Semiconductor Physics, Quantum Electronics & Optoelectronics, 2011. V. 14, N 1. P. 109-113.

PACS 82.45.Xy, 92.60.Jq

Study of nanoporous in humidity-sensitive $MgAl_2O_4$ ceramics with positron annihilation lifetime spectroscopy

H. Klym
Scientific Research Company "Carat", 202, Stryjska str., 79031 Lviv, Ukraine
Lviv Polytechnic National University, 12, Bandera str., 79013 Lviv, Ukraine
Phone: 8-0322-638303 ; e-mail: klymha@yahoo.com, scigroup@novas.com.ua

Abstract. It has been shown that positron annihilation lifetime spectroscopy is a quite promising tool for nanostructural characterization of humidity-sensitive spinel-type $MgAl_2O_4$ ceramics. The results have been achieved using the four-component fitting procedure with arbitrary lifetimes that is applied to mathematically treat the measured spectra. It has been shown that the Tao-Eldrup model is adequate to calculate the nanopore size in $MgAl_2O_4$ ceramics if using the lifetime values of the third and fourth components.

Keywords: nanopore, humidity-sensitive ceramics, sensor, spectroscopy.

Manuscript received 28.04.10; accepted for publication 02.12.10; published online 28.02.11.

1. Introduction

Nowadays, an adequate understanding the correlation between structure and physical-chemical properties of functional ceramics, one of the typical representatives of the so-called topologically disordered substances having wide application, is still in a sphere of sharp scientific and commercial interests for scientists and numerous known electronic firms all over the world [1-4]. The atomic-species structure or spatial order arrangement in atomic positions is typically taken as a main determinant for their properties. In bulk ceramics, in dependence on the sintering temperature, a significant shrinkage of the atomic structure occurs, which leads finally to more or less complicated pore topology [5]. These pores along with specific vacancy-type defects within individual crystalline grains and intergranual boundaries represent free-volume structure of ceramics.

Humidity-sensitive nanoporous $MgAl_2O_4$ ceramics with the spinel structure are one of the most promising materials in view of their application in microelectronics as active elements for humidity sensors [6-9]. Because of significant complications in the microstructure of these ceramics revealed at the levels of individual grains, intergranual boundaries and pores, the further progress in this field depends on the development of new characterization techniques that can be used in addition to the traditional ones. This concerns the positron annihilation lifetime spectroscopy (PALS), the method really applied to ceramics because of significant complications in correct interpretation of the obtained data [9].

Positrons injected to the studied $MgAl_2O_4$ ceramics undergo two positron trapping with two components in positron lifetimes and ortho-positronium o-Ps decaying, these parameters being obtained with the so-called three- and four-component mathematical fitting procedure. Within this approach, the shortest component of the deconvoluted PALS spectra with the positron lifetime τ_1 reflects mainly microstructure specificity of the spinel ceramics, and the middle component with the positron lifetime τ_2 corresponds to extended defects located near intergranual boundaries. The third and fourth components with the lifetimes τ_3 and τ_4 are related to "pick-off" annihilation of o-Ps in nanopores. It is established that the adsorbed water molecules act catalytically on positron trapping in $MgAl_2O_4$ ceramics, and do not change significantly o-Ps decaying modes [10]. This work is aimed at the study of application possibilities of the PALS technique to characterize nanoporous features of humidity-sensitive spinel $MgAl_2O_4$ ceramics.

2. Theoretical approach within the frames of the Tao-Eldrup model

To study o-Ps "pick-off" annihilation processes in $MgAl_2O_4$ ceramics, the mathematical model is needed for adequate description of nanostructured pores in these

humidity-sensitive materials. As this model, the Tao-Eldrup one can be applied.

