Atomic-deficient nanostructurization in water-sorption alumomagnesium spinel ceramics MgAl_2O_4

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Abstract

Atomic-deficient nanostructurization in alumomagnesium MgAl_2O_4 ceramics sintered at 1100–1400 °C caused by water sorption are studied employing positron annihilation lifetime spectroscopy. Detected PAL spectra are reconstructed from unconstrained x4-term decomposition, and further transformed to x3-term form to be applicable for analysis with x3–x2-CDA (coupling decomposition algorithm). It is proved that water-immersion processes reduce positronium (Ps) decaying in large-size holes of ceramics (1.70–1.84 nm in radius) at the expense of enhanced trapping in tiny (~ 0.2 nm in radius) Ps-traps. The water sorption is shown to be more pronounced in structurally imperfect ceramics sintered at $T_s = 1100\text{--}1200$ °C due to irreversible transformations between constituting phases, while reversible physical-sorption processes are dominated in structurally uniform ceramics composed of main spinel phase.

Keywords Positron annihilation · Trapping · Positronium · Spinel ceramics · Water sorption

Background

Alumomagnesium spinel ceramics MgAl_2O_4 are known to be an excellent candidate for humidity sensors possessing a row of functional advantages before known prototypes (Kulwicki 1991; Gusmano et al. 1992; Gusmano et al. 1993; Traversa 1995; Kashi et al. 2012). The mechanism of their remarkable sensing ability is related to a great diversity of chemical and physical water-sorption processes occurring in a rich nanoporous structure of these ceramics (Traversa 1995; Kashi et al. 2012).

At a nanospace, this functionality directly relates to well-known *host–guest chemistry* problems, dealing with filling of some open nanospaces in *host* matrix, which can be occupied by *guest* entities such as embedded atoms, molecules, atomic groups and clusters, distinct particles (Groen et al. 2003; Kobayashi et al. 2007; Hill et al. 2005; Kullmann et al. 2012). To identify such nanometer length–scale inhomogeneities, the method of positron annihilation lifetime (PAL) spectroscopy probing space–time continuum correlations for electron interaction with its antiparticle (positron), i.e.,

dependence between averaged positron lifetime and available free volume, was recognized recently as one of most promising non-destructive tools (Krause-Rehberg and Leipner 1999; Jean et al. 2003).

But possibilities of this method are essentially restricted, when dealing with substances with nanoscale atomic-deficient imperfections, i.e., free-volume elements in nano-substances possessing simultaneously contributions from positrons annihilating in (1) defect-free bulk state, (2) deep ground state of positron-capturing sites (positron traps) and (3) bound positron–electron (positronium, Ps) state. In our preliminary works (Klym et al. 2016a, b), these channels were studied in MgAl_2O_4 ceramics separately due to the PAL spectra reconstructed through unconstrained x4-term decomposition. When nanostructurization takes place as modification of atomic-deficient space, these processes can be tightly interconnected changing ratio between positron-trapping sites and Ps-decaying sites (Ps-traps). In such case of tightly coupling positron- and Ps-related traps, an important information can be gained from additional algorithms, developed to parameterize the PAL spectra under condition of known interconnection between positron- and Ps-related inputs. One of such resolutions referred to as x3–x2-CDA (coupling decomposition algorithm) was proposed recently (Shpotyuk et al. 2015).

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In this work, we check the possibilities of this approach to identify changes in atomic-deficient structure of aluminomagnesium spinel ceramics MgAl_2O_4 responsible for water-sorption processes.

Methods

Ceramics preparation route

The aluminomagnesium MgAl_2O_4 spinel ceramics were sintered at different temperatures (T_s) of 1100, 1200, 1300 and 1400 °C during 2 h, which are deterministic in their microstructure perfectness, the more detailed description of technological route being presented in Klym et al. (2014, 2016b). In respect to X-ray diffraction measurements, the ceramics prepared at lower $T_s = 1100\text{--}1200$ °C are composed of main spinel phase and large amount of additional MgO and Al_2O_3 phases (up to 12%), while the ceramics sintered at high $T_s = 1300\text{--}1400$ °C contain additionally only MgO phase in the amount of 3.5 and 1.5%, respectively.

