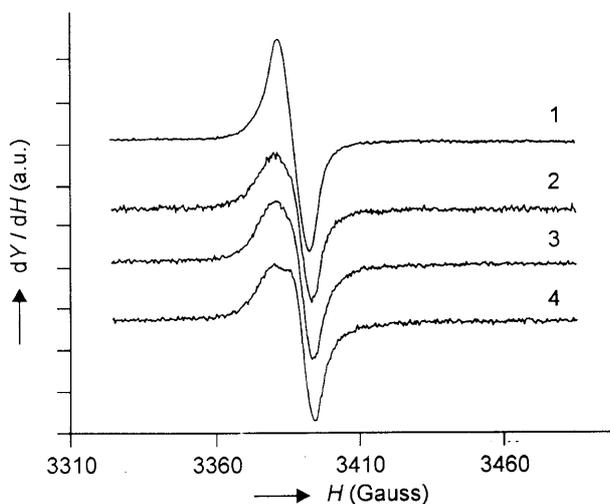


Figure 1. ESR spectra of polycrystalline ZnO - Nd₂O₃ samples. The samples are labelled according to table 1. Microwave frequency 9.2768 GHz.

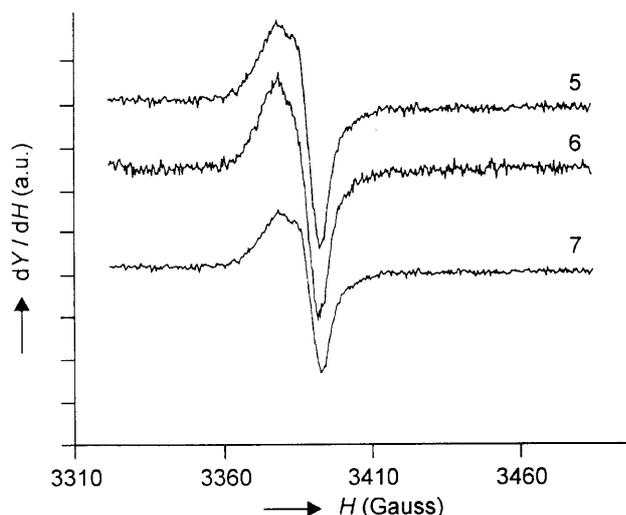


Figure 2. ESR spectra of polycrystalline ZnO - Nd₂O₃ samples. The samples are labelled according to table 1. Microwave frequency 9.2768 GHz.

DISCUSSION

X-ray diffraction diagrams obtained from the samples with the highest Nd₂O₃ content (samples no. 6 and 7) revealed besides ZnO lines also another lines identified as the lines of hexagonal modification of Nd₂O₃. The strongest line of hexagonal Nd₂O₃ positioned

at $2\Theta = 30.7^\circ$ was observed at the samples with lower Nd₂O₃ as a small hump. These results show that the prepared ZnO - Nd₂O₃ samples are heterogeneous and consist of 2 phases: ZnO and Nd₂O₃. Taking into account the method of preparation we can assume, that ZnO crystallites are covered by Nd₂O₃ layer formed by thermal decomposition of Nd(NO₃)₃.

Unit cell parameters of ZnO, from the X-ray diffractograms are given in table 1. An increase in the Nd₂O₃ content results in a decrease of parameter *c*, whereas a decrease of the parameter *a* is relatively small; unit cell volume decreases as well. The observed changes in ZnO lattice parameters due to Nd₂O₃ additions cannot be explained as only due to the chemisorption of oxygen, released from the lattice of the RE oxide, on the surface of ZnO crystallites, as suggested e.g. in [10]. We assume that the observed changes are due to a more pronounced interaction of both the oxides during the heat treatment of their mixture. This interaction can be explained similarly like the changes in ZnO lattice in polycrystalline ZnO - Bi₂O₃ samples [12].

