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THE INVESTIGATION OF VARIATIONS IN OPTICAL PROPERTIES DEPENDING ON SINTERING TEMPERATURE OF Ni:ZNO NANO POWDERS

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Abstract: *In this study, Ni:ZnO nano powders were produced by the sol-gel calcination method to investigate and improve the interaction between sintering temperature and optical properties. ZnO based nano-ceramic materials with superior properties which can be used in several scientific researches and high technology applications and can be easily synthesized were produced by this method. The effect of Ni doping on the optical properties of ZnO nanopowders was investigated through spectrophotometric measurements. The optical band gaps of the samples were calculated from the diffuse reflectance curves using Kubelka-Munk function. It was observed that E_g values of the samples changed depending on the Ni dopant and sintering temperature. As a result of the investigations, it was determined that Ni doping and different sintering temperature have significant effects on the optical properties of ZnO nano powders, and the produced samples can be used in high temperature conductive electrode applications, optoelectronic devices, and sensor production.*

Keywords: *Optical properties, Nanopowders, Ni-doped ZnO, Optical characteristics, Sol-gel calcination method.*

1. Introduction

Semiconductor ZnO has become one of the most popular materials for electrical and optical applications over time. It is a promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thin-film transistor, solar cells, acoustic devices, chemical, and biological sensors. For applications of the transparent and conducting electrode in solar cells and thin-film transistor, the development of low-resistive ZnO films with high transparency is crucial. Due to its large binding energy (60 meV), wide band gap (3.37 eV) and easy facilitate synthesis and assembly methods, the utilization of ZnO has covered various fields such as electric transistors [2], photovoltaic devices [3] and chemical sensors [4]. Nowadays, the nanostructure ZnO materials such as ZnO nanowires [5], nanoparticles [6], and nanotetrapods [7] have attracted the wide attention since their large surface area and enhanced quantum confinement that leads to novel electrical and optical properties for device application. Studies have shown that the surface of ZnO nanocrystals can play an important role in carrier transport. The unbounded oxygen chemisorbed on the nanocrystal surface serves as traps for charge carriers, thus, increasing the interfacial potential and lowering carrier mobility [1]. However, in order to enhance the versatility of ZnO to meet the different requirements of the application, structural modifications have usually been utilized, among which metal ion doping is the most well known and effective approach.

Spintronics (spin-based electronics) based on diluted magnetic semiconductor oxides, is currently an active area of research because spin-based multifunctional electronic devices have several advantages over the conventional charge-based devices regarding data-processing speed, nonvolatility, and higher integration densities [16]. Diluted magnetic semiconductors (DMSs), i.e., semiconductors with a dilute concentration of magnetic dopants are expected to be promising materials for spin-based multifunctional devices. An ideal DMS must satisfy certain conditions, such as high Curie temperature (TC) and the easy incorporation of p- and n-type carriers. Besides the need for materials with high Curie temperature along with high magnetic moments, the critical point is to assure those dopant atoms are uniformly dissolved into the host lattice and that the resulting ferromagnetism (FM) indeed originates from the doped matrices [16,17].

The sol-gel method has advantages such as low cost, easy to handle, safe, and the non-vacuum method, to prepare ZnO materials over conventional synthesis methods such as magnetic sputtering, chemical vapor deposition, and hydrothermal reaction [18]. Moreover, it is easy to realize the incorporation of the dopant using a one-route process simply by modulating the ingredient of the precursors. In this communication, synthesis of nanopowders based on Ni-doped ZnO via the sol-gel calcination method is introduced. Up to our knowledge, there are a few works on the characterization of sol-gel synthesized Ni-doped ZnO nanopowders especially optical band gap calculations based on the measured diffused reflectance. In addition, the diffused reflectance was used to determine the optical constants of Ni-doped ZnO nanopowders.

