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Positron studies of vapour absorption and desorption by melamine–formaldehyde resin

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Abstract

The lifetime spectra of positrons annihilating in vapour-absorbing polymers were measured in order to gain information about the change of dimensions and number of free volume holes during absorption and desorption. Absorption of water, methanol and ethanol vapours in melamine–formaldehyde resin leads to the shortening of *ortho*-positronium lifetime that can be explained by predominant filling larger holes by absorbed molecules, leaving smaller ones empty and accessible for *ortho*-positronium. Removal of molecules by outpumping the vapour increases the lifetime. It was found that the intensity of positronium formation does not follow the rule of proportionality to the number of free volume sites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Positronium; Absorption; Desorption; Melamine–formaldehyde resin

1. Introduction

The processes of moisture intake by resins are of technical importance, as these materials are used in many practical applications: construction elements, insulating layers, etc. The positron annihilation lifetime spectroscopy (PALS) seems to be an attractive tool to study the vapour absorption and desorption, in particular the changes of polymer topology during these processes. The modification of topology reflects in the changes of properties of *ortho*-positronium [1] trapped in nanovoids (low electron density heterogeneities): its lifetime and also formation intensity. A series of papers on the absorption effects in polymers has been published [2–5]. As a rule, the increase of *ortho*-positronium (*o*-Ps) lifetime after absorption of moisture (and other vapours) was observed in linear polymers, while in cross-linked ones the shortening of that lifetime was rather typical. In the papers published so far, the attention was paid mainly to the first stage of polymer–moisture interaction, much less is said on restoring the structure after vapour removal. It seemed to us worthwhile to study the changes in PALS spectra on both stages: absorption and removal of vapour molecules.

2. Experimental

The medium under study was melamine–formaldehyde resin (MFR), prepared by mixing melamine, formaldehyde and polymerization initiator, ageing it during 3 days and heating to 450 K for 3 h. (The resin was prepared at the Department of Adsorption and Planar Chromatography, Maria Curie University, Lublin.) The glass transition point of this resin was near 450 K. Fine-grained resin (diameter 2–8 μm) had the specific surface area of $\sim 6\,\mathrm{m^2\,g^{-1}}$; at this area, the presence of the longest-living annihilation component of intergrain or pore origin in PALS spectra can be neglected. Two layers of grains, separated by Kapton envelope with 0.4 MBq ^{22}Na positron source, were placed inside a small cylindrical container fixed on top of a copper rod with the heating coil, inside a vacuum chamber. Two scintillation counters viewed the sample-source sandwich from outside of the vacuum system. The scintillators were BaF_2 crystals, thus, to avoid the summing effects [6] and the counters were placed at an angle of approximately 135°.

The positron lifetime spectra, i.e. the distribution of time intervals between positron birth and annihilation, were registered using a fast–slow delayed coincidence spectrometer [1] with 213 ps resolution (full width at half maximum). During a 3 h run about 1.3×10^6 coincidences were collected. The vacuum chamber contained an arm with a valve, behind which an ampoule with liquid could be placed. The

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main part of the chamber (containing the sample) was evacuated to ~0.3 Pa and then the valve was opened allowing the vapour to fill the chamber volume. In the majority of cases, the measurements were performed at 298 K. If necessary, the sample container could be heated, while the rest of the whole chamber is remained at the temperature 298 K (i.e. the pressure of saturated vapour was kept constant). After the set of absorption–desorption measurements, the sample was heated to 470 K for 3 h; after such an annealing, the PALS spectra returned almost exactly to the form as before the measurements, i.e. the sample structure was restored.

The PALS spectra were decomposed into three exponentials (convoluted with instrumental resolution curve): the shortest-living component (with fixed lifetime $\tau_1 = 125\,\mathrm{ps}$) was ascribed to the decay of *para*-Ps, the intermediate (lifetime τ_2, intensity I_2) to the annihilation of free positrons, the long-living one—to the annihilation of *o*-Ps atoms trapped in small free spaces inside the polymer structure. The lifetimes τ_3 were found very short (1.0–1.5 ns), and translation of τ_3 into nanovoid size could be safely done using the Tao–Eldrup (TE) model [7] elaborated for small spherical voids:

$$\tau = \frac{1}{\lambda} = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+\Delta R}\right]^{-1} \qquad (1)$$

where R is the void radius, ΔR an empirical parameter ($\Delta R = 0.166\,\mathrm{nm}$), and λ the *o*-Ps decay rate (in ns^{-1}).

