Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 2981–2984
www.elsevier.com/locate/jeurceramsoc

PAL spectroscopy in application to humidity-sensitive $MgAl_2O_4$ ceramics

O. Shpotyuk [a,b,*], A. Ingram [c], H. Klym [a,d], M. Vakiv [a], I. Hadzaman [a], J. Filipecki [b]

[a] *Lviv Scientific Research Institute of Materials of Scientific Research Company "Carat", 202, Stryjska street, Lviv 79031, Ukraine*
[b] *Physics Institute of Pedagogical University of Czestochowa, 13/15, al. Armii Krajowej, Czestochowa 42201, Poland*
[c] *Institute of Mathematics, Physics and Chemistry of Opole Technical University, 75 Ozimska street, Opole 45370, Poland*
[d] *Institute of Telecommunications, Radioelectronics and Electronic Engineering, of Lviv Polytechnic National University, 12 Bandera street, 79013 Lviv, Ukraine*

Available online 5 April 2005

Abstract

It is shown that positron annihilation technique in variant of lifetime spectroscopy is a quite promising tool for nanostructural characterisation of extended free-volume defects in humidity-sensitive spinel-type alumomagnesium $MgAl_2O_4$ ceramics, the best results being achieved provided three-component fitting procedure with arbitrary lifetimes is applied to treat mathematically the measured spectra. Main channels of positron annihilation in the investigated ceramics are supposed to be connected with individual vacancies and vacancy-like clusters, powder particle surfaces, large-angle grain-boundaries and tiny nanostructured voids (pores) with average radius near 3.0 Å, which can capture positronium atoms. The developed approach seems to be especially attractive in tight combination with other experimental structural probes, first of all conventional mercury porosimetry and small-angle X-ray scattering technique.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Spinels; Grain boundaries; Sensors; Porosity; Spectroscopy

1. Introduction

Positron annihilation lifetime (PAL) spectroscopy is one of the most powerful tools for experimental study of extended free-volume defects in solids[1–3]. However, in respect to powder and fine-grained ceramics with functional properties this method has been rarely applied because of complications in correct interpretation of the obtained data. Recently, only a few attempts to develop the phenomenological PAL model for metallic Cu-, W- and Ni-contained powders and perovskite-type $BaTiO_3$ ceramics were made.[1] Nevertheless, the obtained results are sufficiently restricted by specificity of the investigated samples and, consequently, cannot be treated unambiguously for a more large range of functional ceramics.

In 2002, we tried to use the method of PAL spectroscopy for mixed spinel-type transition-metal managanite electroceramics for thermistors.[3] This work is focused on the methodological possibilities of PAL technique for nanostructural characterization of spinel-type alumomagnesium $MgAl_2O_4$ ceramics, extensively investigated as one of the most perspective materials for humidity sensors.[4]

2. Experimental

The studied spinel-type $MgAl_2O_4$ ceramics were prepared in accordance to conventional technological route.[4,5] MgO and Al_2O_3 reagents (with surface area of 17.1 and 1.4 m^2/g, respectively) in a molar ratio of 1:1 were taken as starting components. The above oxides were weighed, mixed with a highly pure acetone, ball-milled during 96 h and dried. The obtained powder with surface area of 16.7 m^2/g was mixed with an organic binder to prepare green body billets in a pellet (disk) form with 15 mm in diameter. These billets were sintered in a special regime with maximal temperature of 1250 °C. In the result, the humidity-sensitive ceramics having the specific surface area of 3.1 m^2/g, total

* Corresponding author. Tel.: +380 322 638303; fax: +380 322 632228.
E-mail address: shpotyuk@novas.lviv.ua (O. Shpotyuk).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.174

porosity of 51.3% and pore sizes from 0.04 to 1.3 μm were obtained.

