First-principles investigation of paramagnetic centers in P_2O_5 based glasses

1st Luigi Giacomazzi
Materials Research Laboratory
(University of Nova Gorica)
Nova Gorica, Slovenia
luigi.giacomazzi@ung.si

2nd Layla Martin-Samos
CNR-IOM Democritos
Trieste, Italy
msamos@sissa.it

3rd Nicolas Richard
DAM-DIF CEA
Arpajon, France
nicolas.richard@cea.fr

4th Matjaz Valant
Materials Research Laboratory
(University of Nova Gorica)
Nova Gorica, Slovenia
mvalant@ung.si

5th Nadege Ollier
LSI-IRAMIS, CEA,
Palaiseau, France
nadege.ollier@polytechnique.edu

***Abstract*—We present a first-principles investigation of paramagnetic centers in P_2O_5 based on the calculation of electron paramagnetic resonance (EPR) parameters (*g*-tensor and Fermi contacts). Calculations of the EPR parameters for the P_1 configuration in crystalline *o'*(P_2O_5) support the previous attribution of the P_1 to a P-defect structurally analogous to the Si-*E′* center. As far as concerns the P_1 center in glassy P_2O_5, the present work suggests the possible occurrence of another configuration besides the analogue of the Si-*E′* center. Such an alternative P_1 center configuration is likely to be relevant for those P_2O_5 based glasses featuring a considerable fraction of Q_1 and Q_2 tetrahedral units besides the Q_3 unit which dominates the structure of pure P_2O_5.**

Keywords—P_2O_5, P_1 center, Si-E' center , first-principles

I. Introduction

Phosphate glasses, due to their low Tg (~300 to 500 ºC) and melting temperature (~800 to 1300 ºC) facilitating the final formation process, are used in various industrial applications. In nuclear waste storage, in particular by means of vitrification processes, iron-phosphate glasses are regarded as a stable storage medium for high-level nuclear waste. In microelectronics, phosphosilicate glass (PSG) is employed to stabilize the field effect transistor (FET) device, since the PSG traps impurity ions, namely Na^+, which would be detrimental for the correct functioning of the device [1]. Furthermore the PSG is used for photovoltaic applications as a dopant source in the fabrication of crystalline silicon solar cells [2]. For optical applications, phosphate glasses are widely used, in particular, doped with rare-earth elements. For instance, phosphate glasses doped with Yb give highly efficient emission at ~1000 nm. As the dissolution of rare-earth ions is much more easier in a phosphate matrix than in silicate glasses, phosphate glasses can be used as laser glass for the production of high-power solid-state lasers systems [3]. Similarly, in silica glass, it has been shown that P-codoping is more efficient to dissolve a rare-earth element such as Yb, than Al-codoping. In fact the P-codoping allows to avoid the Yb cluster formation, which limits the efficiency of Yb^{3+} emission [4].

Ionizing irradiation induces many point defects in phosphate and phospho-silicate glasses [5,6,7]. Several paramagnetic point defects have been detected: the so-called P_1, P_2, P_3, P_4 and r-POHC, and l-POHC centers. The radiation induced generation of the latter phosphorus oxygen hole centers (POHC) has an almost linear dependence on the dose, so that phosphate glasses are nowadays considered also for dosimetry applications [7]. The P_1 center gives rise to an absorption band peaking at about 0.79 eV, which is detrimental for transmission in the infrared domain [6].

Although the P_1 center is commonly accepted to be analogous to the Si-*E′* center [6,8,9], its experimental characterization in phosphate glasses, and in particular in pure P_2O_5 glass, is rather poor (as compared to Si-*E′*) and mainly based on a 30 years old data analysis [5,6]. The present work aims, mainly by means of theoretical first-principles techniques for the calculation of electron paramagnetic resonance (EPR) parameters, to improve our understanding and modelling of point defects, namely of the P_1 center, in P_2O_5 containing glasses.