Due to moderate statistics of the spectra collected in a single 3 h run, the data processing started with the assumption of a simplest model, in which a discrete value of τ_3 was fitted to the experimental data. It is equivalent to the assumption of one, averaged, void radius. The fitting procedure in that case can be POSITRONFIT [8].

3. Results and discussion

The annealed MFR sample was kept under vacuum for 6–9 h, and then the chamber was filled with water vapour and immediately a series of spectra began to be collected. After 24–45 h, when the spectrum parameters τ_i and I_i become stabilized (time-independent), the connection between the sample chamber and liquid was interrupted and the vapour was pumped out; pumping was continued until the end of the measurements. The values of τ_3 and I_3 as a function of treatment time for three selected sample temperatures are shown in Fig. 1.

At low temperatures, the value of τ_3 diminished to new stable value shortly after the contact of the sample with vapour. Evacuation of the chamber led to an equally quick lifetime increase. It means that at least a dominant part of the water molecules was removed from the resin. The scale of lifetime changes diminished with the rise of sample temperature (Fig. 2). The intensity of the long-living component I_3 changed in a different way: during water absorption it decreased, but removal of water resulted in a further reduction of I_3. Above 340 K, the direction of the I_3 changes after vapour absorption was reversed; however, at evacuation the I_3 decrease was still maintained. The reduced value of I_3 after water removal remained low up to the end of measurement, i.e. during 18 h; no recovery effect was observed. The next filling of the chamber with water vapour restored the spectrum parameters to the values observed after the first filling. Regeneration of the sample needed the annealing at 470 K.

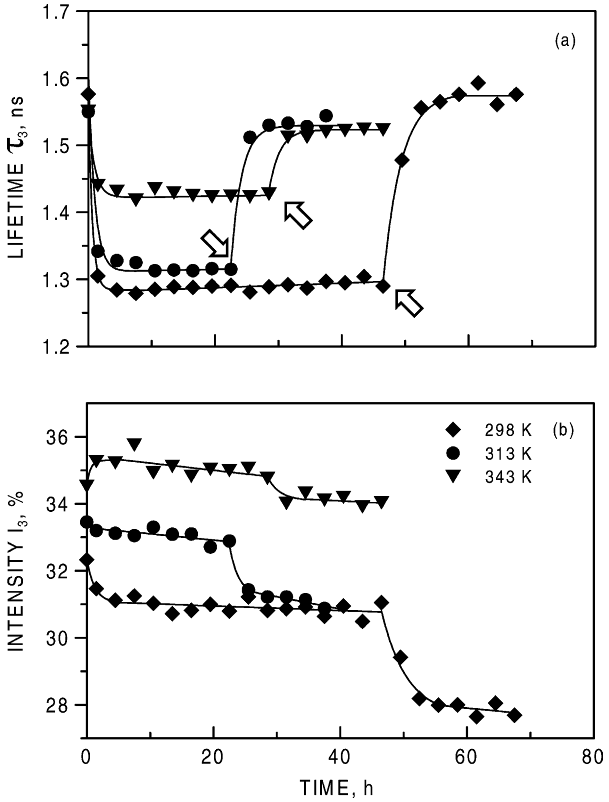

Fig. 1. *o*-Ps lifetime (a) and intensity (b) in MFR resin as a function of the time of treatment with water vapour at various temperatures. Zero of time scale corresponds to the beginning of vapour filling of the sample chamber. The spectrum was decomposed into three exponentials using the POSITRONFIT program. The size of symbols corresponds to the uncertainty limits. The curves serve as eye-guides only, composed of straight lines and exponentials. Arrows indicate the beginning of vapour outpumping.

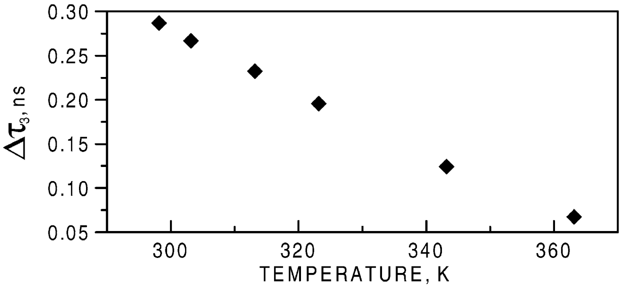

Fig. 2. Decrease of the *o*-Ps lifetime after water vapour absorption as a function of sample temperature.