2. Experimental

2.1. Preparation of Samples

In order to form solutions of ZnO containing Ni in different atomic ratios with the sol-gel method, Nickel(II) acetate tetrahydrate ($Ni(OCOCH_3)_2.4H_2O$) at different atomic ratios (0%, 0.1%, 0.5%, 1%, and 2%) was added into zinc acetate ($(ZnCH_3COO)_2.2H_2O$). All solutions were prepared as 1M, 10 ml. The starting materials with calculated substance quantities were weighed and placed in the test tubes containing the solvent (2-methoxyethanol ($CH_3OCH_2CH_2OH$)). These mixtures were stirred at 800 rpm for 10 min. by the magnetic stirrer at room temperature and then stirred in an ultrasonic mixer for 5 min. to ensure better dissolution. For Ni doping, Nickel(II) acetate tetrahydrate ratios calculated according to the starting material were determined. It was stirred again under the same conditions by adding a dopant source. Monoethanolamine was then added as a stabilizer and the stirring process was repeated under the same conditions. Finally, the solution was stirred at 60 0C for 2 h to obtain the gel form. The production process of the samples is given in Fig. 1.

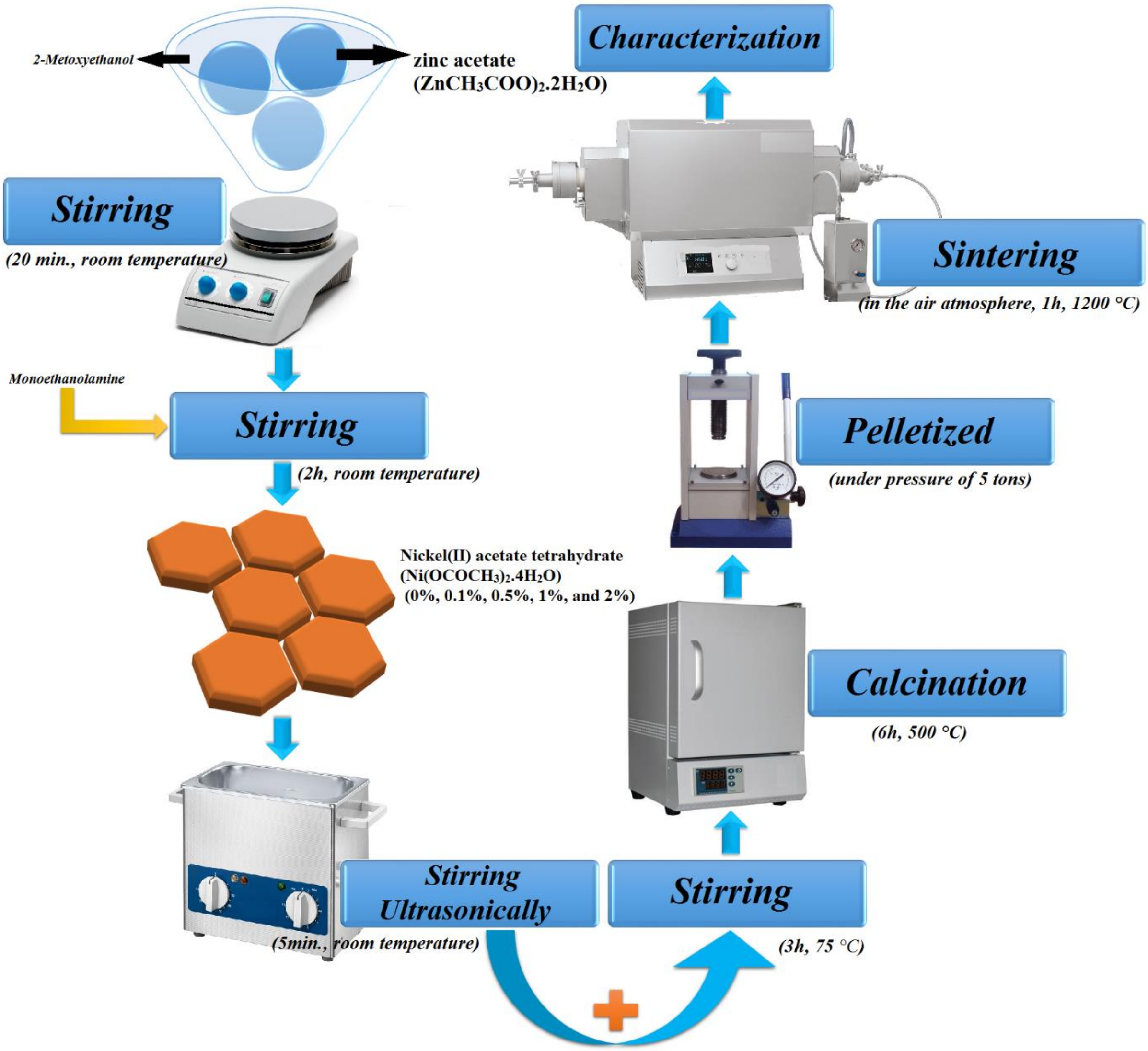

Figure 1. The preparation process of samples

2.2. Characterization Techniques

The optical properties of the prepared nano powders was characterized by spectrophotometer. Measurements of diffuse reflectance (R-λ) of the samples were taken at 200-1200 nm wavelength with a Shimadzu UV-VIS-NIR 3600 spectrophotometer. All measurements were made at room temperature.

3. Results and Discussions

3.1. The reflectance measurements of samples sintered at different temperatures

If the item exposed to the light beam is a semiconductor, many optical phenomena such as absorption, reflection, and transmission occur by the interaction of photons with the material. With this method, the optical characterization of the samples was conducted. Optical characterization of undoped and Ni-doped ZnO thin films obtained with the sol-gel method was carried out at 200-1200 nm scanning zone and room temperature.

