ВІСНИК ЛЬВІВ. УН-ТУ VISNYK LVIV UNIV.
Серія фізична. 2007. Вип.40. С.200-205 Ser.Physic. 2007. N40. P.200-205

PACS number(s): 61.43.Gt, 78.70.Bj, 61.46.Df, 68.35.Dv, 81.05.Je

NANOPOROUS SPINEL-TYPE FUNCTIONAL CERAMICS CHARACTERIZED BY PAL TECHNIQUE

H. Klym[1,2], A. Ingram[3], O. Shpotyuk[1], J. Filipecki[4]

*[1]Institute of Materials of Scientific Research Company "Carat",
202, Stryjska str., UA-79031 Lviv, Ukraine
e-mail: shpotyuk@novas.lviv.ua
[2]Lviv Polytechnic National University,
12, Bandera str., UA-79013 Lviv, Ukraine
[3]Opole University of Technology,
75, Ozimska str., PL-45370 Opole, Poland
e-mail: ingram@wszia.opole.pl
[4]Institute of Physics of Jan Dlugosz University of Czestochowa,
13/15, al. Armii Krajowej, PL-42201 Czestochowa, Poland
e-mail: j.filipecki@wsp.czest.pl*

Nanoporous spinel-type functional $MgAl_2O_4$ ceramics are characterized by positron annihilation lifetime spectroscopy. It is shown, that this method can be used to investigate both extended positron trapping defects and moisture adsorption processes in ceramics bulk.

Key words: spinel, spectroscopy, porosity, positron defects.

It is well known, that positron annihilation lifetime (PAL) spectroscopy is one of the most powerful techniques to study electron-defect structure of solids [1]. Previously, this method was successfully used for investigation of free-volume extended defects in some kinds of functional materials such as perovskite-type $BaTiO_3$ [2, 3] and $SrTiO_3$ [4] ceramics, nanocrystalline ferrites [5], hot-isostatic-pressed transparent $MgAl_2O_4$ ceramics [6], etc. In these materials, the main channels of positron annihilation were ascribed to individual vacancies and vacancy-like clusters, powder particle surfaces, grain-boundaries and nanostructural voids (pores), which can capture positronium atoms. By treating the obtained PAL spectra, the best results were achieved owing to a so-called three-component fitting procedure. But sometimes (as in the case of [6]), there were no numerical information on third component in the deconvoluted spectra, which corresponds to decay of ortho-positronium o-Ps.

In 2002, we tried to use PAL technique for mixed transition-metal managanite electroceramics with thermistor effect [7]. Despite strict confirmation on three-component fitting, a very small number of experimental data with poor statistics sufficiently complicated the final decision on the possibilities channels of positron annihilation in these materials. Therefore, additional attempts are needed now to clarify relations between positron trapping and positronium decay modes in these nanoporous ceramics.

In the last year, we tried to apply PAL method for magnesium aluminate $MgAl_2O_4$ ceramics – one of the most perspective materials for humidity sensors (HS) [8, 9]. In contrast to the previous research [7], it was shown that two channels of positron annihilation are character for these spinel-type ceramics – positron trapping and o-Ps decay modes, the latter process being supposed to occur via a so-called pick-off annihilation of o-Ps in the adsorbed water [10].

In this work, we shall try to confirm the above hypothesis on water-related origin of o-Ps decay modes in humidity-sensitive spinel-type magnesium aluminate $MgAl_2O_4$ ceramics.

The investigated samples of magnesium aluminate $MgAl_2O_4$ ceramics were prepared via conventional sintering route [11].

Starting MgO and Al_2O_3 reagents (with surface area of 17,1 and 10,7 m^2/g, respectively) were taken in a molar ratio of 1:1. These oxides were weighed, mixed with a highly pure acetone, ball-milled during 96 h and dried. The obtained powder with intrinsic surface area of 89.6 m^2/g was mixed with an organic binder to prepare green body disk-shaped billets. Then, these pellets were sintered in a special regime with maximal temperature Ts=1 100 °C. Heating was carried out with rate 100 $^oC/h$ from room temperature to 300 ^oC, next – heating with rate 200 $^oC/h$ to temperature Ts, extract of samples at this temperature during 2 hours and aftercooling in the regime of “furnace off”. In the result, we obtained porous ceramic samples with humidity-sensitive properties.

PAL measurements were performed with an ORTEC spectrometer [12], the full width at half maximum being 270 ps. The ^{22}Na isotope with 0,74 MBq activity was used as a positron source (with 9%), placed between two identical ceramic samples.