In recent 20 years, the relation between the o-Ps lifetime and free volume size has been determined using the Tao-Eldrup model [11, 12]. It assumes that o-Ps trapped inside the spherical free volume (represented by rectangular potential well) may decay spontaneously via three-quantum annihilation or "pick-off" process. In this case, the o-Ps decay constant is

$$\lambda_{T-E} = \lambda_b P + \lambda_T (1-P), \quad (1)$$

where $\lambda_b = \frac{1}{4}\lambda_S + \frac{3}{4}\lambda_T$ is the decay rate of ortho-positronium in bulk material (λ_S = 7.9895 ns and λ_T = 7.0410 ns are the decay rates of para- and o-Ps in vacuum), P is the probability to find o-Ps outside the potential well.

The Tao-Eldrup model was elaborated for small free volumes, like vacancies in solids, voids in polymers, bubbles forced by Ps in liquids. In that case, the spacing of energy levels in small voids is much larger than thermal energy, and thus only the lowest level is populated; Ps wavefunction for this state is the spherical Bessel function. In order to simplify the calculations, the well of finite depth is substituted by infinitely deep one but broadened Δ (nm), which is needed to reproduce the value of P in finite well depth and radius R (nm) [11, 12]. Then,

$$P = 1 - \frac{R}{R+\Delta} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta}\right). \quad (2)$$

The results of calculation for cubic geometry can be compared to spherical (or cylindrical) side length a (nm):

$$a = 2(R+\Delta). \quad (3)$$

The square of o-Ps wavefunction in an infinite potential well is adduced in [11].

3. Experimental

The studied ceramics were prepared from Al_2O_3 with specific surface area of 67 m^2/g and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ with specific surface area of 12.8 m^2/g. The obtained powder is mixed with an organic binder to prepare green body billets. Then, these pellets are sintered using a special technological regime with the maximal temperatures T_s of 1200, 1300 and 1400 °C for 2 h.

Phase composition of $MgAl_2O_4$ ceramics was determined using the X-ray diffractometry (XRD) method. The XRD patterns were recorded at room temperature using HZG-4a powder diffractometer with Cu$K\alpha$ radiation. This equipment was attested with NIST SRM-1976 and Si standards. The measurements were carried out in 2θ step of 0.05° with variable scanning rate, depending on sample quality. The profile analyses were performed using the method of approximation of X-ray reflections by the pseudo-Voigt function. The lattice parameters and crystal structures of phases were refined using the Rietveld method with FULLPROF.2k program [13] from WinPLOTR software [14, 15].

Results obtained with XRD method testify that ceramics sintered at T_s = 1200-1400 °C contain two phases: the main spinel $MgAl_2O_4$ phase (space group $Fd\bar{3}m$) and some additives of MgO (space group $Fm\bar{3}m$). The phase composition of $MgAl_2O_4$ ceramics obtained with XRD method is shown in Table 1.

PALS measurements were performed with an ORTEC spectrometer based on ^{22}Na source placed between two ceramic samples (Fig. 1) at 20 °C and relative humidity of 35%, as it was described in more details elsewhere [16, 18].

The obtained spectra were mathematically treated with the LT computer program [20]. In general, we used 4 to 5 measured spectra for each pair of samples differed by a total number of elementary annihilation events in the range of 0.9-1.2 millions. Each of these spectra was multiply treated owing to slight changes in the number of final channels, annihilation background and time shift of the spectrum. Then, the variance of statistically weighted least-squares deviations between experimental points and theoretical curve was taken into account to compare the obtained results. Only results with deviations quite close to 1.0 (the optimal deviation ranges from 0.95 to ~1.1-1.2) were left for further consideration. In such a way, we obtained the numerical PAL parameters (positron lifetimes τ_1, τ_2, τ_3 and τ_4 as well as intensities I_1, I_2, I_3 and I_4), which correspond to annihilation of positrons in the samples of interest.