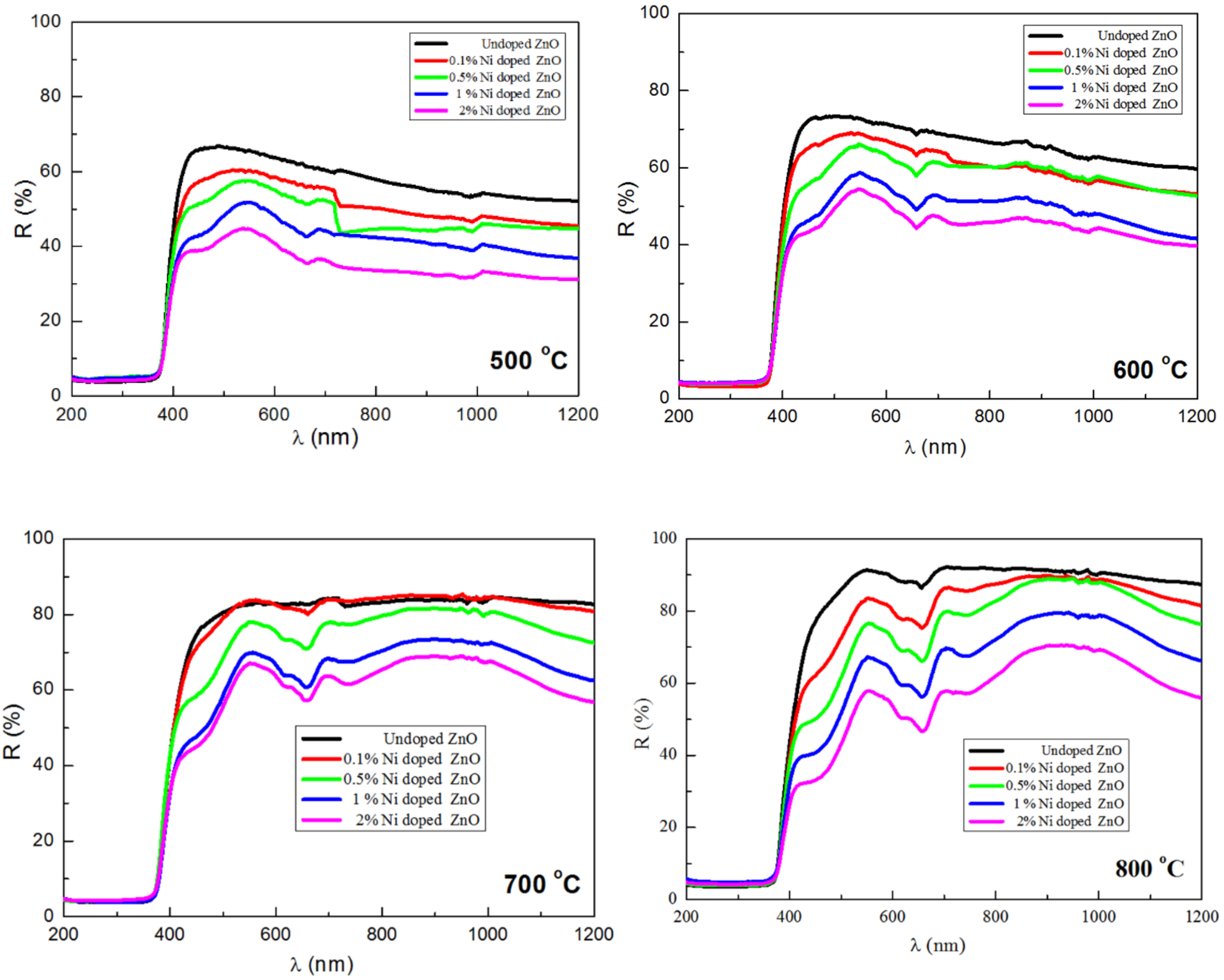

Figure 2. The reflectance graphs of samples sintered at 500, 600, 700 and 800 °C

Fig. 2. shows the reflection spectra of undoped and Ni-doped ZnO samples. As seen in Fig. 2., the reflection curves of the samples showed a decline at about 400 nm wavelength. This decline varied with Ni dopant. This confirmed that the optical band gaps of the films changed with Ni dopant. While the reflection values of the samples decreased at visible region wavelengths, they increased at high wavelengths beyond the visible region. This was associated with the increased interaction of the photons with electrons, atoms or crystal molecules and increased back reflections depending on increasing energy. Furthermore, the reflection values of the samples decreased with Ni dopant. This was associated with the increase in the number of grain boundaries causing optical scattering due to the reduction of the crystal size depending on the doped Ni. Since the grain boundary scattering increased with the increasing number of grain boundaries, the optical reflection values of the samples were thought to decrease.

