Positron annihilation sites in nano lead sulfide powders

A A Rempel¹, A A Valeeva¹, K Sato³, N S Kozhevnikova¹
¹Institute of Solid State Chemistry, the Ural Branch of the Russian Academy of Sciences, Pervomaiskaya 91, Ekaterinburg 620990, Russia
²Ural Federal University named after First President of Russia B.N. Yeltsin, Mira 19, Ekaterinburg, 620002, Russia
³Department of Environmental Sciences, Tokyo Gakugei University, Nukuikita 4-1-1, Koganei, Tokyo 184-8501, Japan

E-mail: rempel@ihim.uran.ru

Abstract. The coincident Doppler broadening of the positron-electron annihilation radiation has been applied for the identification of vacancies in nano lead sulfide (nano-PbS) powders. The results of the positron annihilation studies on nano-PbS with different particle size are presented. Nano-PbS specimens have been synthesized by the chemical bath deposition in aqueous medium. Independently of the size of nanoparticles (from 12 to 16 nm) the positron lifetime (PLT) for all specimens has been found to be the same and equal to 391±1 ps. Independently of the size of nanoparticles the chemical surrounding of positron annihilation sites identified by coincident Doppler broadening measurements was the same, namely lead (Pb).

Introduction
Coincident measurements of the Doppler broadening of the positron-electron annihilation radiation is a powerful tool for the site detection of vacancies in complex substances. The coincident Doppler broadening of positron annihilation radiation (CDBPAR) gives access to the electron momentum distribution of the core electrons (CE) of the atoms surrounding the annihilation site. In case of positron trapping at vacancies in binary compounds this element-specific information allows for the identification of the sublattice on which the vacancies are located [1].

Lead sulfide (PbS) has been used as a functional material in infrared photon detectors [2]. Since decade after development of the synthetic routes for quantum dots this material has been applied for studies of quantum-confinement effects in nanoparticles [3]. Such studies might extend the detection application to near infrared wave range in near future. That is why a lot of recent scientific activities are devoted to nano-PbS synthesis, structure, and properties [4, 5, 6]. Valuable information on the positron lifetimes for a set of chalcogenide semiconductors is available in [7, 8, 9, 10].

In this paper we present our recent results on vacancies identification in nano-PbS powders. It should be noted that the method of synthesis of nano-PbS is of great importance, because it depends on the method what kind of defects the compound will contain, i.e. structural vacancies in metal or nonmetallic sublattices, agglomerates of vacancies, vacancies in interfaces etc.

¹ Corresponding author Andrey A Rempel

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
**Experimental**

Positron lifetime spectra with $1-2 \times 10^6$ counts were measured by means of a fast-slow $\gamma \gamma$ spectrometer with a time resolution of 205 ps. The Doppler broadening of the positron-electron annihilation radiation was measured by coincident detection of the two annihilation quanta for background suppression using two Ge detectors with high energy resolution (FWHM = 1.2 keV). Two-dimensional energy spectra ($N(E_1,E_2)$) of the pairs of annihilation photons were recorded with a total number of $3-5 \times 10^7$ counts within 3 days. One-dimensional CDBAR spectra with optimum statistics were obtained by cutting the two-dimensional energy spectra along diagonal $E_1 + E_2 = 1022$ keV with an energy width of 1 keV. Since the one-dimensional spectra were symmetric with respect to the 511 keV, the right- and left-hand sides of the spectra were superimposed. The one-dimensional CDBAR spectra with low background ($< 10^{-5}$) extend up to an energy shift $|\Delta E| = 12.8$ keV corresponding to an electron momentum of $50 \times 10^{-3} m_0 c$, where $m_0$ is the electron rest mass and $c$ is the velocity of light.

The chemical bath deposition (CBD) of nano-PbS was performed by the direct reaction between water-soluble lead acetate Pb(OAc)$_2$ and sodium sulfide Na$_2$S in aqueous medium:

$$\text{Pb(OAc)}_2 + \text{Na}_2\text{S} = \text{PbS} \downarrow + 2 \text{NaOAc}$$

Primary concentrations of the precursors for nano-PbS synthesis by chemical bath deposition and size of nanoparticles are listed in Table 1. By XRD, SEM and TEM it was determined that the average size of crystallites for different nano-PbS was in the range between 12 and 16 nm [11].

![Figure 1](image_url)

**Figure 1.** XRD spectra showing a broadening of lines due to small nanosized grains of nano-PbS as compared with coarse-grained bulk PbS. Insert shows TEM of nano-PbS powder [11]

According to XRD analysis the structure of synthesized samples of nano-PbS corresponds to $B1$ (rock salt) structure. Nano-PbS is homogeneous and contains only one phase. The XRD spectrum of nano-PbS (Figure 1) shows a huge broadening of diffraction doublet lines (331), (420), (422) as compared...
with the XRD spectrum of bulk PbS with narrow diffraction reflections split into CuKα1,2 doublet. The average size of nanoparticles (Table 1) was calculated from the broadening of the lines by means of the Williamson-Hall method [12, 13]. For positron annihilation studies the nano-PbS powders were compacted by uniaxial pressing of $P = 20$ kgf/cm$^2$ into disk-shaped pellets.