PAL spectra measurement procedure

The PAL spectroscopic measurements were performed using ORTEC instrument equipped with ^{22}Na source placed between two identical sandwiched ceramics samples. The measurements were conducted at 22 °C and relative humidity $\text{RH} = 35\%$ for ceramics samples taken just after initial drying and 7-days water-vapor exposure in desiccator ($\text{RH} = 100\%$). To analyze both short and more prolonged PAL components, the spectra were collected within 6.15 and 61.5 ps channel widths, and further analyzed with LT software (Kansy 1996).

In our previous works (Filipecki et al. 2007; Klym et al. 2011), the MgAl_2O_4 ceramics were studied using x3-term fitting procedure under normal statistical analysis of PAL spectra accumulated near 1 M of elementary positron annihilation events. This decomposition route allows studying only one annihilation channel directly related to water-sorption processes, namely the catalytic effect revealed due to preferential Ps decaying in open pores filled with adsorbed water (Filipecki et al. 2007). At high-statistical measurements (more than 1 M counts), the best results were obtained with unconstrained x4-term decomposition (Klym et al. 2016a; Klym et al. 2016b), which allow to study nanopores of more extended sizes, responsible for *o*-Ps decaying. Each PAL spectrum was processed multiple times owing to slight changes in the number of channels, annihilation background and time shift of the 0-th channel. In such a way, we obtained fitting parameters (positron lifetimes $\tau_1, \tau_2, \tau_3, \tau_4$ and corresponding unity-normalized intensities I_1, I_2, I_3, I_4),

which correspond to annihilation of positrons in the samples of interest within a quite reliable error-bar.

The decaying of bound positron–electron positronium (Ps) states forms important channel of PAL spectrum in substances possessing long-lived lifetime components (Krause-Rehberg and Leipner 1999; Jean et al. 2003). Basically, the Ps exists as para-Ps (*p*-Ps) with antiparallel positron–electron spins, decaying intrinsically with two γ -quanta and lifetime of 0.125 ns (in a vacuum), as well as ortho-Ps (*o*-Ps) with parallel positron–electron spins, decaying with three γ -quanta and lifetime of 142 ns (these states are occupied as 1:3). In a matter, since positron wave function overlaps with electron outside, the annihilation with such electron decreases lifetime to 0.5–10 ns (two γ -rays “pick-off” annihilation). Correspondingly, the Ps localized in free-volume spaces gives indication on their mean radii R in terms of long-lived τ_3 lifetime (the relative intensity of this component I_3 correlates with density of Ps sites) in respect to Tao-Eldrup equation:

$$\tau = 0.5 \times \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \times \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right], \quad (1)$$

where $\Delta R = 0.166$ nm is fitted empirical layer thickness (Jean et al. 2003).

By fitting Eq. (1) with measured τ_3 values, the R_3 and spherical free volumes V_f can be determined.

Ps-to-positron-trapping conversion processes by x3–x2-CDA

For inhomogeneous solids, where annihilation is expected through mixed interconnected positron-Ps channels, the formalism of Ps-to-positron trapping conversion (Shpotyuk et al. 2015) can be applied to identify the changes occurring in atomic-deficient structure. The embedded *guest* entities (GEs) like water molecules, for instance, occupy some open spaces of Ps-decaying sites in *host* ceramics matrix, resulting in increased annihilation contribution from remnants of these traps.