Firstly, the PAL measurements were carried out in as-prepared ceramic samples at 20 ^oC temperature and ~35% relative humidity. In order to verify hypothesis on water-related origin of o-Ps decay modes in these ceramics, which were well worked previously for cement pastes [13, 14], we placed these samples into distillated water for 12 h. Later, PAL measurements were repeated at the same conditions. One month later, these samples were investigated again.

The obtained PAL spectra were decomposed by LT computer program of J. Kansy [15] using a sum of a few weighted exponential functions convoluted with measured resolution function of the spectrometer. We used three measured PAL spectra for each investigated pair of samples, differing by a total number of counts. Each spectrum was multiply treated owing to slight changes in the number of final channels, background of annihilation and time shift of PAL spectrum. The best results were chosen by comparing the FITs, determined as statistically weighted least-squares deviations between experimental points and theoretical curve. In such a way, we formed a few groups of results containing different number of experimental points within each mathematical treatment procedure. Only results with FIT values close to 1,0 (the optimal FIT deviates from 0,95 up to ~1,1–1,2) were left for further consideration.

At the next stage, this FIT values and determined PAL parameters were controlled in dependence on the background of annihilation and time shift of PAL spectrum, the results showing slight changes being chosen. It should be noted that source correction and spectrometer resolution function were kept unchangeably for all PAL spectra.

The normalized positron lifetime spectra for investigated $MgAl_2O_4$ ceramics obtained in as-prepared, 12 h water-immersed and one-month natural-dried after water-immersion samples was shown in fig. Each of them is a superposition of a few spectra with different positron lifetimes. The obtained dependences are characterized by a narrow peak and region of long fluent decaying of coincidence counts in a time. The mathematical decay of such shape curve is represented by a sum of decreasing exponential functions with different values of power-like indexes inversed to positron lifetime [16].

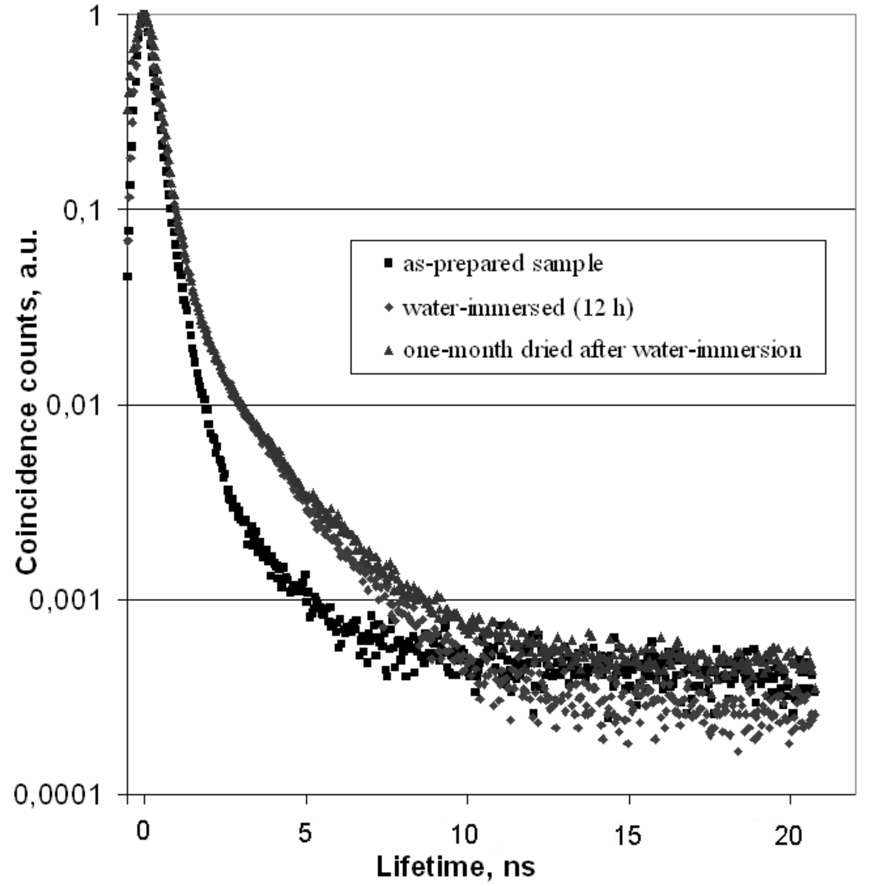

Fig. Peak-normalized positron lifetime spectra of magnesium aluminate $MgAl_2O_4$ ceramics (a comparison between as-prepared, 12 h water-immersed and one-month dried after water-immersion samples)

As we shown early [8], at mathematical treatment of PAL spectra of $MgAl_2O_4$ ceramics by LT computer program, the best results were obtained at three-component fitting procedure.

