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Investigation of Sintering Kinetics of NiO using Photoacoustic Spectroscopy

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Abstract:
Sintering kinetics of NiO was investigated using photoacoustic spectroscopy. This method was used to follow the change of phase and amplitude of the photoacoustic signal of nickel-oxide samples sintered at 1373 K for 15-240 min. as a function of modulation frequency of the laser beam. Fitting of experimental data enabled determination of photoacoustic properties including thermal diffusivity of sintered nickel-oxide. Analysis of the change of sample density during sintering showed that the sintering process of this material can be observed from the viewpoint of activated volume and the change of thermal diffusivity can be correlated with the change of density of this material.
Keywords: *Sintering kinetics, NiO, Photoacoustic spectroscopy.*

1. Introduction

The method of photoacoustic spectroscopy has lately been used much more often for the characterization of different materials [1-4]. Besides applications for characterization of electronic, optical and defects structures of semiconductors [4] this method can be applied for the characterization of electronic states and structural disorders of ceramic materials [1]. In a typical photoacoustic experiment the sample is placed in a closed photoacoustic cell exposed to radiation with a modulated laser beam. The dependence of the obtained photoacoustic signal on the rate of diffunded heat through the sample enables thermal characterization of the sample, i.e. determination of different properties of the analyzed material including thermal diffusivity [3].

Nickel-oxide is a very interesting anti-ferromagnetic semiconductor of the p-type. It is characterized by a high resistivity that is the consequence of an expressed ionic bond nature. In this work the method of photoacoustic spectroscopy is viewed from the viewpoint of transport of activated volume having in mind the relation between this parameter and the density of sintered samples.

2. Experimental work

Nickel-oxide powder (Johnson Mathey and Co Ltd) 99.95% pure was pressed with

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1.5 GPa into pellets 10 mm in diameter. The average green density was 3.724 g/cm^3. Green samples were then isothermally sintered at 1373 K for 15-240 min. Densities of sintered samples were determined and the values obtained are given in table I.

The method of photoacoustic spectroscopy was used to follow changes in phase and amplitude of the photoacoustic signal of obtained sintered samples. Samples were placed in a photoacoustic cell protected from external influences described in detail in [5]. A 10 mW He-Ne laser modulated with a mechanical chopper was used as the optical source in the way described in [6]. The experimental setup for a photoacoustic measurement is given in fig. 1.

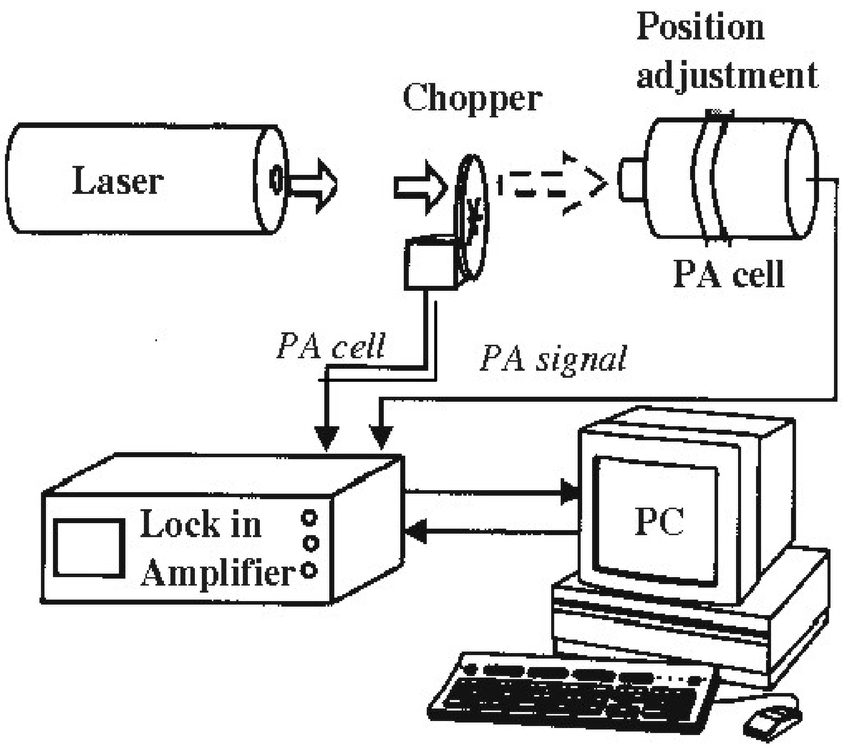

Fig. 1 Experimental setup for a photoacoustic experiment

3. Results and discussion

A theoretical analysis of experimentally obtained data was performed using the method described in detail in [6] based on the Rozenzweig-Gersho model [7]. Normalized experimental photoacoustic phase and amplitude diagrams were fitted with theoretically calculated photoacoustic signals for nickel-oxide. On fig. 2 an example of the phase and amplitude of the photoacoustic spectra for nickel-oxide sintered at 1373 K for 240 minutes is given. A fitting procedure described in detail in [4] was used for determining thermal parameters of nickel-oxide, including thermal diffusivity. The obtained values are given in table I. With the increase of sintering time the thermal diffusivity value increases reaching 80% of the value obtained for monocrystal nickel-oxide (1.2×10^{-4} m^{2}s^{-1} [8]) for the maximum sintering time of 240 min.