Zinc oxide annealed at 1000 °C reveals an oxygen deficit which results in n-type electrical conductivity of ZnO. This electron conductivity is explained by the pre-

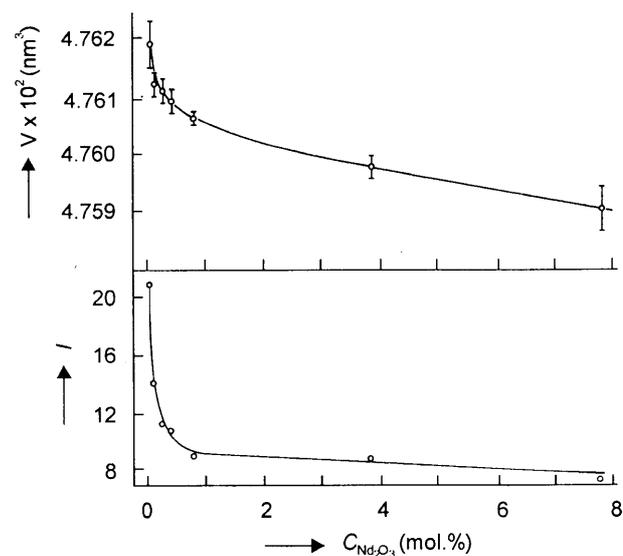


Figure 3. The dependences of the elementary unit cell volume (*V*) of ZnO and the strength of the ESR band (*I*) on the content of Nd₂O₃ in the polycrystalline samples ZnO - Nd₂O₃.

sence of oxygen vacancies [13,14] or interstitial zinc atoms [15,16] in the crystal structure of ZnO. According to [17] in the ZnO crystal lattice both types of native defects can be present. On the other side, Nd₂O₃ deposited as a layer on the surface of ZnO crystallites as a p-type semiconductor, reveals an overstoichiometric content of oxygen. In its crystal structure the presence of vacan-

cies in the cation substructure is assumed in [18], whereas interstitial oxygen atoms are supposed to be present in Nd_2O_3 according to [19].

Therefore we assume that at the interface of both these phases oxygen atoms are transported from the O-richer Nd_2O_3 onto the surface of O-poorer ZnO phase which can be not only adsorbed on the surface, but also diffused into the ZnO crystal lattice filling the oxygen vacancies in the ZnO anion sublattice. Supposing the presence of Zn interstitials, a simultaneous diffusion of overstoichiometric Zn atoms towards ZnO - Nd_2O_3 interface can take place, where they can combine with oxygen atoms supplied from Nd_2O_3 forming thus ZnO.

The above described processes will result in a decrease of the oxygen deficit in ZnO crystal structure i.e. a decrease of the concentration of oxygen vacancies and Zn interstitials. This processes should lead to a decrease in the volume of the ZnO unit cell, which is in a good agreement with the obtained experimental results. The suggested explanation of experimental results is supported also by recent investigations of Jasim [20] who studied thermal stability of RE oxides. From thermoanalytical curves he found that on heating Nd_2O_3 loses an appreciable amount of oxygen at about 285 °C.

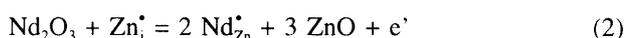
The suggested transfer of oxygen from overstoichiometric Nd_2O_3 into ZnO, should result also in changes in the crystal lattice parameters of Nd_2O_3 due to a decrease in the concentration of vacancies in its cation sublattice or interstitial oxygen atoms. When we compare the values of the lattice parameters of Nd_2O_3 in the ZnO - Nd_2O_3 samples with those for pure Nd_2O_3 obtained under the same conditions by thermal decomposition of $\text{Nd}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ like Nd_2O_3 - ZnO samples (see table 2) we can see that the unit cell volume of Nd_2O_3 in the mixed samples is smaller than that of "pure" Nd_2O_3 . These results also support our model of the mutual interaction of both the oxides.

Nevertheless, we can not exclude a possibility of diffusion of Zn atoms into Nd_2O_3 lattice as well, especially, when considering the diffusion of Zn interstitials towards the Nd_2O_3 -ZnO interface. We have to consider also an incorporation of some Zn atoms into Nd_2O_3 crystal lattice, where they can enter vacant sites in the cation sublattice, which could also result in a decrease of the unit cell volume of Nd_2O_3 .