In our PAL-experiments with ORTEC spectrometer,[2,3,6] the full width at half maximum was 0.270 ns and the ^{22}Na isotope with 0.74 MBq activity was used as a positron source (with input of 9%), placed between two identical ceramic samples. The measured PAL spectra were fitted by LT computer program of Kansy,[7] using a sum of a few weighted exponential functions, convoluted with the measured resolution function of the spectrometer. We used three measured PAL spectra for the investigated pair of samples, they differing by total number of counts or, in other words, ordinary annihilation evens in the range of 800,000–1,200,000. Each of these spectra was multiply treated owing to slight changes in the number of final channels, background of annihilation and time shift of the spectrum. The best results were selected at the basis of FIT (short abbreviation originated from "fitting"), determined as statistically weighted least-squares deviation between experimental points and theoretical curve.[6] We formed a few groups contained different number of experimental points N within each kind of the chosen mathematical treatment procedure. Only results with FIT values close to 1.0 (the optimal FIT deviation range from 0.95 up to ∼1.1 to 1.2) were considered as optimal ones. At the next stage, this FIT values and determined PAL characteristics were controlled in dependence on background of annihilation and time shift of PAL spectrum, the results showing only slight changes being chosen by us. It should be noted that source correction and spectrometer resolution function were kept unchangeable in the above algorithm.

In order to anticipate the possible kinds of positron annihilation channels, the scanning electron microscopy (SEM) investigations were performed on freshly prepared chips of the investigated ceramic samples using LEO 982 field emission microscope.

3. Results and discussion

As it testified from visual inspection of micrograph shown in Fig. 1, a large variety of positron trapping sites, such as grain boundaries, intrinsic surfaces of pores, incomplete intergranual contacts between some grains with incorporated pores of different geometrical sizes and shapes, etc. exist in the investigated ceramics. Additionally, a possibility for positronium Ps formation should be taken into account, as it was accepted previously for some other kinds of glassy-like, powder and fine-grained porous materials.[1–3] Since Ps is basically formed in two states (75% as ortho-positronium o-Ps with parallel spins and 25% as para-positronium p-Ps with antiparallel spins) and $\tau = 0.125$ ns is the best theoretical value for p-Ps lifetime,[1] it is reasonably to check a number of multi-component fitting procedures, which include this lifetime as fixed value. It should be noted that PAL spectroscopy would be especially sensitive only to tiny intrinsic

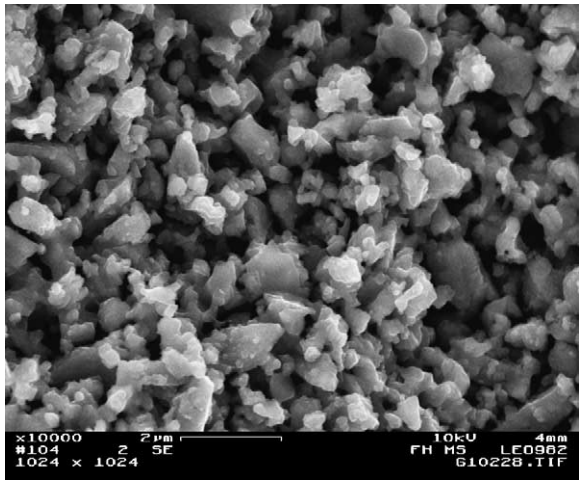

Fig. 1. SEM-micrograph of the freshly prepared chip of $MgAl_2O_4$ ceramics.

pores and very small free-volume voids with geometrical sizes less than ≤ 10 Å[1] because of small size of Ps (1.59 Å).

Taking into account that a total number of simultaneously distinguished PAL components in the decomposed PAL spectra does not exceed typically 4–5,[1] the following cases of mathematical fitting procedures are considered in order to develop the phenomenological model for multichannel positron annihilation in the investigated ceramics:

- one-component fitting procedure,
- two-component fitting procedure with arbitrary PAL parameters,
- three-component fitting procedure with arbitrary PAL parameters,
- four-component fitting procedure with arbitrary PAL parameters,
- three-component fitting procedure with fixed $\tau_1 = 0.125$ ns,
- four-component fitting procedure with fixed $\tau_1 = 0.125$ ns.