### Table 1. Lattice constant, average size of nanoparticles and primary concentrations of the precursors for nano-PbS synthesized by CBD

| Specimen | $a_{B1}$, pm | $<D>$, nm | Synthesis conditions |
|----------|--------------|-----------|---------------------|
| PbS 1    | 591.8        | 12        | [Pb(OAc)$_2$], mol/l [Na$_2$S], mol/l |
| PbS 2    | 594.0        | 15        | 0.05 0.05           |
| PbS 3    | 593.5        | 16        | 0.25 0.25           |

**Results and discussion**

In present paper the positron annihilation studies (PAS) results on nano-PbS with different size of particles synthesized by CBD are presented.

![Figure 2](image_url)  
**Figure 2.** Ratios of the coincidence Doppler broadened spectra for the PbS specimens (PbS 1, PbS 2, PbS 3 and for sulfur (S crystal) to the Doppler broadened spectrum of defect-free pure lead (pure Pb).

According to the positron lifetime measurements in nano-PbS powders an exclusively single positron lifetime component was observed. Independently of the size of nanoparticles the positron lifetime for all specimens was the same and equal to 391±1 ps.

The attribution of the positron lifetimes to defects is made by the analysis of CDBAR spectra, analogous to that suggested earlier in [1, 14]. It could be seen from Figure 2 that the position and the slope of the all three curves of nano-PbS in the CE range (from $20\times10^{-3} m_0c$ to $40\times10^{-3} m_0c$ ) are very similar to each other. The curve for sulfur (S crystal) has very different position and slope in the CE...
range. The nearly zero slope of the curves ratio and ratio values close to 1 for the Doppler broadening spectra ratio to bulk lead (pure Pb) spectrum means that positron annihilation sites in nano-PbS are surrounded by, mostly, Pb atoms and to a small extent by S atoms. These results are compared with the results of our previous studies on nano-PbS synthesized using another methodology of CBD described in [15]. In our previous study we observed two components in PLT spectrum, which were ascribed to positron trapping in the lattice vacancies on lead sublattice (204 ps, 20 %) and in interfaces (340 ps, 80 %). The contribution by interfaces in case of nanopowders with smaller particle size (from 12 to 16 nm) was much larger (about one order of magnitude), than in case of nanopowders with larger particle size (180 nm [15]). Newly obtained and previous data will be consistent if positron trapping rates in lattice vacancies and interfaces do not change drastically upon particle size in nanoscale regime. In this case for nano-PbS specimens with smaller particles almost all the positrons are trapped at interfaces. A little bit larger (15 %) positron lifetime in interfaces (391 ps) with smaller particles is due to higher contribution of free volumes in triple junctions in such nanomaterial.

Summary

The CDBPAR techniques reported here are expected to be of interest for an identification of defects and specific investigation of defects and atomic processes in complex condensed matter in general, etc. It has been found that independently of the size of nanoparticles (from 12 to 16 nm) the positron lifetime (PLT) for all specimens of nano-PbS is the same 391±1 ps. The chemical surrounding of positron annihilation sites identified by coincident Doppler broadening measurements is mostly Pb and to small extent S.

Acknowledgements

The authors would like to thank S.I. Sadovnikov for his assistance. This work was partially financially supported by the Russian Foundation for Basic Research (RFBR No. 11-08-00314) and by the Ural Branch of the RAS (12-P-234-2003).

References

[1] Rempel A A, Sprengel W, Blaurock K, Reichle K J, Major J and Schaefer H-E 2002 Phys. Rev. Letters 89 185501, Strite S and Morkoc H 1992 J. Vac. Sci. Technol. B 10 1237
[2] Liu X and Zhang M 2000 Int. J. Infrared Millimeter Waves 21 1697
[3] Mcdonald S A, Konstantatos G, Zhang S, Cyr P W, Klem E J D, Levina L and Sargent E H 2005 Nat. Mater. 4 138
[4] Zagorac D, Doll K, Schön J C and Jansen M 2011 Phys. Rev. B 84 045206
[5] Rempel A A , Kozhevnikova N S, Leenaers A J G and van den Berghe S 2005 J. Cryst. Growth 280 300
[6] Sadovnikov S I and Rempel A A 2009 Phys. Solid State 51 2375
[7] Polity A, Krause-Rehberg R, Zlomanov V, Stanov V, Chatchaturov A and Mäkinen S 1993 J. Cryst. Growth 131 271
[8] Plazaola F, Seitsonen A P and Puska M J 1994 J. Phys.: Condens. Matter 6 8809
[9] Eijt S W, Mijnarends P E, van Schaarenburg L C, Houtepen A J, Vanmaekelbergh D, Barbiellini B and Bansil A 2009 Applied Physics Letters 94 091908
[10] Sharma S K, Sudarshan K, Maheshwari P, Dutta D, Pujari P K, Shah C P, Kumar M and Bajaj P 2011 European Physical Journal B 82 335
[11] Sadovnikov S I, Kozhevnikova N S, Pushin V G and Rempel A A 2012 Inorg. Mater. 48 21
[12] Hall W H 1949 Proc. Phys. Soc., Sect. A (London) 62 741.
[13] Hall W H and Williamson G K 1951 Proc. Phys. Soc. Sect. B. (London) 64 937
[14] Valeeva A A, Rempel A A, Sprengel W and Schaefer H-E 2003 Phys. Chem. Chem. Phys. 5 2304
[15] Rempel A A, Valeeva A A and Kozhevnikova N S 2010 JETP Letters 92 146