Atomic-deficient nanostructurization in water-sorption alumomagnesium spinel ceramics MgAl$_2$O$_4$

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Abstract
Atomic-deficient nanostructurization in alumomagnesium MgAl$_2$O$_4$ 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 $T_s = 1100–1200$ °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$_2$O$_4$ 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 nanopores 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$_2$O$_4$ 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).
In this work, we check the possibilities of this approach to identify changes in atomic-deficient structure of alumomagnesium spinel ceramics MgAl₂O₄ responsible for water-sorption processes.

**Methods**

**Ceramics preparation route**

The alumomagnesium MgAl₂O₄ spinel ceramics were sintered at different temperatures (Tₛ) 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 Tₛ = 1100–1200 °C are composed of main spinel phase and large amount of additional MgO and Al₂O₃ phases (up to 12%), while the ceramics sintered at high Tₛ = 1300–1400 °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 ²²Na source placed between two identical sandwiched ceramics samples. The measurements were conducted at 22 °C and relative humidity RH = 35% for ceramics samples taken just after initial drying and 7-days water-vapor exposure in desiccator (RH = 100%). To analyze both short and more prolonged drying and 7-days water-vapor exposure in desiccator measurements were conducted at 22 °C and relative humidity between two identical sandwiched ceramics samples. The slight changes in the number of channels, annihilation backshift of the 0-th channel. In such a way, we obtained fitting parameters (positron lifetimes τ₁, τ₂, τ₃, τ₄ and corresponding unity-normalized intensities I₁, I₂, I₃, I₄), 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 τ₃ lifetime (the relative intensity of this component I₃ correlates with density of Ps sites) in respect to Tao-Eldrup equation:

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

where ΔR = 0.166 nm is fitted empirical layer thickness (Jean et al. 2003).

By fitting Eq. (1) with measured τ₃ values, the R₃ and spherical free volumes V₃ 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 τᵢᵣ lifetime and Iᵢᵣ intensity in the second component of the reconstructed x₂-term PAL spectrum for GE-modified matrix, provided compensating (τᵢᵣ, Iᵢᵣ) 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 \( \left( \tau_n, I_n \right) \) and \( \left( \tau_{\text{int}}, I_{\text{int}} \right) \) 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 (nanostructured) matrix evolving Ps- and positron-trapping sites, these being defect-specific \( \tau_{\text{int}} \) and defect-free bulk \( \tau_{\text{GE}} \) lifetimes, trapping rate in defects \( k_{\text{GE}} \), and some derivative characteristics, such as signature of trap size in terms of equivalent number of vacancies defined by \( \left( \tau_{\text{int}}, I_{\text{GE}} \right) \) difference and nature of these traps defined by \( \tau_{\text{int}}/\tau_{\text{GE}} \) ratio (Krause-Rehberg and Leipner 1999).

### Results and discussion

The raw PAL spectra for initially dried and water-immersed MgAl\(_2\)O\(_4\) 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 \( \tau_2 \) lifetime and increasing \( I_2 \) intensity in water-immersed MgAl\(_2\)O\(_4\) 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 \( \tau_3 = 2.24–2.50 \) ns for MgAl\(_2\)O\(_4\) 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 \( \tau_4 = 62–70 \) ns for aluminogidge ceramics in decaying \( T_s \) sequence) to 1.54–1.64 nm (equivalent of \( \tau_4 = 53–59 \) 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 ~ 60–70 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 \( (\tau_1^{**}, I_1^{**}) = (\tau_1, I_1) \), third component \( (\tau_3^{**}, I_3^{**}) \) taken as previous fourth \( (\tau_4, I_4) \), and second component \( (\tau_2^{**}, I_2^{**}) \) determined as averaged value from previous second \( (\tau_2, I_2) \) and third \( (\tau_3, I_3) \) components:

\[
\tau_2^{**} \times I_2^{**} = \tau_2 \times I_2 + \tau_3 \times I_3 \tag{2}
\]

\[
I_2^{**} = I_2 + I_3 \tag{3}
\]

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\(_2\)O\(_4\) 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\(_2\)O\(_4\) ceramics at the expense of enhanced

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### Table 1.