Within this approach (which is valid only for substances allowing one type of trapping changes, when Ps-decaying sites are substituted by the same positron-trapping sites), we deal with x3-term decomposed PAL spectrum transformed to the generalized x2-term form for both reference and GE-modified substances. The second component in this generalized x2-term spectrum involves all possible contributions, arising from positron trapping, *o*-Ps decaying and *p*-Ps self-annihilation. Such simplification allows resolving additional input with defect-specific τ_{int} lifetime and I_{int} intensity in the second component of the reconstructed x2-term PAL spectrum for GE-modified matrix, provided compensating (τ_n, I_n) input in first component obeys complete inter-channel balance. Parameterization of Ps-to-positron trapping

conversion in modified matrix (caused by GEs embedded in Ps-decaying sites) can be performed accepting (τ_n , I_n) and (τ_{int} , I_{int}) as corresponding first and second components of x2-term PAL spectrum employing conventional two-state simple trapping model (West 1973; Krause-Rehberg and Leipner 1999; Tuomisto and Makkonen 2013; Saarinen et al. 1998). The trapping modes derived within this approach are signatures of hypothetical GE-modified (nanostructurized) matrix evolving Ps- and positron-trapping sites, these being defect-specific τ_{int} and defect-free bulk $\tau_{\text{b}}^{\text{GE}}$ lifetimes, trapping rate in defects $\kappa_{\text{b}}^{\text{GE}}$, and some derivative characteristics, such as signature of trap size in terms of equivalent number of vacancies defined by ($\tau_{\text{int}}\tau_{\text{b}}^{\text{GE}}$) difference and nature of these traps defined by $\tau_{\text{int}}/\tau_{\text{b}}^{\text{GE}}$ ratio (Krause-Rehberg and Leipner 1999).

Results and discussion

The raw PAL spectra for initially dried and water-immersed MgAl_2O_4 spinel ceramics (obtained at different sintering temperatures T_s) were reconstructed from constraint-free x4-term decomposition (Klym et al. 2016a), the corresponding fitting parameters being gathered in Table 1. These data clearly indicate that positrons are trapped more strongly in spinel ceramics prepared at lower T_s , as it reflected in the increased values of second component intensity I_2 (see Table 1). Preferential decrease of defect-specific τ_2 lifetime and increasing I_2 intensity in water-immersed MgAl_2O_4 ceramics is due to intensification of positron trapping processes in free-volume defects near grain boundaries filled with water (Filipecki et al. 2007).

The water–vapor sorption in ceramics results also in essential evolution of third and fourth Ps-decaying components. The radii of Ps-sites corresponding to third component calculated with known Tao-Eldrup Eq. (1) using $\tau_3 = 2.24\text{--}2.50$ ns for MgAl_2O_4 ceramics in growing T_s sequence (Table 1) are only slightly changed under water sorption being in the range of 0.31–0.33 nm. In contrast, the radii of Ps-sites corresponding to fourth component

are decreased substantially under water sorption from 1.70–1.84 nm (equivalent of $\tau_4 = 62\text{--}70$ ns for alumomagnesium ceramics in decaying T_s sequence) to 1.54–1.64 nm (equivalent of $\tau_4 = 53\text{--}59$ ns). Under water sorption, the intensities I_3 reveal the same growing tendency as I_2 , while intensities I_4 demonstrate an opposite dropping trend. These findings confirm Ps annihilation in water-filled pores of ceramics due to “bubble” mechanism (Klym et al. 2016a) with third PAL spectrum component responsible for these changes, whereas the fourth component can be undoubtedly ascribed to formation of thin layers of water molecules covering walls of inner pores with larger radii of $\sim 60\text{--}70$ nm (Golovchak et al. 2012).

