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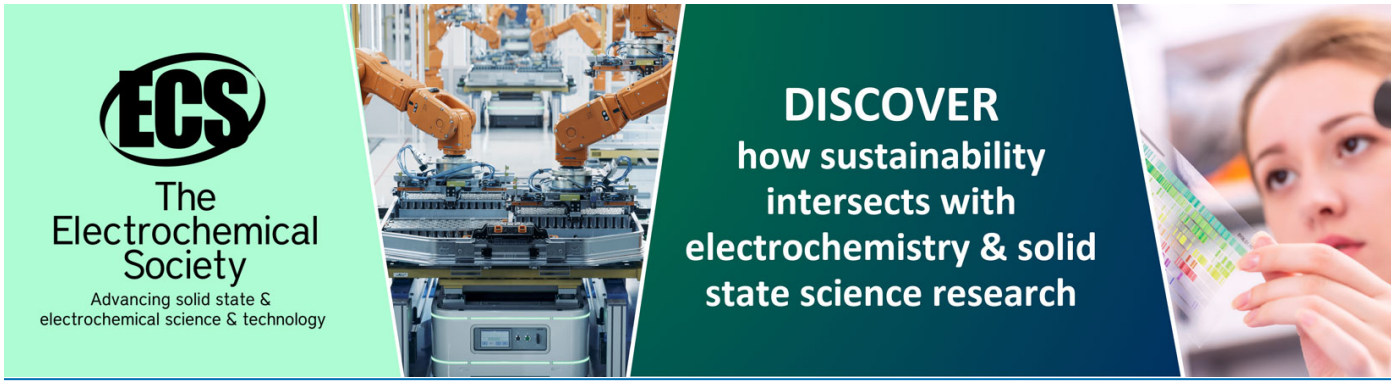

Monovacancies and Na substitutional defects in PbTe: theoretical positron annihilation study

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Abstract. The electron structures of cubic PbTe and substitutional defects are investigated using the state of the art pseudo-potential plane wave method, in the framework of the density functional theory within the generalized gradient approximation. The structural dependent positron annihilation in cubic PbTe was calculated and the positron lifetimes of the bulk, the Pb mono-vacancy, the Te mono-vacancy and the Na atom substituting on Pb were calculated respectively. The study provides evidence that positrons can distinguish between mono-vacancies and in situ substitutional Na doping. The positron lifetime values were found to be too similar to be distinguished. But calculations of the positron annihilation momentum distribution spectra did show clear differences between the two types of defect and may be exploited to characterize substitutional defects.

1. Introduction

Thermoelectric materials are solid-state energy converters whose combination of thermal, electrical, and semiconducting properties allows them to be used to convert waste heat into electricity or electrical power directly into cooling and heating [1]. To obtain optimized thermoelectric figure of merit (ZT) of a material, a large Seebeck coefficient, high electrical conductivity and low thermal conductivity are simultaneously required. Since the total thermal conductivity includes the two aspects of electronic and lattice-related phonon components, and point defects scatter phonons with a scattering cross section varying as the fourth power of frequency while other interaction processes vary more slowly with frequency, doping has been proposed as an approach to increase the electrical conductivity and decrease the thermal conductivity. PbTe-based compounds exhibit a great figure of merit for thermoelectric generators for the direct conversion of waste heat into electricity in the temperature range 400–800K, with a very low lattice thermal conductivity as well as a large Seebeck coefficient when appropriately p-type and n-type doped, and a good electrical conductivity [2]. In order to optimal control the doping effect on the thermoelectric properties, it is necessary to study in detail the influence of the substitution associated defects behavior in such thermoelectric materials.

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Measurements of positron annihilation constitute the reliable experimental tools for studying the electronic structures of condensed media. The annihilation characteristics depend on the type of defect in which the positron is trapped. Such measurements, such as positron lifetime method, could yield information regarding the electron density in the region of electron-positron overlap. It is well known that the experimental measures of total annihilation rate only contain the average electron-positron overlap in the crystal and could not yield information about the details of the overlap. By contrast, the positron lifetime or of data related to the momentum content of the annihilating electron-positron pair in a specific environment could produced accurately basing on the theoretical and computational simulations and more detailed information could be available.