The structure of free volume voids in polymers is usually a complex one. No single well-defined size is observed, but rather a broad distribution of sizes, which leads to the distribution of the lifetimes. From this point of view, the processing of spectrum as composed of three discrete exponentials is too simple. Such an oversimplification reflected in the variance of fit, which was always above unity. Thus, in order to account the distribution of *o*-Ps lifetimes the spectra were processed using the LT program [9]. In that program, the distribution of *o*-Ps decay rates $S(\lambda)$ is approximated by Gaussian in a logarithmic scale:

$$S(\lambda) \sim \exp\left[-\frac{\ln^2(\tau_p\lambda)}{2\sigma^2}\right] \qquad (2)$$

where τ_p is the lifetime at the peak of distribution. The width of Gaussian σ is an additional fitting parameter. With this kind of data processing, the variance of the fit substantially improved. The values of τ_{3p}, σ and I_3 are shown in Fig. 3 for the spectra taken at 298 K (lower curve in Fig. 1). The decrease of lifetime τ_{3p} was accompanied by evident reduction of the distribution width σ. Removal of water molecules gave a new value of τ_{3p}, higher than in the fresh, annealed sample, but the intensity of the long-living component repeated the sequence observed at the POSITRONFIT processing: both absorption and subsequent desorption of water lowered I_3.

The shortening of lifetime after absorption of water can be explained as result of two processes:

1. Expansion of the free volume hole when a vapour molecule is located in it; this expansion reduces the sizes of neighbouring empty voids in which Ps can be trapped.
2. Water molecules fill the pre-existing bigger free volumes only, the smaller ones remain empty. The width of the distribution of voids accessibles for Ps becomes narrower, the average void size seen by Ps is smaller, and the number of free volume sites also diminishes.

The lifetimes before and after absorption are relatively short, the values τ_{3p} fitted by the LT program are 1.16 and 1.08 ns, respectively, which correspond to the most probable void radii according to the Tao–Eldrup model (Eq. (1)): 0.190 and 0.177 nm. However, the radius of the water molecule is 0.15 nm, thus such a molecule should not distort the surrounding of the site in which it is located. That points rather to the process (2); in particular, the narrowing of the σ speaks in favour of such a mechanism. On the other hand, the most probable lifetime fitted by LT to the spectrum at room temperature after vapour desorption is about 1.3 ns (TE radius equal to 0.209 nm). It means that the free volume holes after desorption are (as average) larger than before vapour treatment, i.e. a certain expansion of the free volume hole exists and, moreover, such a distortion is permanent (this concerns the temperature 298 K; at higher temperatures τ_{3p} returns to the initial value only). One can suppose that both processes mentioned above accompany the absorption.