The first channel of positron annihilation in ceramics bulk was attributed with shortest (lifetime τ_1 and intensity I_1) and middle (lifetime τ_2 and intensity I_2) PAL components. This channel can be attributed to positron trapping modes, the trapping defects being individual vacancies and small vacancy-like clusters within ceramics bulk (τ_1=0,24 ns) and positron trapping defects in the form of neutral or negatively charged clusters of charge-compensating vacancies located at grain-boundaries (τ_2=0,50 ns).

In addition, the following positron trapping parameters were calculated for this case: the mean positron lifetime $\tau_{av.} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$, which reflects cumulative defect environment prevailing in the sample [5]; bulk lifetime $\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}$, associated with positron trapping in defect-free bulk [2, 5, 6, 15] and positron trapping rate in defects $k_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right)$ [12]. In the investigated $MgAl_2O_4$ ceramics, the difference (τ_2-τ_b) can be treated as size measure of trapping defect [5, 17], whereas τ_2/τ_b value represents the nature of this defect [6] (see Table).

Table

PAL characteristics of magnesium aluminate $MgAl_2O_4$ ceramics mathematically treated with three-component fitting procedure

Sample pre-history	**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.	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	τ_2 - τ_b, ns	τ_2/τ_b
as-prepared	0,24	0,68	0,50	0,30	2,59	0,02	0,32	0,28	0,7	0,21	1,7
water-immersed for 12 h	0,24	0,56	0,50	0,29	1,88	0,15	0,33	0,29	0,7	0,21	1,7
one-month natural-dried after water-immersion	0,18	0,56	0,42	0,35	2,02	0,09	0,27	0,23	1,2	0,19	1,8

The second channel of positron annihilation described by longest PAL component (lifetime τ_3 and intensity I_3) can be attributed to o-Ps decay modes. In as-prepared ceramics, the lifetime τ_3 equals 2,59 ns. But after 12 h water-immersion, this lifetime was decreased to 1,88 ns, the value close to o-Ps pick-off lifetime in water [10]. Respectively, the intensity at this component increased from 0,02 to 0,15. This increase was accompanied by the corresponding decrease in the first PAL component (see Table), while the second component left without any significant changes.

So, like to cement pastes [13], in humidity-sensitive magnesium aluminate $MgAl_2O_4$ ceramics the process of pick-off annihilation of o-Ps in volume pores filled with water occurs [18]. After one-month natural drying of water-immersed samples, the irreversible changes occur in the structure of $MgAl_2O_4$ ceramics. These changes are probably caused by separation of other phases in the pores and water remainders (I_3 = 0,09). In the result, the positron-trapping defect centres are modified by drying (the positron trapping rate increases from 0,7 to 1,2 ns^{-1}).

PAL investigation was confirmed that two channels of positron annihilation are character for nanoporous humidity-sensitive magnesium aluminate ceramics – positron trapping and o-Ps decay modes. The first channel is connected with positron trapping defects in the form of individual vacancies, small vacancy-like clusters and vacancies located at grain-boundaries. The second channel is linked with pick-off o-Ps annihilation in the adsorbed water. The PAL method can be applied to investigate the processes of structural changes in magnesium aluminate $MgAl_2O_4$ ceramics.