Obtained results are gathered in Table 1.

It is obvious that one-component fitting procedure is fully unacceptable to describe quantitatively the process of positron annihilation in the investigated $MgAl_2O_4$ ceramics because of too high FIT values (as high as 6.321). This fact testifies in a favour that free-volume defect-related processes are significant in these specimens to be neglected in comparison with free positron annihilation channel, as it takes place in some kinds of crystalline materials with low concentration of positron traps.[1]

If two-component fitting procedure with arbitrary PAL parameters is applied, the accuracy of mathematical treatment is only poor (the FIT value achieved 1.284 and 1.687 for two groups of results, contained $N = 9$ and $N = 13$ experimental points, respectively). So, more than one free-volume defect is probably formed in the ceramics body. The high value of long positron lifetime τ_2 in the decomposed PAL spectra testifies in a favour of Ps formation.

Table 1
PAL characteristics of alumomagnesium $MgAl_2O_4$ ceramics, treated with one-, two-, three- and four-component fitting procedures (the best result is bold-distinguished)

N	|FIT − 1.000|	PAL characteristics (lifetimes, intensities)							
		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.)
One-component fitting procedure									
5	6.321	0.27	1.00	–	–	–	–	–	–
Two-component fitting procedure with arbitrary PAL parameters									
9	0.284	0.22	0.98	1.51	0.02	–	–	–	–
13	0.687	0.23	0.94	0.94	0.06	–	–	–	–
Three-component fitting procedure with arbitrary PAL parameters									
14	0.002	0.18	0.74	0.40	0.24	1.62	0.02	–	–
9	0.006	0.19	0.78	0.43	0.20	1.68	0.02	–	–
8	**0.000**	**0.20**	**0.81**	**0.45**	**0.17**	**1.72**	**0.02**	**–**	**–**
31	0.020	0.21	0.83	0.51	0.15	1.93	0.02	–	–
Three-component fitting procedure with fixed τ_1 ($\tau_1 = 0.125$ ns) value									
3	0.286	0.125	0.20	0.26	0.75	1.10	0.05	–	–
2	0.555	0.125	0.30	0.27	0.66	1.19	0.04	–	–
2	0.384	0.125	0.43	0.29	0.53	1.27	0.04	–	–
Four-component fitting procedure with arbitrary PAL parameters									
14	0.004	0.19	0.77	0.41	0.20	1.29	0.03	6.9	0.004
17	0.007	0.20	0.80	0.43	0.18	1.38	0.02	4.8	0.002
Four-component fitting procedure with fixed τ_1 ($\tau_1 = 0.125$ ns) value									
18	0.052	0.125	0.002	0.20	0.82	0.49	0.16	1.9	0.02
9	0.072	0.125	0.28	0.24	0.59	0.61	0.11	2.1	0.02

Only three- and four-component fitting procedures can be more or less successfully used to correctly describe the obtained PAL data, since the corresponding FIT value is quite close to 1.000. However, if shortest lifetime is fixed at theoretically calculated level of p-Ps lifetime ($\tau_1 = 0.125$ ns), the accuracy of mathematical fitting falls down (the FIT value tends to 1.286 in the best group of selected experimental results, which contains too small number of points, $N = 3$) in respect to arbitrary-determined procedures. It means that Ps formation is a slight channel in positron annihilation, taking place only in a few kinds of structurally intrinsic pores. In fact, four-component fitting procedure leads to three-component one, because the intensity of fourth PAL component tends to 0.

Therefore, the best result ($\tau_1 = 0.20$ ns, $I_1 = 0.81$; $\tau_2 = 0.45$ ns, $I_2 = 0.17$; $\tau_3 = 1.72$ ns, $I_3 = 0.02$) can be obtained using three-component fitting procedure with arbitrary PAL parameters, the corresponding FIT value being equal to theoretically best one.