Tab. I Measured density and calculated thermal diffusivity of nickel-oxide sintered for different time intervals

Sintering time (min)	Density (g/cm^3)	Thermal diffusivity (m^2s^{-1}) x10^{-5}
15	4.76	0.67
30	4.88	0.75
60	5.01	0.87
120	5.22	0.91
240	5.29	0.97

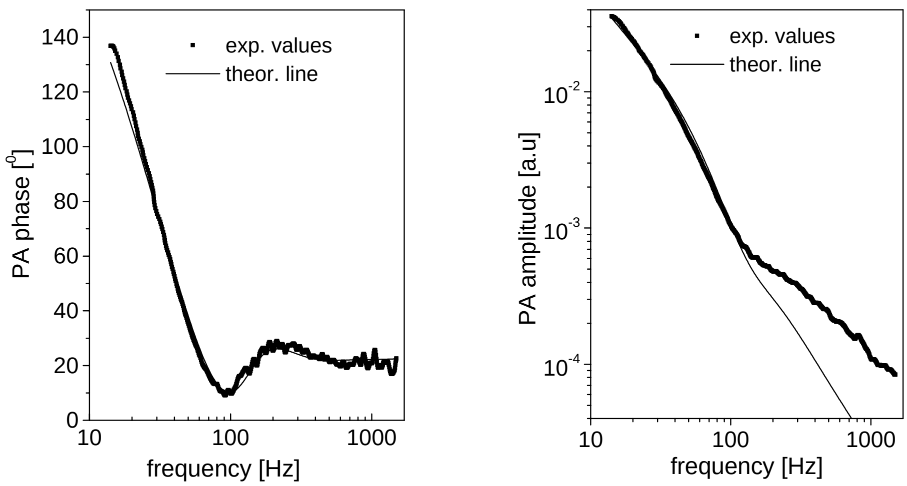

Fig. 2 Phase and amplitude of the photoacoustic spectra of nickel-oxide sintered at 1373 K for 240 min

Analysis of experimental data of sample density change during sintering for different time periods has shown that the sintering kinetics of this material can be analyzed from the viewpoint of activated volume (fig. 3).

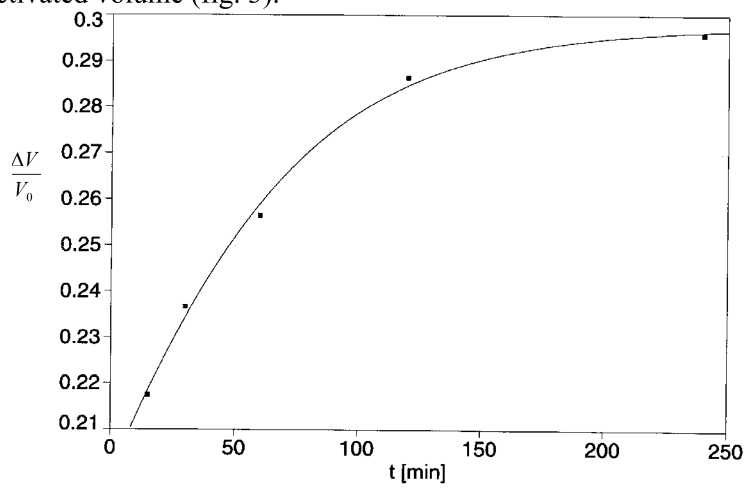

Fig. 3 Change of relative volume of nickel-oxide during isothermal sintering (the full line represents the curve obtained using eq. (1), while the points represent experimental data)

Mass transport during the sintering process can be presented as the movement of effective activated volume in the system [9]. In any moment of the sintering process the effective activated volume gravitates towards the value of equilibrium activated volume.

If density is expressed as the change of relative volume ($\Delta V / V_0 = 1 - \rho_0 / \rho$) then the dependence described in detail in [9] can be used:

$$\frac{\Delta V}{V_0} = \frac{K}{1 + C\exp(-st)} \cdot (st)^n \tag{1}$$

where K – the process rate constant, C – a constant defining the relationship between the starting effective activated volume and the equilibrium effective activated volume, s – a norming parameter, n – a constant dependent of the process mechanism. In our experiment the following parameter values were obtained: $K = 0.297$, $C = 0.4885$, $s = 0.0197$, $n = 3.69\ 10^{-5}$.

Analysis of values obtained for thermal diffusivity for different sintering times has shown that the value of this parameter increases with sintering time and the form of this curve resembles the density change curve (fig. 4).