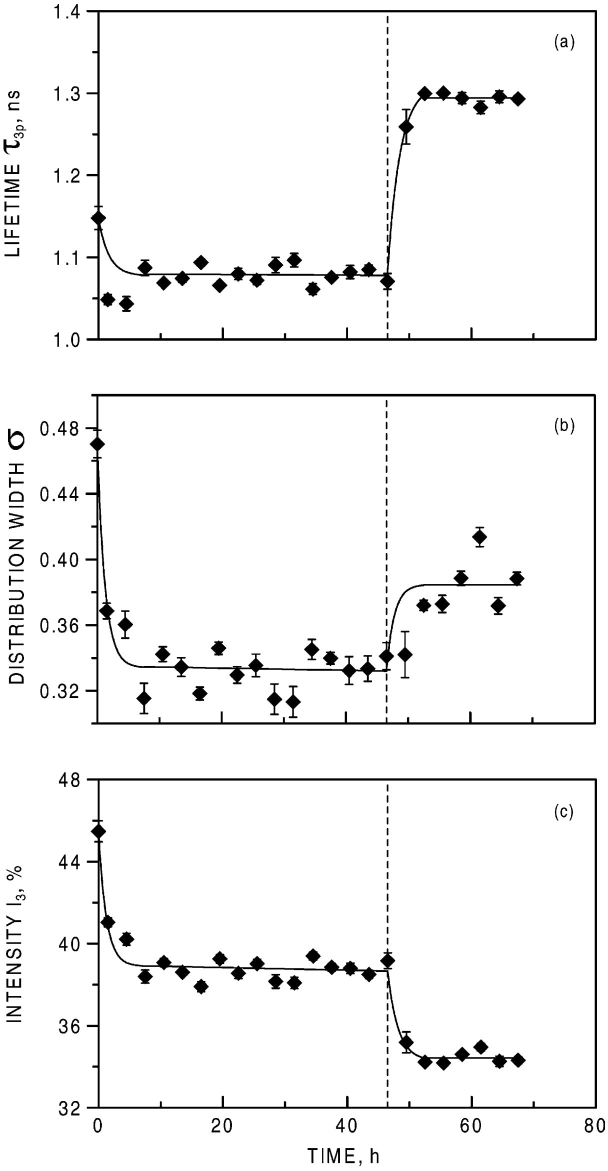

Fig. 3. *o*-Ps lifetime in the peak of distribution (a), the width of lifetime distribution (b) and its intensity (c) as a function of time of MFR resin treatment with water vapour at 298 K. LT spectrum fitting program. The vertical dashed line (in this figure and next ones) represents the beginning of evacuation of the sample chamber.

The decrease of I_3 after water absorption can be tentatively ascribed to several effects. In the annihilation studies of polymers, it is commonly accepted that the intensity is linearly dependent on the number of free volume sites [10–12]; however, it seems to be a rather crude approximation. At a high concentration of the sites, the intensity I_3 (Ps formation probability) must tend to a saturation value determined by spur processes [13,14]. It was shown [15] that a controlled and well-defined number of free volume sites which can be introduced into an organic solid produces the long-living component; its intensity is proportional to the void concentration below 10^{-4} only. In polymers, we can expect much

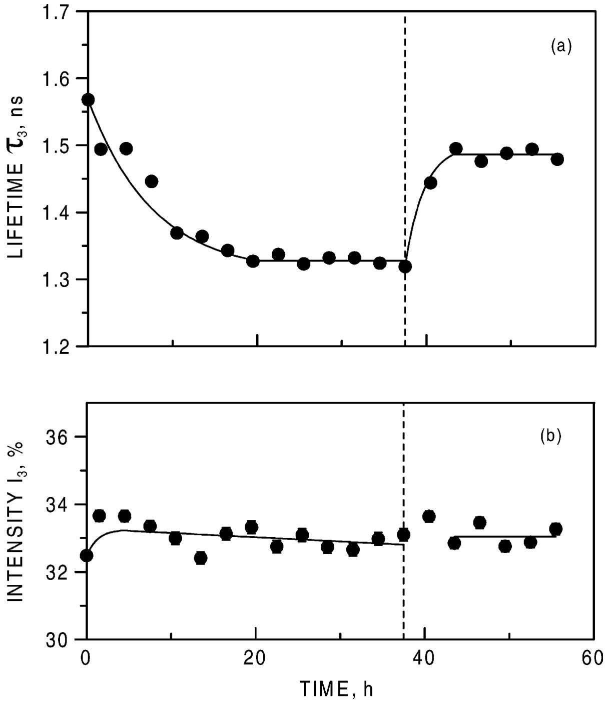

Fig. 4. *o*-Ps lifetime (a) and intensity (b) in MFR resin as a function of exposure time onto ethanol vapour at 298 K. Fitting program was POSITRONFIT.

higher concentrations, thus if the dependence of I_3 on the number of free volume sites still exists, it is not linear and greatly weakened. The step down in I_3 after water absorption could be understood in the framework of the "linear model" from Refs. [10–12], as simple result of the reduction in the number of empty holes. However, more probable are alternative explanations based on spur properties:

- Presence of water increases the effective dielectric permittivity and in consequence reduces the Onsager radius [16].
- One can also suppose that the introduction of polar water molecules shortens the positron localization (solvatation) time.

In both cases, the e^+e^- binding probability is reduced.