II. Methods & Models

The calculations presented in this work are based on density functional theory (DFT). The codes we used are freely available with the Quantum-Espresso (QE) package [10]. We used the QE-GIPAW code that exploits the gauge including projector augmented wave (GIPAW) method for the calculation of the EPR parameters [10,11] The Perdew-Burke-Ernzerhof exchange correlation functional (PBE) has been adopted for the present calculations [12]. Norm-conserving Trouiller-Martins gipaw pseudopotentials are used and Kohn-Sham wavefunctions are expanded in a basis of plane waves up to a kinetic cutoff of 70 Ry. The defect configurations here analyzed have been obtained by using a o'(P_2O_5) crystal model and a recently generated vitreous P_2O_5 model both consisting of a 112 atoms supercell with 32 regular corner-sharing PO_4 tetrahedral units. Regular PO_4 units exhibit three normal P-O bonds and one P=O double bond, and are sometimes labelled as Q_3 units [13]. Configurations of paramagnetic centers (POHC, P_1 P_2) are obtained by removing a terminal oxygen from one PO_4 tetrahedron and then by performing a first-principles relaxation of the atomic structure which is put in a

978-1-7281-0940-4/19/$31.00 ©2019 IEEE

positive charge state. Next EPR parameters (*g*-tensors and Fermi-contacts) are calculated by using the QE-GIPAW code. The calculations of the computationally expensive *g*-tensor have been carried out only for a selected number of configurations.

III. Results

A. *g-tensor and Fermi-contact analysis of selected paramagnetic configurations in P_2O_5*

Despite we are not aware of any EPR measurements on irradiated crystalline o'(P_2O_5) we still begin our investigation by considering oxygen vacancies, at terminal oxygen atoms, in o'(P_2O_5) where there is no issue concerning the structural arrangement of atoms. The spin density of our P_1 defect configuration in o'(P_2O_5) is shown in Fig. 1: the spin-density mainly localizes on a sp^3 dangling bond at the three-fold P atom, similarly to a Si-*E'* center. However, terminal oxygen atoms of nearby [(O-)$_3$P=O] tetrahedra also show some spin-density localization. For the three-fold P atom shown in Fig. 1, the average O-P-O bond angle is 106.3° and P-O bond length is 1.57 Å. The calculated *g*-principal values and Fermi contacts are g_1 =2.0023, g_2 =2.0038, g_3 =2.0063, and $A_{iso}(^{31}P)$ = 105.8 mT. Such values are in a reasonable agreement with the available experimental data [5]: $\langle g \rangle$=2.005, $A_{iso}(^{31}P)$ =95 mT, and provide a solid ground for further investigations in P_2O_5 based glasses. Note that although only the average value $\langle g \rangle$ was given in [5] a certain anisotropy could be expected on the basis of the experimental EPR parameters of the P_1 center in P-doped silica: $g_{//}$=2.002, $g_{\perp}$=1.999, and A_{iso} (^{31}P)=91 mT [6]. As previously shown by Abarenkov *et al* [14], the top of the valence band of P_2O_5 mainly comprises of O *2p* states which, given the large number of terminal oxygen atoms, implies an ease of formation of phosphorus-oxygen hole centers (POHC). In fact, by applying the same procedure used to generate a P_1 center in the o'(P_2O_5) crystal (i.e. removing one terminal oxygen atom and one electron and subsequently carrying out an *ab-initio* relaxation of the atomic structure, see also the following discussion on the Fermi contacts distribution) we have generated P_1, P_2 and also POHC-like center (Fig. 2) in our glass model of P_2O_5. The *g* principal values calculated for the configuration shown in Fig. 2 are g_1 =2.013, g_2 =2.018, g_3 =2.019, which indeed speak for a center resembling a POHC [6]. Note that this configuration features a (neutral) three coordinated P atom with average P-O bond length of 1.67 Å and O-P-O angle of 96.7°. Only a few terminal oxygen sites in the glass allowed for the generation of a P_1 center configuration similar to the one discussed here above in the crystalline o'(P_2O_5) model structure. Moreover, from a direct inspection of the spin-density, only one configuration shows a spin-density very close to the ideal sp^3 typical of *E'* centers, whereas the others all shows spin-density localization on a fourth nearby oxygen atom, thus reminiscing of the spin-density of a P_2 center. The calculated *g*-principal values and Fermi contacts of our "ideal" P_1 configuration are g_1 =2.0018, g_2 =2.0026, g_3 =2.0036, and Aiso(P) = 98.5 mT. The formation energy [9] calculated for the neutral oxygen vacancy at this site is about 2.7 eV (for a few other oxygen vacancy sites we found formation energies to be in the range 2.3 to 2.8 eV), about 2 eV less than reported for neutral oxygen vacancies in silica [9]. In the neutral charge state, the average P-O bond length is 1.67 Å, and O-P-O angle is 97.7°, while once it is positively charged the P-O bond length becomes 1.57 Å and O-P-O 108.8°.