Fitting parameters describing PAL spectra of MgAl\(_2\)O\(_4\) ceramics sintered at different temperatures \( T_s \) reconstructed from x4-term decomposed PAL spectra (Klym et al. 2016a)

| \( T_s \) \(^\circ\text{C}\) | \( \text{Ceramics state} \) | \( \tau_1, \text{ns} \) | \( I_1, \text{a.u.} \) | \( \tau_2, \text{ns} \) | \( I_2, \text{a.u.} \) | \( \tau_3, \text{ns} \) | \( I_3, \text{a.u.} \) | \( \tau_4, \text{ns} \) | \( I_4, \text{a.u.} \) |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1100 | Initial dried | 0.169 | 0.680 | 0.462 | 0.280 | 2.240 | 0.017 | 70.14 | 0.025 | 2.025 |
| 1100 | Water-immersed | 0.170 | 0.660 | 0.483 | 0.280 | 1.820 | 0.044 | 53.05 | 0.009 | 0.799 |
| 1200 | Initial dried | 0.164 | 0.730 | 0.443 | 0.240 | 2.347 | 0.011 | 70.51 | 0.020 | 1.666 |
| 1200 | Water-immersed | 0.167 | 0.640 | 0.426 | 0.310 | 2.047 | 0.038 | 58.67 | 0.004 | 0.524 |
| 1300 | Initial dried | 0.155 | 0.820 | 0.414 | 0.160 | 2.426 | 0.008 | 68.74 | 0.014 | 1.149 |
| 1300 | Water-immersed | 0.161 | 0.760 | 0.400 | 0.210 | 2.619 | 0.018 | 58.33 | 0.007 | 0.683 |
| 1400 | Initial dried | 0.152 | 0.880 | 0.388 | 0.110 | 2.504 | 0.007 | 62.32 | 0.008 | 0.709 |
| 1400 | Water-immersed | 0.160 | 0.770 | 0.409 | 0.200 | 2.562 | 0.022 | 57.35 | 0.006 | 0.577 |
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 \( \tau_{\text{int}} \sim 0.6–0.7 \) ns in respect to Eq. (1), and \( (\tau_{\text{int}}-\tau_{b}), \tau_{\text{int}}/\tau_{b} \sim 2.7–3.4 \) (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 \( \sim 0.2 \) nm calculated in respect to Tao-Eldrup Eq. (1).

Thus, the water-induced trapping conversion in spinel MgAl\(_2\)O\(_4\) ceramics occurs between large-size \( (1.70–1.84 \) nm in radius) and tiny \( (\sim 0.2 \) nm in radius) Ps-trapping sites. This process is captured in the nearest environment of spinel phase, as it follows from \( \kappa_{b}^{\text{GE}} \sim 1.3–1.5 \) ns\(^{-1}\). In contrast, the reversible physical-sorption processes are dominated in more structurally uniform alumomagnesium ceramics prepared at higher sintering temperatures \( T_{s} \sim 1300–1400 \) °C, which are composed preferentially of main spinel phase.

### Conclusions

Atomic-deficient nanostructurization in alumomagnesium spinel ceramics MgAl\(_2\)O\(_4\) 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\(_2\)O\(_4\) ceramics (having 1.70–1.84 nm in radius) at the expense of enhanced trapping in tiny \( (\sim 0.2 \) nm in radius) Ps-traps. The water sorption is more pronounced in structurally imperfect ceramics sintered at \( T_{s} \sim 1100–1200 \) °C due to irreversible transformations between constituting phases, while reversible physical-sorption processes are dominated in more structurally uniform ceramics \( (T_{s} \sim 1300–1400 \) °C) composed preferentially of main spinel phase.

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### Table 2

| \( T_{s} \), ceramics state   | Fitting parameters |
|-----------------------------|------------------|
| \( \tau_{\text{int}}, \) ns | \( I_{\text{int}}, \) 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

| \( T_{s} \) | x3–x2-CDA modes |
|-------------|-----------------|
| \( \tau_{\text{int}}, \) ns | \( I_{\text{int}}, \) a.u. |
| \( \tau_{b}, \) ns | \( I_{b}, \) a.u. |
| \( \kappa_{d}^{\text{GE}}, \) ns\(^{-1}\) | \( \tau_{b}^{\text{GE}}, \) ns |
| \( \tau_{\text{int}}/\tau_{b}^{\text{GE}}, \) a.u. |
| 1100 °C      | 0.178 0.437 0.738 0.204 0.150 0.235 1.35 0.503 3.14 |
| 1200 °C      | 0.169 0.543 0.614 0.295 0.092 0.181 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 |
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