The next step in decrease of I_3, i.e. after pumping out the vapour, is hard to explain. In the literature, there are no data suggesting such a decrease as a rule or an exception. For sake of comparison, an analogous experiment was performed with other vapours composed of small polar molecules: ethanol and methanol. The results of processing by POSITRONFIT are shown in Figs. 4 and 5. The most characteristic feature of the I_3 intensity is the lack of sensitivity on the presence or outpumping of vapour. In the limits

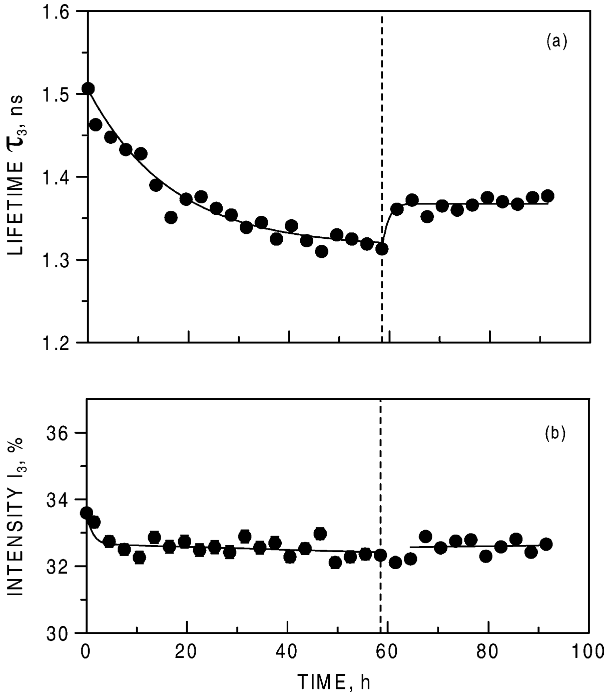

Fig. 5. *o*-Ps lifetime (a) and intensity (b) in MFR resin as a function of exposure time onto methanol vapour at 298 K. Fitting program was POSITRONFIT.

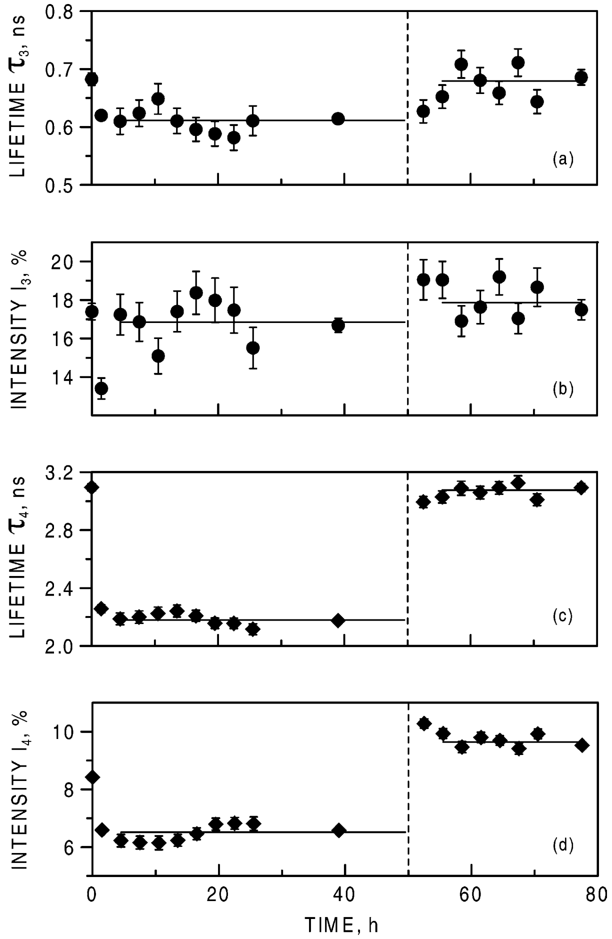

Fig. 6. *o*-Ps lifetime (a, c) and intensity (b, d) in phenol–formaldehyde resin exposed into water vapour at 298 K (compare with Fig. 1). Other data as in Figs. 4 and 5. Two long-living components are assumed. The experimental points at 0, 40 and 78 h represent the measurements with greatly increased statistics.

of error, the intensity was the same during the whole sample treatment sequence. Generally, absorption and desorption, well visible in the *o*-Ps lifetimes, do not find a reflection in the intensity of Ps formation.