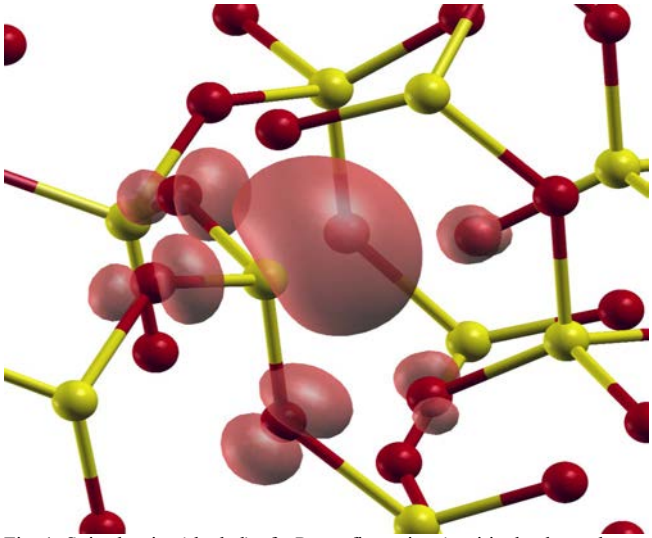

Fig. 1: Spin-density (shaded) of a P_1 configuration (positively charged oxygen vacancy obtained from removal of a terminal oxygen) in o'(P_2O_5).

In the glass, we also generated a considerable number of P_2 center configurations. The calculated *g*-principal values and Fermi contacts of a typical P_2 configuration are g_1 =2.0002, g_2 =2.0027, g_3 =2.0038, and $A_{iso}(^{31}P)$ = 142.5 mT which is in reasonable agreement with [5]. The PO_4 tetrahedron of this P_2 configuration is remarkably distorted, as previously found for P_2 centers in P-doped silica [15], and shows a wide O-P-O angle of 163.6° between two long P-O bonds (1.69 and 1.95 Å), while the other two P-O bonds are shorter (1.61 Å) and form a O-P-O angle of 101.1°.

An alternative model for the P_1 center, not structurally analogous to the Si-*E'* center, was obtained by adding a PO_2 unit nearby a terminal oxygen atom and then by carrying out a first principles relaxation of the structure. The spin-density of the final configuration is shown in Fig. 3.

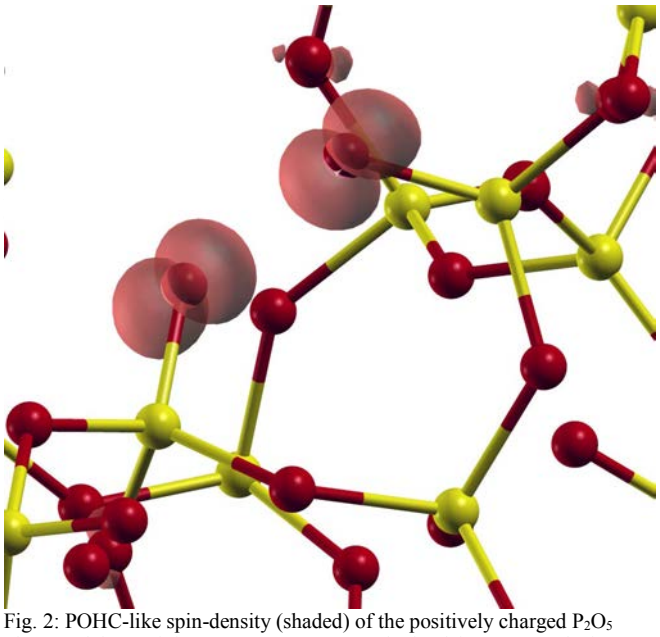

Fig. 2: POHC-like spin-density (shaded) of the positively charged P_2O_5 glass model containing an oxygen vacancy obtained from removal of a terminal oxygen atom.

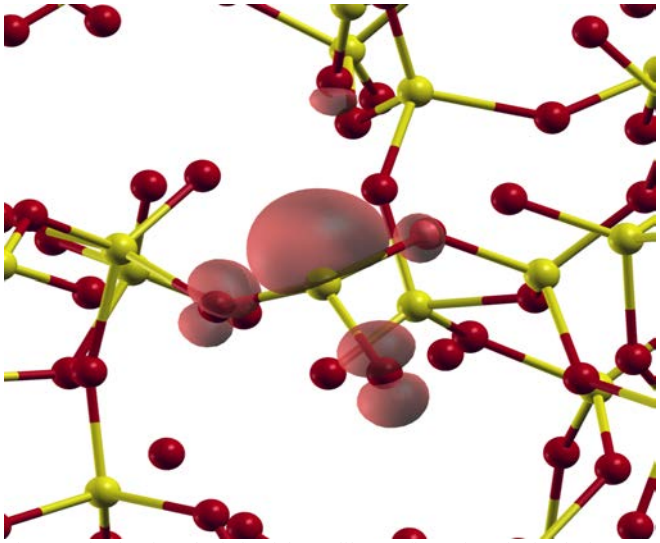

Fig. 3: Spin-density (shaded) of the P_1-like configuration obtained after placing an extra PO_2 unit nearby a terminal oxygen in a P_2O_5 glass model.