On the other side, we can not exclude also a possibility of the dissolution of a small amount of Nd_2O_3 in ZnO, i.e. an incorporation of traces of Nd atoms or ions into ZnO crystal lattice. Such a process would create two new types of point defects - Nd interstitial or substitutional defects in ZnO. As the neodymium atoms or ions have a relatively high radii, when comparing with those of Zn ($r_{\text{Zn}^{2+}} = 0.074 \text{ nm}$, $r_{\text{Nd}^{3+}} = 0.108 \text{ nm}$), we assume the incorporation of Nd ions or atoms into ZnO lattice as interstitial, suggested in [6], to have a low probability.

We assume that a partial absorption of ZnO luminescence in the presence of RE atoms, observed in [6], can be associated with the two-phase structure of the samples consisting of a layer of RE oxide on the ZnO surface. Such a layer of RE oxide can function as a partially-absorbing filter of the luminescent radiation.

The formation of substitutional defects of Nd^{3+} ions replacing Zn^{2+} ions (Nd_{Zn}^*) is more plausible. The formation of such defects in the ZnO crystal structure containing oxygen vacancies (for simplicity we consider only single-charged O vacancies) or Zn interstitial, can be described by the following equations:



According to these equations the formation of Nd_{Zn}^* substitutional defects is associated with the suppression of the concentration of oxygen vacancies or interstitial defects in ZnO. An increase in the volume of ZnO unit cell due to the formation of Nd_{Zn}^* defects (Nd^{3+} has a larger volume than Zn^{2+}) is partially compensated by a decrease in the concentration of native defects in ZnO.

We assume that the formation of Nd_{Zn}^* defects has a low probability in comparison with the above described oxygen transport from Nd_2O_3 into ZnO, because the solubility of Nd_2O_3 in ZnO is very small. This conclusion is supported by the observed dependence of the ZnO unit cell volume on the Nd_2O_3 content (see figure 3), where no an extreme has been found, within the sensitivity limits of the X-ray diffraction measurement.

When a trace amount of Nd is incorporated into ZnO crystal lattice as Nd_{Zn}^* point defects, according to the equations (1) and (2) it is evident, that Nd impurities in ZnO behave as donors. This conclusion is in agreement with [3], according to which additions of RE oxides behave in ZnO crystal lattice as donors causing a shift of bands in the luminescence spectrum of ZnO.

An interesting information on the point defects character in ZnO crystal structure bring also ESR spectra. As can be seen in figure 1, ESR spectrum of the starting ZnO is manifested by a slightly nonsymmetric band with the value of g-factor equal to 1.958. According to [21-23] the ESR band with $g = 1.957$ is ascribed to an unpaired electron localized on the oxygen vacancy, i.e. to the point defect V_O^* and thus its presence in the ESR spectrum gives evidence for the presence of V_O^* defects in our ZnO samples. From the observed asymmetry of the ESR band we can deduce two values of the g-factor: $g_1 = 1.958$ and $g_2 = 1.964$; the signal with g_2 is associated probably with distortions in the axial symmetry of the paramagnetic defect center.

From the obtained ESR spectra of ZnO - Nd_2O_3 samples, shown in figures 1 and 2, we can make the following conclusions:

- a) The additions of Nd₂O₃ to starting ZnO results in a substantial decrease in the strength of the ESR band (see figure 3). With the application of the results of [21-23] we assume that this decrease is associated with a decrease in the concentration of oxygen vacancies V_O[•] in the ZnO structure. This result is in a good agreement with our model proposed above, according to which the interaction of ZnO with Nd₂O₃ leads to the suppression of nonstoichiometry in the starting ZnO crystallites. It complies also with the process of formation of Nd_{Zn}[•] defects ascribed by equation (1).
- b) With an increasing amount of Nd₂O₃ in the ZnO - Nd₂O₃ samples, the asymmetry of the ESR band is more pronounced. This effect is manifested in figure 4 by comparing ESR absorption bands of the starting ZnO (broken line) with that of the sample 5 (full line). In the latter ESR band an increase in the strength of the component with g₂ is evident. This results gives evidence for a decrease in the symmetry of the coordination neighbourhood of the V_O[•] paramagnetic centrum. This effect is probably associated with changes around this paramagnetic centrum due to the occupation of other non-paramagnetic oxygen vacancies (uncharged V_O^x and double-charged V_O^{••}) by oxygen atoms or eventually by the suppression of the concentration of interstitial defects Zn_i in the ZnO crystal lattice and the formation of substitutional defects Nd_{Zn}[•].