The lifetime τ_3 behaved similarly as in the case of water. It decreased after absorption, although with a much lower rate, in particular in the case of methanol (in spite of the larger saturated vapour pressure); in that case the time constant of τ_3 decrease was ∼17 h. The regaining τ_3 value after desorption of methanol was by far incomplete. The analysis of spectrum by the LT program gave qualitatively the same results.

The decrease of I_3 after sample evacuation was seen in the case of water only, thus we decided to perform an additional test using other resin, phenol–formaldehyde one, and exposing it into the water vapour. In that polymer, the positron lifetime spectrum contained two distinct long-living components, with lifetimes of about 0.7 and 3 ns. The result of the treatment, similar as in previous cases, is shown in Fig. 6. The component with the lifetime of 0.6 ns was practically insensitive on vapour treatment, which can be easily explained by the size of voids producing that component, i.e. their radius (∼1.05 nm) is too small to accommodate any molecule. In the case of the fourth longest-living component, the decrease of lifetime is very large and its value is restored after sample evacuation. Again, no decrease of I_4 after pumping out the vapour was observed.

4. Conclusions

Absorption of water vapour by MFR (as well as phenol–formaldehyde one) reduces both lifetime and intensity of *o*-Ps; this kind of behaviour seems to be typical for cross-linked polymers [2]. Evacuation of the chamber containing the samples (desorption of vapours) restores the lifetime distribution (except the case of MFR—methanol system); however, the intensity of the *o*-Ps component need not to be the same as before sample treatment with vapours. In particular, removal of water gives an unexpected decrease of I_3, but only in the case of MFR resin. Generally, evacuation of vapour should increase the number of accessible free volume holes, thus, reduction of intensity, or its constancy, is an indication that there is no simple linear dependence between these two quantities. This lack of linearity I_3 vs. number of free sites should be kept in mind in the discussion of free volumes in polymers determined by positronic methods. The deviation from the simple rule is particularly strong in the case of MFR + water vapour system, which deserves more attention.

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References

[1] O.E. Mogensen, Positron Annihilation in Chemistry, Springer, Berlin, 1995.

[2] T. Miura, T. Suzuki, Y. Oki, M. Numajiri, K. Kondo, Y. Shiomi, Y. Ito, J. Phys. IV 3 (1993) 249.

[3] Y. Ito, in: M.R. Tant, A.J. Hill (Eds.), Structure and Properties of Glassy Polymers, ACS Symposium Series 710, American Chemical Society, Washington, DC, 1998 (Chapter 23).

[4] C.L. Soles, F.C. Chang, B.A. Bolan, H.A. Hristov, D.W. Gidley, A.F. Yee, J. Polym. Sci. B 36 (1998) 3035.

[5] C.L. Soles, A.F. Yee, J. Polym. Sci. B 38 (2000) 792.

[6] T. Goworek, W. Gorniak, J. Wawryszczuk, Nucl. Instr. Meth. A 321 (1992) 560.

[7] M. Eldrup, D. Lightbody, J.N. Sherwood, Chem. Phys. 63 (1981) 51.

[8] P. Kirkegaard, N.J. Pedersen, M. Eldrup, Risø M2740 Report, Risø, 1989.

[9] J. Kansy, Nucl. Instr. Meth. A 374 (1996) 235.

[10] Y.Y. Wang, H. Nakanishi, Y.C. Jean, T.C. Sandreczki, J. Polym. Sci. B 24 (1986) 1247.

[11] Y. Kobayashi, W. Zheng, E.F. Meyer, J.D. McGervey, A.M. Jamieson, R. Simha, Macromolecules 22 (1989) 2302.

[12] J. Krištiak, J. Bartoš, K. Krištiaková, O. Šauša, P. Bandžuch, Phys. Rev. B 49 (1994) 6601.

[13] Y. Ito, J. Radioanal. Nucl. Chem. 210 (1996) 327.

[14] S.V. Stepanov, C.-L. Wang, Y. Kobayashi, V.M. Byakov, K. Hirata, Radiat. Phys. Chem. 58 (2000) 403.

[15] T. Goworek, C. Rybka, Phys. Stat. Sol. B 81 (1977) 565.

[16] S.J. Tao, Appl. Phys. 10 (1976) 67.