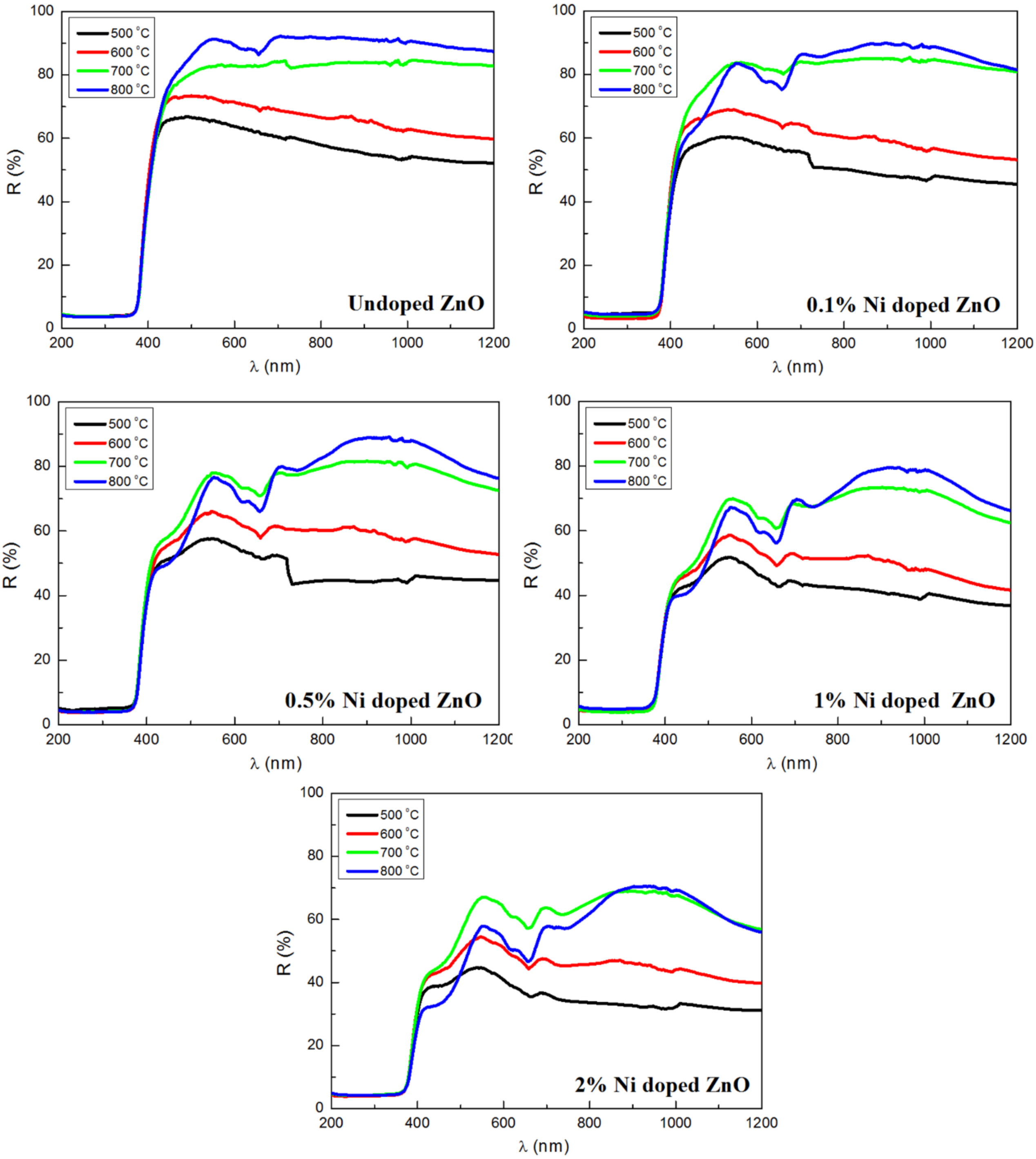

Figure 3. The comparison of reflectance values of samples with different sintering temperature with the same additive ratio

Fig. 3. shows the diffuse reflectance curves obtained from the ZnO-based nano-electroceramics at different temperature. As can be seen from the reflection spectra given in Fig. 2, optical reflections also increased with the increasing sintering temperature. The lowest reflection values were observed in undoped ZnO sample. The reflection curves of the samples show that the optical reflection increased

with increasing wavelength but decreased when shifting to short wavelengths. This was caused by the fact that the photons less interacted with electrons, atoms or crystal molecules and the back reflection decreased since the energy of photons decreased.

3.2. Determination of forbidden energy ranges of samples

In order to determine E_g values of undoped and Ni-doped ZnO nano electroceramics, diffuse reflectance spectra given in Fig. 2 were used based on The Kubelka-Munk theory. With this method, reflectance values can be converted into absorption values by means of the Kubelka-Munk function. Kubelka-Munk function is defined by [19]:

$$F(R) = \frac{(1-R)^2}{2R} \tag{1}$$