---

1. *Banerjiee A., Chaudhuri B.K Sarkar A., Sanyal D.* et al. The design of an electrostatic variable energy positron beam for studies of defects in ceramic coatings and polymer films // Phys. B. 2001. Vol. 229. P. 130–134.
2. *Langhammer H.T, Müller T., Polity A., Felgner K.-H.* et al. On the crystal and defect structure of manganese-doped barium titanate ceramics // Mater. Lett. 1996. Vol. 26. P. 205–210.
3. *Massoud A. M., Krause-Rehberg R., Langhammer H.T.* et al. Defect studies in $BaTiO_3$ ceramics using positron annihilation spectroscopy // Mater. Sci. Forum. 2001. Vol. 263-365. P. 144–146.
4. *Zhi Y., Chen A.* A positron annihilation study of $SrTiO_3$-based ceramics // J. Phys., Condens. Matt. 1993. Vol. 5. P. 1877–1882.
5. *Ghosh S., Nambissan P.M.G., Bhattacharya R.* Positron annihilation and Mössbauer spectroscopic studies of In^{3+} substitution effects in bulk and nanocrystaline $MgMn_{0.1}Fe_{1.9-x}O_4$ // Phys. Lett. A. 2004. Vol. 325. P. 301–308.
6. *He J., Lin L., Lu T., Wang P.* 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. Instr. Meth. Phys. Res. B. 2001. Vol. 191. P. 596–599.
7. *Shpotyuk O., Filipecki J., Vakiv M., Balitska V.* et al. Characterisation possibilities of positron annihilation lifetime spectroscopy in application to spinel-based functional ceramics // Steinfurter-Keramik-Seminar. 2002. Vol. 18. P. 1–5.
8. *Shpotyuk O., Ingram A., Klym H., Vakiv M., Filipecki J.* PAL spectroscopy in application to humidity-sensitive $MgAl_2O_4$ ceramics // J. Europ. Ceram. Soc. 2005. Vol. 25. P. 2981–2984.
9. *Traversa E.* Ceramic sensors for humidity detection: the state-of-the-art and future development // Sensors and Actuators. 1995. Vol. 23. P. 135–156.
10. *Kotera K., Saito T., Yamanaka T.* Measurement of positron lifetime to probe the mixed molecular states of liquid water // Phys. Lett. A. 2005. Vol. 345. P. 184–190.
11. *Sheftel I. T.* Thermoresistors. Moscow: Nauka, 1972. 416 p.
12. *Krause-Rehberg R, Leipner H.S.* Positron Annihilation in Semiconductors. Defect Studies // Springer-Verlag, Berlin-Heidelberg-New York. 1999. 378 p.
13. *Consolati G., Dotelli G., Quasso F.* Investigation of nanostructures in ordinary cement through positron annihilation lifetime spectroscopy // J. Appl. Phys. 1999. Vol. 86. N 8. P. 4225–4231.
14. *Consolati G., Dotelli G., Quasso F.* Drying and rewetting of mature cement pastes studied through positron annihilation lifetime spectroscopy // J. Am. Ceram. Soc. 2001. Vol. 84. N 1. P. 227–229.
15. *Kansy J.* Microcomputer program for analysis of positron annihilation lifetime spectra // Nucl. Instr. Meth. Phys. Res. 1996. Vol. A 374. P. 235–244.

16. *Bigg D.M.* A review of positron annihilation lifetime spectroscopy as applied to the physical aging of polymers // Polym. Engin. Sci. 1996. Vol. 36. N 6. P. 737–743.
17. *Nambissan P.M.G., Upadhyay C., Verma H.C.* Positron lifetime spectroscopic studies of nanocrystalline $ZnFe_2O_4$ // J. Appl. Phys. 2003. Vol. 93. N 10. P. 6320–6326.
18. *Goldanskyy V.I.* Physical chemistry of positron and positronium. Moskov, 1968. 174 p.

НАНОПОРИСТА ФУНКЦІОНАЛЬНА КЕРАМІКА ШПІНЕЛЬНОГО ТИПУ, ОХАРАКТЕРИЗОВАНА ЗА ДОПОМОГОЮ ТЕХНІКИ ПАС

Г. Клим[1,2], А. Інграм[3], О. Шпотюк[1], Я. Філіпецькі[4]

[1]Науково-виробнич підприємство "Карат",
вул. Стрийська, 202,79031 Львів, Україна
e-mail: shpotyuk@novas.lviv.ua
[2]Національний університет „Львівська політехніка"
вул. Бандери, 12, 79013 Львів, Україна
[3]Опольський технічний університет,
вул. Озімска, 75, 45370 Ополє, Польща
e-mail: ingram@wszia.opole.pl
[4]Інститут фізики університету Яна Длугоша в Ченстохові,
вул. Армії Крайової, 13/15, 42201 Ченстохова, Польща
e-mail: j.filipecki@ajd.czest.pl

Охарактеризовано нанопористу функціональну кераміку шпінельного типу $MgAl_2O_4$ методом позитронної анігіляційної спектроскопії. Показано, що цей метод може бути використано для дослідження в кераміці як об'ємних дефектів, так і процесів вологопоглинання.

Ключові слова: шпінель, спектроскопія, пористість, позитронні дефекти.

Стаття надійшла до редколегії 29.05.2006
Прийнята до друку 26.02.2007