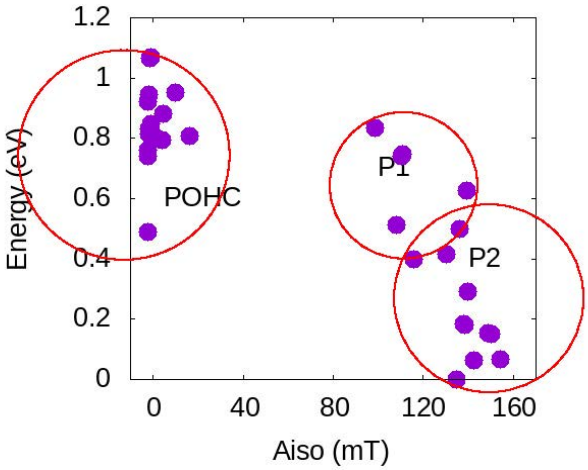

Fig. 5: Fermi-contacts $A_{iso}(^{31}P)$ distribution of oxygen vacancies (at a non-bridging oxygen atom) in a P_2O_5 glass model.

The P atom bearing the unpaired spin in Fig. 3 forms one double bond with a terminal oxygen (1.49 Å) and two bonds with bridging oxygen atoms (1.87 Å and 1.55 Å). The spin-density shown in Fig. 3 is very similar to the one shown in Fig. 1, thus suggesting its classification as a P_1 center configuration. Moreover, the Fermi contact A_{iso} (^{31}P)=101.3 mT and the g principal values g_1 =1.9969, g_2 =2.0023, g_3 =2.0049 calculated for the configuration shown in Fig. 3 further support its attribution to a paramagnetic defect of the P_1 center type [6]. In the table Tab. 1, we summarize the results of our EPR calculations for the three P_1-like configurations generated in the present work, according to the number of non-bridging oxygen (NBO) atoms.

B. *Fermi contacts $A_{iso}(^{31}P)$ distribution of oxygen vacancies in P_2O_5 glass*

The Weeks & Bray paper [5] is to our knowledge, the only paper which addresses the irradiation induced generation of paramagnetic centers in pure P_2O_5. However, also because the information on g-tensors given in [5] is rather scarce, we have dedicated more attention to the hyperfine splittings and in particular we have obtained the distribution of Fermi contacts $A_{iso}(^{31}P)$ calculated for all the paramagnetic configurations generated at a terminal oxygen site in our model of vitreous P_2O_5. In agreement with Weeks & Bray [5], the present investigation shows (Fig. 4) that in pure P_2O_5 the presence of oxygen vacancies (at the terminal oxygen) leads to the three kinds of EPR centers mentioned here above (P_1, P_2, POHC), so that the occasional presence of centers other than the three under discussion should be ascribed to the occurence of impurities in P_2O_5 [5]. Among the three kinds of centers which are emphasized in Fig. 4 with circles, the lowest (relative) energy one corresponds to P_2 centers which exhibit Fermi contacts in the range ~130-150 mT. P_1 centers and POHC centers have a larger relative energy 0.6-1.0 eV. However these differences, when considering a non-equilibrium condition (irradiation) are rather small and do not imply necessarily a preference for the generation of P_2 centers. Moreover, we here only generated a few P_1-like configurations so that, with a more statistically significative set of configurations, their average relative energy difference with respect to P_2 could become smaller.