Where *R* is diffuse reflectance and *F(R)* is the Kubelka-Munk function corresponding to the absorbance value. *F(R)* value is converted to the absorption coefficient by the following equation [20] :

$$\alpha = \frac{F(R)}{t} = \frac{Absorbance}{t} \tag{2}$$

Where t is the sample thickness. In this case, the equation used for determining the optical band gaps of the samples can be written as follows [21]:

$$\left(\frac{F(R)h\nu}{t}\right) = A\,.\,(h\nu - E_g)^n \tag{3}$$

Where *A* is an energy-independent constant, $h\nu$ is the photon energy, E_g is the optical band gap and *n* is ½ (for direct transitions). With the help of sample thicknesses, $(\alpha h\nu)^{1/n}$ graphs of the samples against $h\nu$ were plotted. Energy value of the point where the line corresponding to the linear part of the graph intersects with *the* $h\nu$ axis at $(\alpha h\nu)^n = 0$ gives the value of the optical band gap of that material. If the value of *n* is 2, then the material has an indirect band gap, if n is ½, then the material has a direct band gap. When *n* was replaced with ½ in the obtained graphs, the best linearity was obtained. Thus, it was determined that the samples had the direct band pass. Fig. 4 shows $h\nu$-$(\alpha h\nu)^2$ graphs of the samples. Table.1 shows the optical band gap values calculated with the help of these curves.