In such presentation as given in Table 1, these results cannot be treated unambiguously with x3–x2-CDA, because of additional Ps-decaying component in the detected PAL spectra. The resolution occurs to be very simple accepting that second and third components in the x4-term decomposed PAL spectra behave in a similar way that may be due to catalytic effect of positron annihilation in water-immersed medium, while fourth component reflects annihilation of positrons in water-free spaces of larger voids. With this in mind, it is possible to transform the unconstrained x4-term decomposed PAL spectra in modified x3-term form with unchanged first component (τ_1^{**}, I_1^{**}) = (τ_1, I_1), third component (τ_3^{**}, I_3^{**}) taken as previous fourth (τ_4, I_4), and second component (τ_2^{**}, I_2^{**}) determined as averaged value from previous second (τ_2, I_2) and third (τ_3, I_3) components:

$$\tau_2^{**} \times I_2^{**} = \tau_2 \times I_2 + \tau_3 \times I_3, \quad (2)$$

$$I_2^{**} = I_2 + I_3. \quad (3)$$

The results of such transformation are presented in Table 2.

With these data, the x3–x2-CDA procedure (Shpotyuk et al. 2015) can be applied, accepting dried MgAl_2O_4 ceramics as reference and water-immersed ceramics as modified, the calculated trapping modes being given in Table 3.

It is seen that water-immersion processes reduce Ps decaying in MgAl_2O_4 ceramics at the expense of enhanced

Table 1 Fitting parameters describing PAL spectra of MgAl_2O_4 ceramics sintered at different temperatures T_s reconstructed from x4-term decomposed PAL spectra (Klym et al. 2016a)

T_s , ceramics state	Fitting parameters								$\tau_{\text{av}}^{\Sigma}$, ns
	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.	
1100 °C, initial dried	0.169	0.680	0.462	0.280	2.240	0.017	70.14	0.025	2.025
1100 °C, water-immersed	0.170	0.660	0.483	0.280	1.820	0.044	53.05	0.009	0.799
1200 °C, initial dried	0.164	0.730	0.443	0.240	2.347	0.011	70.51	0.020	1.666
1200 °C, water-immersed	0.167	0.640	0.426	0.310	2.047	0.038	58.67	0.004	0.524
1300 °C, initial dried	0.155	0.820	0.414	0.160	2.426	0.008	68.74	0.014	1.149
1300 °C, water-immersed	0.161	0.760	0.400	0.210	2.619	0.018	58.33	0.007	0.683
1400 °C, initial dried	0.152	0.880	0.388	0.110	2.504	0.007	62.32	0.008	0.709
1400 °C, water-immersed	0.160	0.770	0.409	0.200	2.562	0.022	57.35	0.006	0.577

Table 2 Fitting parameters describing modified x3-term PAL spectra of MgAl_2O_4 ceramics derived from x4-term decomposed PAL spectra (Klym et al. 2016a)

T_s , ceramics state	Fitting parameters					
	τ_1^{**} , ns	I_1^{**} , a.u.	τ_2^{**} , ns	I_2^{**} , a.u.	τ_3^{**} , ns	I_3^{**} , a.u.
1100 °C, initial dried	0.169	0.680	0.564	0.297	70.14	0.025
1100 °C, water-immersed	0.170	0.660	0.665	0.324	53.05	0.009
1200 °C, initial dried	0.164	0.730	0.526	0.251	70.51	0.020
1200 °C, water-immersed	0.167	0.640	0.603	0.348	58.67	0.004
1300 °C, initial dried	0.155	0.820	0.510	0.168	68.74	0.014
1300 °C, water-immersed	0.161	0.760	0.575	0.228	58.33	0.007
1400 °C, initial dried	0.152	0.880	0.515	0.117	62.32	0.008
1400 °C, water-immersed	0.160	0.770	0.622	0.222	57.35	0.006

Table 3 Nanostructurization in water-immersed MgAl_2O_4 ceramics within x3–x2-CDA using modified x3-term fitting data from Table 2