TABLE I. G-TENSORS AND FERMI CONTACTS (MT) OF P_1 CONFIGURATIONS IN P_2O_5 AS CALCULATED BY FIRST-PRINCIPLES

Number of NBO	*structure*	g_1	g_2	g_3	$A_{iso}(P)$
0	o'(P_2O_5)	2.0023	2.0038	2.0063	105.8
0	glass	2.0018	2.0026	2.0036	98.5
1	glass	1.9969	2.0023	2.0049	101.3

IV. CONCLUSIONS

We performed first-principles calculations of the structure and of the EPR parameters for the P_1, P_2 and POHC paramagnetic centers in o'(P_2O_5) and P_2O_5 glass. The results are satisfactory and confirm the validity of the adopted theoretical approach to model paramagnetic defects in phosphate glasses and support for the P_1 a structural analogy to the Si-*E'* center. It should be noted however that only a minor fraction (~15%) of the oxygen vacancy sites in the glass here considered allow for the generation of a P_1-like configuration. In fact, the vast majority of the terminal oxygen vacancy sites allows for the generation of POHC and P_2 centers in a similar amount. As far as concerns the P_1 center in glassy P_2O_5, the present work suggests the possible occurrence of another configuration besides the previous one, i.e. a three-fold P atom featuring a P=O double bond and two normal P-O bonds. Such an alternative P_1 center configuration is likely to be relevant for those glasses featuring a considerable fraction of Q_1, Q_2 tetrahedral units besides the Q_3 unit which dominates the structure of pure P_2O_5 glass [13].

ACKNOWLEDGMENT

We acknowledge support through the ARRS-CEA Bilateral Project "REPHLES" NC-0008.

REFERENCES

[1] P. Balk and J. M. Eldridge, "Phosphosilicate glass stabilization of FET devices," Proceed. IEEE, vol. 57, no. 9, pp. 1558-1563, September 1969.

[2] H. Wagner et al, "Optimizing phosphorus diffusion for photovoltaic applications: peak doping, inactive phosphorus, gettering, and contact formation," J. Appl. Phys, vol. 119, no. 18, pp. 185704, May 2016.

[3] J. H. Campbell, J. S. Hayden, and A. Marker, "High-power solid-state lasers: a laser glass perspective,"J. Appl. Glass Sci. vol. 2, no. 1, pp. 3-29, February 2011.
[4] B. Schaudel, P. Goldner, M. Prassas, and F. Auzel, "Cooperative luminescence as a probe of clustering in Yb^{3+} doped glasses," J. Alloys Compd, vol. 300-301, pp. 443-449, April 2000.
[5] R. A. Weeks and P. J. Bray, "Electron spin resonance spectra of gamma-ray-irradiated phosphate glasses and compounds: oxygen vacancies," J. Chem. Phys, vol. 48, no. 1, pp. 5-13, January 1968.
[6] D.L. Griscom, E. J. Friebele, K. J. Long, and J. W. Fleming, "Fundamental defect centers in glass: Electron spin resonance and optical absorption studies of irradiated phosphorus doped silica glass and optical fibers,"J. Appl. Phys, vol. 54, no. 7, pp. 3743, March 1983.
[7] Z. M. Da Costa, W. M. Pontuschka, J. M. Giehl, and C. R. Da Costa, "ESR dosimeter based on P_2O_5-CaO-Na_2O glass system," J. Non-Cryst. Solids, vol. 352, no. 32-35, pp. 3663-3667, September 2006.
[8] L. Giacomazzi *et al.*, "EPR parameters of *E'* centers in v-SiO_2 from first-principles calculations," Phys. Rev. B, vol. 90, no. 1, pp. 014108, July 2014.
[9] L. Giacomazzi *et al.*, "Photoactivated processes in optical fibers: generation and conversion mechanisms of twofold coordinated Si and Ge atoms," Nanotechnology, vol. 28, no. 19, pp. 195202, April 2017.
[10] P. Giannozzi *et al.*, "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials," J. Phys. Condens. Matter, vol. 21, no. 39 pp. 395502, September 2009.
[11] C. J. Pickard and F. Mauri, "First-principles theory of the EPR g-tensor in solids: defects in quartz," Phys. Rev. Lett, vol. 88, no. 8-25, pp. 086403, February 2002.
[12] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., vol. 77, no. 18, pp. 3865-3868, October 1996.
[13] N. Shcheblanov *et al.*, "Vibrational and structural properties of P_2O_5 glass: advances from a combined modeling approach," unpublished.
[14] I. V. Abarenkov, I. I. Tupitsyn, V. G. Kuznetsov, and M. C. Payne, "Electronic structure of crystalline phosphorus pentoxide and the effect of an Ag impurity," Phys. Rev. B, vol. 60, no. 11, pp. 7881-7885, September 1999.
[15] G. Pacchioni, D. Erbetta, D. Ricci, and M. Fanciulli, "Electronic structure of defect centers P_1,P_2, and P_4 in P-doped SiO_2", J. Phys. Chem. B, vol. 105, no. 26, pp. 6097-6102, March 2001.