By comparing this result with known previous data for other kinds of electroceramics,[1,3] we can put forward the following supposition:

- the middle positron lifetime $\tau_2 = 0.45$ ns can be connected with positron annihilation on structurally intrinsic free-volume positron traps, such as extended vacancy-like clusters, powder particle surfaces, grain-boundaries, etc.;
- the input of bulk positron lifetime τ_b is probably revealed in the shortest (τ_1) PAL component, being interconnected with one (or two) shortest defect-related lifetimes corresponding to vacancies or small vacancy-like clusters in ceramics bulk;
- by supposed that semi-empirical expression connecting o-Ps lifetime τ_3 and pore (void) radius in spherical approximation in some kinds of polymer substances[1] is valid in the case under consideration, the average radius R of pores attributed to the third PAL component is estimated to be at the level of ∼3.0 Å.

The further development of this approach should be spread for other kinds of functional ceramics. No more important will be experimental study of effect of external influences (thermal treatment including thermally-stimulated ageing tests, high-energetic irradiation, etc.) and technological parameters (temperature and duration of sintering, etc.) on PAL data in ceramics of different chemical compositions. Especially attractive this experimental method seems to be in tight combination with other experimental structural probes, first of all conventional mercury porosimetry and small-angle X-ray scattering.

4. Conclusions

The PAL spectroscopy is a quite promising tool for nanostructural characterisation of spinel-type alumomagnesium $MgAl_2O_4$ ceramics, giving information on extended free-volume defects, such as:

- positron traps in the form of individual vacancies and small vacancy-like clusters, attributed to the shortest PAL component with $\tau_1 \approx 0.20$ ns and $I_1 = 0.81$;

- positron traps in the form of extended vacancy-like clusters, powder particle surfaces, large-angle grain-boundaries, attributed to the middle PAL component with $\tau_2 \approx 0.45$ ns and $I_2 = 0.17$;
- nanostructured free-volume voids in ceramics bulk (presumably, between individual grains owing to incomplete intergranual contacts), which can capture Ps.

Acknowledgements

This work was carried out in the framework of activity of Science and Technology Center in Ukraine (Project STCU # 3119). The microstructure characterisation of ceramics was performed in Fachhochschule Münster/University of Applied Sciences (Steinfurt, Germany) in accordance to the Agreement on cooperation with Lviv Scientific Research Institute of Materials of SRC "Carat" (Lviv, Ukraine).

References

1. Krause-Rehberg, R. and Leipner, H. S., *Positron Annihilation in Semiconductors Defect Studies*. Springer-Verlag, Berlin, Heidelberg, New York, 1999, 378 p.
2. Shpotyuk, O. and Filipecki, J., *Free-Volume in Vitreous Chalcogenide Semiconductors: Possibilities of Positron Annihilation Lifetime Study*. WSP w Czestochowie, Czestochowa, 2003, 114 p.
3. Shpotyuk, O., Filipecki, J., Vakiv, M., Balitska, V., Hadzaman, I. and Hyla, M., Characterisation possibilities of positron annihilation lifetime spectroscopy in application to spinel-based functional ceramics. In *6 Steinfurter-Keramik-Seminar: Materialfrschung und Anwendung Vol 18*, 2002, pp. 1–5.
4. Traversa, E., Ceramic sensors for humidity detection: the state-of-the-art and future developments. *Sens. Actuators*, 1995, **23**, 135–156.
5. Sheftel, I. T., *Thermoresistors*. Nauka, Moscow, 1973.
6. Shpotyuk, O., Filipecki, J., Kozdras, A. and Hyla, M., Two-state positron trapping model for vitreous arsenic triselenide. In *Contributions to Non-Crystalline Semiconductor Physics and to Optoelectronics*. Chisinau, Moldova, 2003, pp. 140–151.
7. Kansy, J., Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl. Instr. Meth. Phys. Res*, 1996, **A 374**, 235–244.