T_s	x3–x2-CDA modes									
	τ_n , ns	I_n , a.u.	τ_{int} , ns	I_{int} , a.u.	$\tau_n \cdot I_n$, ns	$\tau_{\text{int}} \cdot I_{\text{int}}$, ns	τ_b^{GE} , ns	κ_d^{GE} , ns ⁻¹	$\tau_{\text{int}} \cdot \tau_b^{\text{GE}}$, ns	$\tau_{\text{int}} / \tau_b^{\text{GE}}$, a.u.
1100 °C	0.178	0.437	0.738	0.204	0.078	0.150	0.235	1.35	0.503	3.14
1200 °C	0.169	0.543	0.614	0.295	0.092	0.181	0.227	1.50	0.387	2.70
1300 °C	0.166	0.451	0.598	0.134	0.075	0.080	0.199	1.00	0.399	3.00
1400 °C	0.163	0.517	0.667	0.142	0.064	0.095	0.195	1.00	0.473	3.43

positron trapping revealed in $(\tau_{\text{int}}, I_{\text{int}})$ channel. The character sizes of these traps, which appear in water-immersed ceramics instead of Ps-decaying holes in dried ones, correspond to longer lifetimes $\tau_{\text{int}} \sim 0.6\text{--}0.7$ ns in respect to Eq. (1), and $(\tau_{\text{int}} - \tau_b^{\text{GE}}) \sim 0.39\text{--}0.50$ ns, $\tau_{\text{int}} / \tau_b^{\text{GE}} \sim 2.7\text{--}3.4$ (Table 3). Therefore, these remnants of initial empty voids filled with water molecules can be attributed rather to Ps (not positron) traps with character sizes of ~ 0.2 nm calculated in respect to Tao-Eldrup Eq. (1).

Thus, the water-induced trapping conversion in spinel MgAl_2O_4 ceramics occurs between large-size (1.70–1.84 nm in radius) and tiny (~ 0.2 nm in radius) Ps-trapping sites. This process is captured in the nearest environment of spinel phase, as it follows from $\tau_b^{\text{GE}} = 0.195\text{--}0.235$ ns, the values approaching defect-free bulk positron lifetimes in MgAl_2O_4 ceramics sintered at different T_s (Klym et al. 2014; Klym et al. 2016b). The water sorption is more pronounced in structurally imperfect ceramics sintered at $T_s = 1100\text{--}1200$ °C due to irreversible transformations within inner pores between constituting MgO and Al_2O_3 phases (resulting in increased $\kappa_b^{\text{GE}} \sim 1.3\text{--}1.5$ ns⁻¹). In contrast, the reversible physical-sorption processes are dominated in more structurally uniform alumomagnesium ceramics prepared at higher sintering temperatures $T_s = 1300\text{--}1400$ °C, which are composed preferentially of main spinel phase.

Conclusions

Atomic-deficient nanostructurization in alumomagnesium spinel ceramics MgAl_2O_4 sintered at 1100–1400 °C caused by water sorption are studied by employing the method of positron annihilation lifetime (PAL) spectroscopy. The PAL spectra are reconstructed from constraint-free x4-term decomposition, and further transformed to x3-term form to be applicable for analysis with x3–x2-CDA (coupling decomposition algorithm). It is proved that water-immersion processes reduce Ps decaying in large-size holes of MgAl_2O_4 ceramics (having 1.70–1.84 nm in radius) at the expense of enhanced trapping in tiny (~ 0.2 nm in radius) Ps-traps. The water sorption is more pronounced in structurally imperfect ceramics sintered at $T_s = 1100\text{--}1200$ °C due to irreversible transformations between constituting phases, while reversible physical-sorption processes are dominated in more structurally uniform ceramics ($T_s = 1300\text{--}1400$ °C) composed preferentially of main spinel phase.