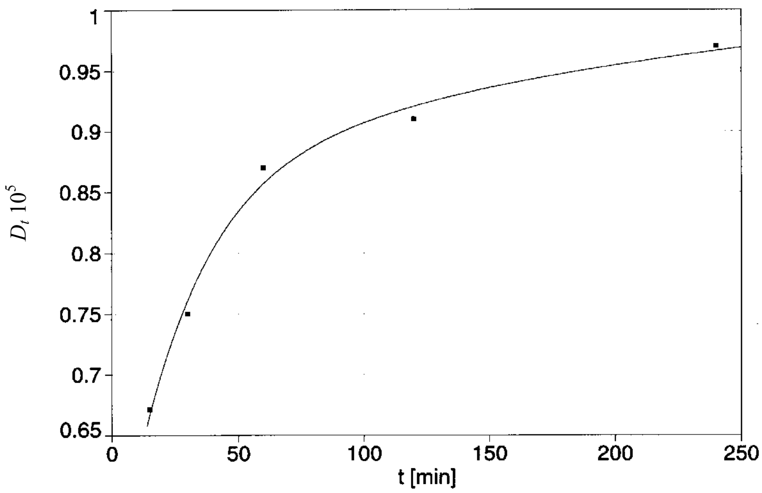

Fig. 4 Change of thermal diffusivity with sintering time

By definition thermal diffusivity is

$$D_t = \frac{\lambda}{C_t \rho} \tag{2}$$

where λ – the thermal conductivity, C_t – the thermal capacity, ρ- the density.

From a phenomenological viewpoint the dependence of thermal diffusivity on sintering time is characterized by a principle with formally the same form as eq. (1):

$$D_t = \frac{K_t}{1 + C_t\ \exp(-s_t t)} \cdot (s_t t)^{n_t} \tag{3}$$

This would in principle indicate that activated volume has a certain role in the change of thermal diffusivity during the sintering process as both thermal conductivity and thermal capacity depend on the materials density. It can thus be concluded that the thermal diffusivity of this material changes in accordance with the change of material density during the sintering process.

4. Conclusion

In this paper photoacoustic phase and amplitude diagrams of sintered nickel-oxide were measured in relation to the frequency of the chopped laser beam. It was shown that thermal diffusivity of this material increases with the sintering time achieving for maximal sintering time 80% of the value obtained for the nickel-oxide monocrystal. The change of density of nickel-oxide during the sintering process can be analyzed from the viewpoint of activated volume. It has been shown that the change of thermal diffusivity of this material occurs in correlation with the change in density.

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References

1. T. Toyoda, S. Shimamoto, Materials Science and Engineering B54 (1998), 29-32
2. J. Soldner, K. Stephan, Chemical Engineering and Processing 38 (1999), 585-591
3. N. A. George, T. Paul, P. Radhakrishnan, V. P. N. Nampoori, C. P. G. Vallabhan, M. T. Sebastian, Journal of Materials Science Letters 19 (2000), 499-501
4. P. M. Nikolić, D. Vasiljević, M. Miletić, Glas CCCLXXX of the Serbian Academy of Sciences and Arts, Department of Technical Sciences, vol. 32, 1996, 27-34
5. D. M. Todorović, P. M. Nikolić, Opt. Eng. 36 (1997), 432
6. P. M. Nikolić, M. V. Nikolić, D. Luković, S. Savić, M. M. Ristić, Zeitschrift fur Metallkunde, 95 (2004), 147-150
7. A. Rosencwaig, A. Gersho, J. Appl. Phys 47 (1976), 11
8. P. M. Nikolić et al, to be published J. of Phys. Condensed Matter
9. M. V. Nikolić, Fenomenological laws of the kinetics of the sintering process", Ph.D. thesis, Belgrade, 2003

***Резюме**: Кинетика спекания NiO исследована при помощи фотоакустической спектроскопии. Наблюдались изменение фазы и амплитуды фотоакустического сигнала в функции частоты модуляции лазерного пучка для образцов NiO, спеченных при температуре 1373 K с выдержкой 15-240 мин. Фитованием экспериментальных данных определены фотоакустические свойства, включая и термодиффузию спеченного NiO. Анализ изменения плотности образца в процессе спекания показывает что процесс спекания данного материала можно рассматривать с точки зрения переноса активированного объема и что процесс термодиффузии протекает в корреляции с изменением плотности данного материала.*
***Ключевые слова**: Кинетика спекания, NiO, фотоакустическая спектроскопия.*

***Садржај**: Кинетика синтеровања NiO проучена је коришћењем фотоакустичне спектроскопије. Овом методом праћена је промена фазе и амплитуде фотоакустичног сигнала у функцији учестаности модулације ласерског снопа за узорке никл-оксида синтероване на температури од 1373 K у току 15-240 мин.. Фитовањем експерименталних података одређена су фотоакустична својства, укључујући и топлотну дифузивност синтерованог никл-оксида. Анализа промене густине узорка током процеса синтеровања показала је да се процес синтеровања овог материјала може посматрати са гледишта транспорта активиране запремине,* *као и да се промена топлотне дифузивности одвија у корелацији са променом густине овог материјала.*

***Кључне речи**: Кинетика синтеровања, NiO, фотоакустична спектроскопија.*