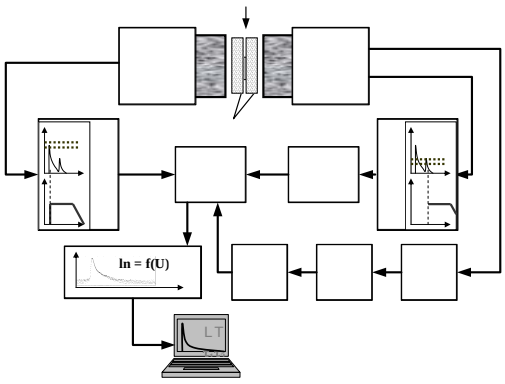

Fig. 1. Block-scheme of conventional sample-source "sandwich" arrangement for PALS measurements using the ORTEC apparatus [17, 19]: *1* – foil-covered ^{22}Na source, *2* – two identical samples, *3.1* and *3.2* – scintillators of γ-quanta (plastic KL detectors), *4.1* and *4.2* – photomultipliers (model RCA 8575), *5.1* and *5.2* – constant fraction discriminators (model 473A), *6* – delay line (model 425A), *7* – time-pulse height converter (model 467), *8* – preamplifier (model 113), *9* – amplifier (model 471), *10* – single channel analyzer (model 455), *11* – multichannel analyzer (model 6420B), *12* – personal computer.

Table 1. Phase composition of $MgAl_2O_4$ ceramics.

T_s, °C	$MgAl_2O_4$ – weight fraction, %	MgO – weight fraction, %
1200	93.63(0.78)	**6.37(0.27)**
1300	94.12(0.80)	**5.88(0.30)**
1400	94.05(0.78)	**5.95(0.34)**

The positron trapping modes in the sintered $MgAl_2O_4$ ceramics were calculated using the known formalism for the two-state positron trapping model [17, 21]:

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \quad \kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right), \tag{4}$$

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}, \tag{5}$$

where τ_b is the positron lifetime in defect-free bulk, τ_{av} – average positron lifetime, κ_d – positron trapping rate of defect. In addition, the $\tau_2 - \tau_b$ difference was accepted as a size measure for extended free-volume defects where positrons are trapped (in terms of equivalent number of monovacancies), as well as the τ_2/τ_b ratio was taken in a direct correlation to the nature of these defects [22].

3. Results and discussion

In accordance with the scanning electron microscopy data presented in [23], the observed additional phases are non-uniformly distributed within ceramics bulk, being more clearly pronounced near intergranual boundaries. These phase extractions serve as specific trapping centers for positrons penetrating ceramics. So, using the PALS method we could study more carefully structural peculiarities of the $MgAl_2O_4$ ceramics sintered at various T_s.

Taking into account the model described in [16, 22, 23], the shortest lifetime component in the studied ceramics reflects mainly the microstructure specificity of the spinel with character octahedral and tetrahedral cation vacancies. It is shown (see Table 2) that the lifetime τ_1 of this first component and intensity I_1 are not practically changed with T_s. The second component with the positron lifetime τ_2 corresponds to extended defects located near intergranual boundaries. The fitting parameters of this lifetime component (τ_2 and I_2) decrease with T_s. Consequently, the corresponding positron trapping modes of extended defects near intergranual boundaries will be changed, too. The third and fourth components with the lifetimes τ_3 and τ_4 are caused by "pick-off" annihilation of o-Ps in nanopores [23].

These changes are related with a more branched structure of open pores in the ceramics sintered at higher T_s (1300 and 1400 °C). With T_s growing, the o-Ps "pick-off" decay occurs preferentially in the nanopores filled by absorbed water, while the ceramic samples sintered at relatively low T_s (1200 °C) show this process in both water-filled and water-free nanopores.

The positron trapping modes such as the average τ_{av}, defect-free bulk τ_b and difference $\tau_2 - \tau_b$ are insignificantly changed with the sintering temperature.

Table 2. PALS Characteristic of $MgAl_2O_4$ ceramics mathematically treated with the four-component fitting procedure.