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References

- Filipecki J, Ingram A, Klym H, Shpotyuk O, Vakiv M (2007) Water-sensitive positron trapping modes in nanoporous magnesium aluminate ceramics. *J Phys Conf Ser* 79(1):012015-1–012015-4
- Golovchak R, Wang Sh, Jain H, Ingram A (2012) Positron annihilation lifetime spectroscopy of nano/macroporous bioactive glasses. *J Mater Res* 27(19):2561–2567
- Groen JC, Pefferer LAA, Perez-Ramirez J (2003) Pore size determination in modified micro- and mesoporous materials. pitfalls and limitations in gas adsorption data analysis. *Microporous Mesoporous Mater* 60:1–17
- Gusmano G, Montesperelli G, Traversa E, Bearzotti A, Petrocco G, D'amico A, Di Natale C (1992) Magnesium aluminium spinel as humidity sensor. *Sens Actuators B Chem* 7:460–463
- Gusmano G, Montesperelli G, Traversa E, Mattogno G (1993) Microstructure and electrical properties of MgAl_2O_4 thin films for humidity sensing. *J Am Ceram Soc* 76(3):743–750
- Hill AJ, Freeman BD, Jaffe M, Merkel TC, Pinnau I (2005) Tailoring nanospace. *J Molec Structure* 739:173–178
- Jean YC, Mallon PE, Schrader DM (2003) Principles and application of positron and positronium chemistry. World Sci. Publ. Co. Pte. Ltd., New Jersey
- Kansy J (1996) Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl Instrum Methods Phys Res A* 374:235–244
- Kashi MA, Ramazani A, Abbasian H, Khayyatian A (2012) Capacitive humidity sensors based on large diameter porous alumina prepared by high current anodization. *Sens Actuators A* 174:69–74
- Klym H, Ingram A, Shpotyuk O, Filipecki J, Hadzaman I (2011) Structural studies of spinel manganite ceramics with positron annihilation lifetime spectroscopy. *J Phys: Conf Ser* 289(1):012010
- Klym H, Ingram A, Hadzaman I, Shpotyuk O (2014) Evolution of porous structure and free-volume entities in magnesium aluminate spinel ceramics. *Ceram Intern* 40(6):8561–8567
- Klym HI, Ingram A, Shpotyuk O, Hadzaman I, Solntsev V (2016a) Water-vapor sorption processes in nanoporous $\text{MgO-Al}_2\text{O}_3$ ceramics: the PAL spectroscopy study. *Nanoscale Res Lett* 11:133-1–133-7
- Klym H, Ingram A, Shpotyuk O, Hadzaman I, Hotra O, Kostiv Yu (2016b) Nanostructural free-volume effects in humidity-sensitive $\text{MgO-Al}_2\text{O}_3$ ceramics for sensor applications. *J Mater Eng Perform* 25:866–873
- Kobayashi Y, Ito K, Oka T, Hirata K (2007) Positronium chemistry in porous materials. *Rad Phys Chem* 76:224–230
- Krause-Rehberg R, Leipner HS (1999) Positron annihilation in semiconductors. Defect studies. Springer, Berlin
- Kullmann J, Enke D, Thraenert S, Krause-Rehberg R, Beiner M (2012) Characterization of pore filling of mesoporous host systems by means of positronium annihilation lifetime spectroscopy (PALS). *Opt Appl XLII(2):281–286*
- Kulwicki BM (1991) Humidity sensors. *J Am Ceram Soc* 74(4):697–708
- Saareninen K, Hautajarvi P, Corbel C (1998) Positron annihilation spectroscopy of defects in semiconductors. *Semicond semimet* 51A:210–285
- Shpotyuk O, Filipecki J, Ingram A, Golovchak R, Vakiv M, Klym H, Balitska V, Shpotyuk M, Kozdras A (2015) Positronics of subnanometer atomistic imperfections in solids as a high-informative structure characterization tool. *Nanoscale Res Lett* 10:77-1–77-5
- Traversa E (1995) Ceramic sensors for humidity detection: the state-of-the-art and future developments. *Sens Actuators B Chem* 23(2):135–156
- Tuomisto F, Makkonen I (2013) Defect identification in semiconductors with positron annihilation: experiment and theory. *Rev Mod Phys* 85:1583–1631
- West RN (1973) Positron studies of condensed matter. *Adv Phys* 22:263–383

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