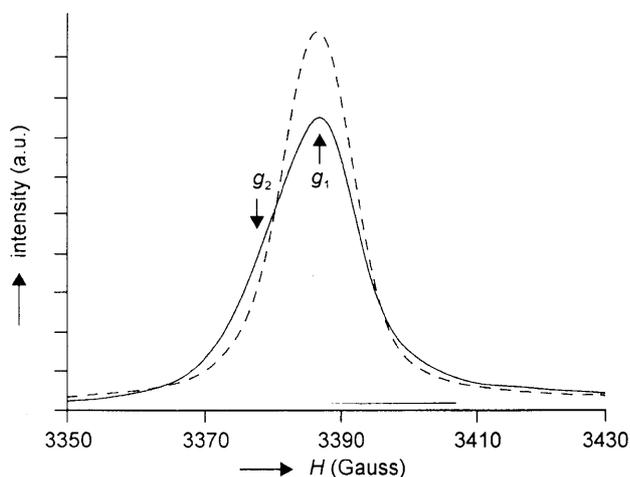


Figure 4. Absorption ESR spectra of the samples of pure ZnO (broken line) and ZnO + 3.81 mol.% Nd₂O₃ (full line). Microwave frequency 9.2768 GHz.

In this way the results of ESR spectra measurements of ZnO - Nd₂O₃ samples support the above described model of the interaction of both oxides proposed from the interpretation of the results of X-ray diffraction measurements.

CONCLUSION

The investigation of ZnO - Nd₂O₃ polycrystalline samples by X-ray diffraction and ESR spectra measurements lead to the following conclusions:

1. ZnO - Nd₂O₃ samples form a two-phase system of ZnO crystallites covered by a layer of Nd₂O₃.
2. Mutual interaction of both oxides during their heat treatment results in a decrease of the nonstoichiometry of both ZnO and Nd₂O₃.
3. The interaction of both oxides leads to a decrease in the concentration of oxygen vacancies and/or interstitial Zn atoms in the ZnO crystal lattice; on the other side, the concentration of vacancies in the cation sublattice or oxygen interstitials in Nd₂O₃ crystal lattice are suppressed.

Besides the above described interactions we assume that trace amounts of Nd atoms can be incorporated into the ZnO crystal structure, forming thus Nd_{Zn}[•] substitutional defects.

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INTERAKCE OXIDŮ V SYSTÉMU ZnO - Nd₂O₃

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Polykrystalické vzorky směsí oxidů zinečnatého a neodymitého, které jsou v praxi používány k výrobě varistorové kera-

miky, složení ZnO + x mol% Nd₂O₃ ($x = 0 - 7$) byly charakterizovány rentgenodifrakční analýzou a měřením EPR spekter.

Bylo zjištěno, že studované materiály jsou dvoufázové - na povrchu krystalitů ZnO je deponována vrstva Nd₂O₃. Přídavek Nd₂O₃ k ZnO vyvolává zmenšení objemu elementární buňky krystalové ZnO a snížení intenzity EPR pásu s hodnotou faktoru $g = 1.958$; současně bylo pozorováno zvýraznění asymetrie tohoto pásu.

Tyto výsledky jsou vysvětleny vzájemnou interakcí obou komponent směsi, mající za následek snížení nestechiometrie struktur ZnO i Nd₂O₃. Vychází se přitom ze známé skutečnosti, že ZnO vykazuje deficit kyslíku, zatímco Nd₂O₃ je charakterizován nadstechiometrickým obsahem kyslíku. Je předpokládáno, že v krystalových strukturách obou oxidů, v důsledku vzájemné interakce, dochází k poklesu koncentrace přirozených poruch, tj. intersticiálních atomů, resp. iontů, zinku a kyslíkových vakancí ve struktuře ZnO a vakancí v substruktuře neodymu, resp. intersticiálů kyslíku, jejichž existence je předpokládána ve struktuře Nd₂O₃.