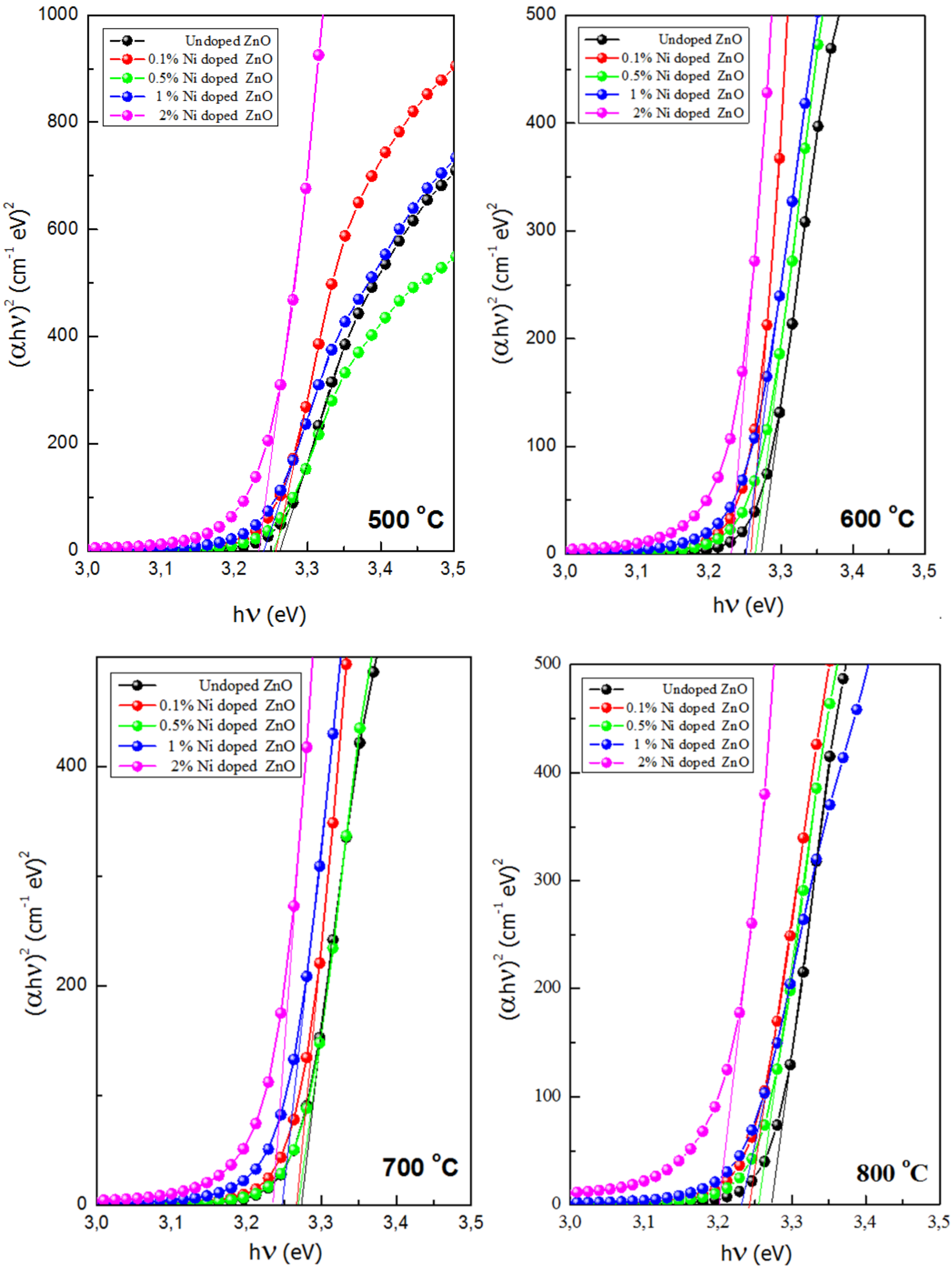

Figure 4. The plots of $(\alpha h\nu)^2$vs. the photon energy of the undoped and Ni-doped ZnO nanoceramics sintered at 500, 600, 700 and 800 °C