T_s, °C	Fitting parameters								Positron trapping modes				
	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.	τ_4, ns	I_4, a.u.	τ_{av}, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2-\tau_b$, ns	τ_2/τ_b
1200	0.16	0.65	0.38	0.33	2.03	0.010	48.4	0.011	0.24	0.20	1.07	0.18	1.89
1300	0.15	0.67	0.35	0.32	1.98	0.007	40.8	0.005	0.22	0.19	0.85	0.20	2.03
1400	0.15	0.67	0.35	0.31	1.94	0.008	42.4	0.005	0.22	0.19	0.81	0.21	2.10

Table 3. o-Ps lifetime as a function of the pore size within the range of free volume for sphere, cube and capillaries with circular and square cross-sections, when assuming the side length $a = 2R$ (T = 293 K).

o-Ps life-times, ns	Pore size, nm/geometry					
	spherical		cubic	cylindrical		cuboidal
	Δ = 0.166 nm	Δ = 0.18 nm	Δ = 0.18 nm	Δ = 0.19 nm	Δ = 0.18 nm	Δ = 0.18 nm
τ_3 2.03	0.28	0.31	0.28	0.25	0.2	0.22
1.98						
1.94						
τ_4 48.4	1.60	1.80	1.70	1.52	1.4	1.35
40.8	1.40	1.55	1.45	1.30	1.2	1.17
42.4	1.45	1.60	1.50	1.36	1.3	1.20

In addition, the positron trapping centre (τ_2/τ_b) is formed on a typical for $MgAl_2O_4$ ceramics level of ~1.9-2.0 [22], which testifies to the same nature of trapping sites, whatever the content of absorbed water. In contrast, most significant changes in positron trapping in $MgAl_2O_4$ ceramics are reflected in the positron trapping rate in defect κ_d (see Table 2).

In addition, the size of nanopores for $MgAl_2O_4$ ceramics in spherical, cylindrical, cubical and cuboidal approximations can be calculated using the o-Ps "pick-off" lifetime (third and fourth components with the lifetimes τ_3 and τ_4) within the frames of the Tao-Eldrup model [11, 12]. The size of nanopores for spinel-structured $MgAl_2O_4$ ceramics calculated with the above model using τ_3 has been shown in Table 3.

4. Conclusions

Thus, positron annihilation lifetime spectroscopy can be successfully used for experimental studies of structural defects and nanoporosity in humidity-sensitive $MgAl_2O_4$ ceramics. The Tao-Eldrup model can be applied to calculation of the nanopore size in ceramic materials for sensor electronics.

5. Acknowledgement

The author thanks to Dr. I. Hadzaman (Drohobych Ivan Franko State Pedagogical University, Drohobych, Ukraine) for sample preparation and Dr. A. Ingram (Opole University of Technology, Poland) for assistance in PALS experiments.