Table 1. E_g values of the undoped and Ni-doped ZnO nanoceramics sintered at 500, 600, 700 and 800 °C

	E_g at 500 °C (eV)	E_g at 600 °C (eV)	E_g at 700 °C (eV)	E_g at 800 °C (eV)
Undoped	3.27	3.28	3.28	3.28
0.1% Ni	3.26	3.26	3.27	3.24
0.5% Ni	3.25	3.27	3.27	3.26
1% Ni	3.23	3.25	3.25	3.23
2% Ni	3.21	3.23	3.24	3.20

As it is seen in Table 1, the optical band gap of the samples significantly decreased with increasing Ni ratio. In addition, when the temperature increases, the forbidden energy ranges decrease. This is because the carrier concentration increased with increasing Ni ratio [22]. The sample having the lowest optical band gap was 2% Ni-doped ZnO at 800 °C. The obtained optical band gap values were compatible with the theoretical values in the literature and Eg values of ZnO-based materials synthesized with different methods [23]. The variation of the forbidden energy ranges depending on the sintering temperature is shown in Fig. 5.

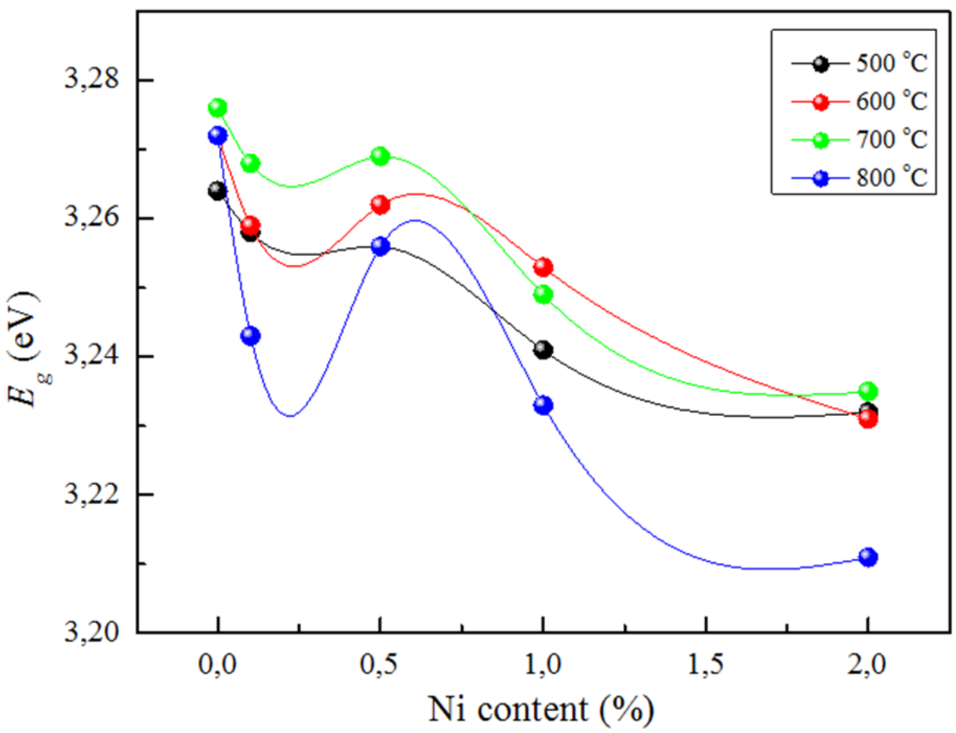

Figure 5. The change of the E_g with temperature

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