References

1. P.M.G. Nambissan, C. Upadhyay, H.C. Verma, Positron lifetime spectroscopic studies of nanocrystalline $ZnFe_2O_4$ // *J. Appl. Phys.* **93(**10**)**, p. 6320-6326 (2003).
2. S. Ghosh, P.M.G. Nambissan, R. Bhattacharya, Positron annihilation and Mössbauer spectroscopic studies of In3+ substitution effects in bulk and nanocrystalline $MgMn_{0.1}Fe_{1.9-x}In_xO_4$ // *Phys. Lett. A*, **325**, p. 301-308 (2004).
3. J. He, L. Lin, T. Lu, P. Wang, Effects of electron- and/or gamma-irradiation upon the optical behavior of transparent $MgAl_2O_4$ ceramics: different color centers induced by electron-beam and γ-ray // *Nucl. Instrum. Meth. Phys. Res. B* **191**, p. 596-599 (2001).
4. T. Gron, J. Wolff, Th. Hehenkamp, K. Bärner, I. Okonska-Kozlovwska, I. Jendrzejewska, E. Malicka, Positron trap studies in $Zn_{1-x}Cu_xCr_2Se_4$ spinels // *J. Phys. IV France*, p. C1-273-274 (1997).
5. I.T. Sheftel, *Thermoresistors*. Nauka, Moscow, 1973, p. 415 (in Russian).
6. E. Traversa, Ceramic sensors for humidity detection: the state-of-the-art and future developments // *Sensor and Actuators B* **23**, p. 135-156 (1995).
7. G. Gusmano, G. Montesperelli, E. Traversa, Microstructure and electrical properties of $MgAl_2O_4$ thin film for humidity sensors // *J. Amer. Ceram. Soc.* **76**, p. 743-750 (1993).
8. G. Gusmano, G. Montesperelli, E. Traversa, A. Bearzotti, G. Petrocco, A. D'Amico, C. Di Natale, Magnesium aluminate spinel thin film as a humidity sensor // *Sensor and Actuators B* **7**, p. 460-463 (1992).
9. T. Seiyama, N. Yamazoe, H. Arai, Ceramic humidity sensors // *Sensor and Actuators* **4**, p. 85-96 (1983).
10. J. Filipecki, A. Ingram, H. Klym, O. Shpotyuk, M. Vakiv, Water-sensitive positron-trapping modes in nanoporous magnesium aluminate ceramics // *J. Phys.: Conf. Ser.* **79**, 012015-1-4 (2007).
11. P.B. Johns. A symmetrical condensed node for the TLM method // *IEEE Trans. Microwave Theory Tech.*, **MTT-35**, p. 370-377 (1997).
12. V. Trenkic, C. Christopoulos, T.M. Benson, Efficient computational algorithms for TLM // *1st Intern. Workshop TLM*, Univ. Victoria, Canada, p. 77-80 (1995).
13. J. Rodriguez-Carvajal, Recent developments of the program FULLPROF // *Commission on Powder Diffraction (IUCr)*, Newsletter, **26**, p. 12-19 (2001).
14. T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a windows tool for powder diffraction patterns analysis // *Materials Science Forum, Proc. Seventh European Powder Diffraction Conference,* Barcelona, p. 118-123 (2004).
15. R.J. Hill, C.J. Howard, Quantitative phase analysis from neutron powder diffraction data using the Rietveld method // *J. Appl. Crystallography* **20**, p. 467-474 (1987).
16. V. Balitska, J. Filipecki, A. Ingram, O. Shpotyuk, Defect characterization methodology in sintered functional spinels with PALS technique // *Phys. status solidi* (*c*) **4(**3**)**, p. 1317-1320 (2007).
17. O. Shpotyuk, J. Filipecki, *Free Volume in Vitreous Chalcogenide Semiconductors: possibilities of Positron Aannihilation Lifetime Study*. Częstochowa, 2003, p. 114.
18. O. Shpotyuk, A. Kovalskiy, J. Filipecki, T. Kavetskyy, Positron annihilation lifetime spectroscopy as experimental probe of free volume concepts in network glasses // *Phys. Chem. Glasses: Eur. J. Technol. B* **47(2)**, p. 131-135 (2006).
19. R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors. Defect Studies*. Springer-Verlag, Berlin-Heidelberg-New York, 1999, p. 378.

20. J. Kansy, Positronium trapping in free volume of polymers // *Radiation Phys. and Chem.* **58**, p. 427-431 (2000).
21. H. Klym, A. Ingram, O. Shpotyuk, I. Hadzaman, Water-sorption effects in nanoporous $MgAl_2O_4$ ceramics for humidity sensors // *Semiconductor Physics, Quantum Electronics and Optoelectronics*, **12(1)**, p. 31-34 (2009).
22. O. Shpotyuk, A. Ingram, H. Klym, M. Vakiv, I. Hadzaman, J. Filipecki, PAL spectroscopy in application to humidity-sensitive $MgAl_2O_4$ ceramics // *J. Europ. Ceram. Soc.*, **25**, p. 2981-2984 (2005).
23. H. Klym, A. Ingram, Unified model of multichannel positron annihilation in nanoporous magnesium aluminate ceramics // *J. Phys.: Conf. Ser*. **79**, 012014-1-6 (2007).