In the present paper we shall focus on the influence of the Na substitution associated defects on positron annihilation in rocksalt structure PbTe, recent experiments have shown that doping Na can result in significant increases to power factor [3]. The electron structures of rocksalt structure PbTe and substitutional defects are investigated using the state of the art pseudo-potential plane wave method, in the framework of the density functional theory within the generalized gradient approximation. And the structural dependent positron lifetimes of the bulk, the mono-vacancy of Pb and Te, and of the Na atom substituting on Pb site were also studied respectively.

2. Method

One of the fundamentally important inputs for a clear understanding of the positron annihilation characteristics is the positron state. For the electronic structure calculations we employed the pseudopotential plane wave method (PP-PW), in the framework of the density functional theory within the generalized-gradient approximation (GGA). PbTe adopts the rocksalt structure with 64 atoms in a supercell. The valence electron configurations were $5d^{10}5s^25p^2$, $5s^25p^4$ and $3s^1$ for Pb, Te and Na, respectively. A plane-wave energy cutoff of 400eV and a 4×4×4 grid of Monkhorst-Pack k points were chosen in this study to ensure well convergence of the calculated structure. Then, the calculations for localized positron states at defects in rocksalt structure PbTe are achieved basing on the "conventional" scheme in which the positron does not affect the average electron density around the defects. Once the positron and electron densities are known, the total positron annihilation rate is obtained by

$$\begin{aligned}\lambda &= \pi r_0^2 c \int dr \cdot n_p(r) \cdot n_e(r) \cdot \gamma(n_e) \\ &= \int dr \cdot n_p(r) \cdot \Gamma(n_e)\end{aligned} \tag{1}$$

with r_0 denotes the classical electron radius, c denotes the speed of light, $\Gamma(n_e)$ denotes the positron annihilation rate in a homogenous electron gas with density ne and the so-called enhancement factor $\gamma(n_e)$ is a manifestation of electron-positron interaction and it is always a crucial ingredient when calculating the positron lifetime.

The enhancement factor is always a crucial ingredient in the context of calculating the correct positron lifetimes in solids. Local-density parameterizations in which the enhancement is parameterized as a function of the unscreened electron density, n_e, at the positron, have been introduced to account for the inhomogeneity of real systems. In this study, the concrete form of enhancement factor parameterized by Boroński and Nieminen (BN model) was chosen which can give reliable results compared with the experiment than other interpolation formula [4]:

$$\Gamma(n_e) = \pi r_0^2 c n_e (1 + 1.23 r_s + 0.8295 r_s^{1.5} - 1.26 r_s^2 + 0.3286 r_s^{2.5} + (1 - 1/\varepsilon) \cdot (r_s^3/6)) \tag{2}$$

where ε is the high-frequency dielectric constant and r_s is the electron density parameter.

3. Results and Discussion

The ground-state structural optimization was achieved firstly by a fit to the third-order Birch-Murnaghan equation of state (BMEOS) with the total energy as a function of the cell volume. The optimized values for the lattice parameters of PbTe are a=b=c=6.552Å, which are agreement with

experimental results within the acceptable error and other theoretical calculations, as summarized in table 1.

Table 1. Theoretical and experimental lattice constants a_0, bulk modulus B and its pressure derivatives B' of rocksalt structure PbTe at T=0 and P=0.

	This work	Other calculations	experiments
a_0(Å)	6.552	6.565[a] 6.44[b]	6.4611(3)[c]
B(MBar)	0.401	0.44[a] 0.517[b]	0.398[d]
B'	4.53	3.352[a] 4.52[b]	

[a] reference 5; [b] reference 6; [c] reference 7; [d] reference 8.

The decomposition of the positron lifetime spectrum is explained by the trapping model which gives the rate equations for the positron annihilating in delocalized states and in localized states. Possibly existing vacancy-type defects can trap positrons, but the results were widely different. The comparison of defect structures yields distinct differences in the electron and positron density distributions as demonstrated in figure 1. Despite the only major internal distinction between the defect-free and its substitution is the fact that the presence of a Na atom with lower atomic number, the positron density distribution difference could not be disregarded.

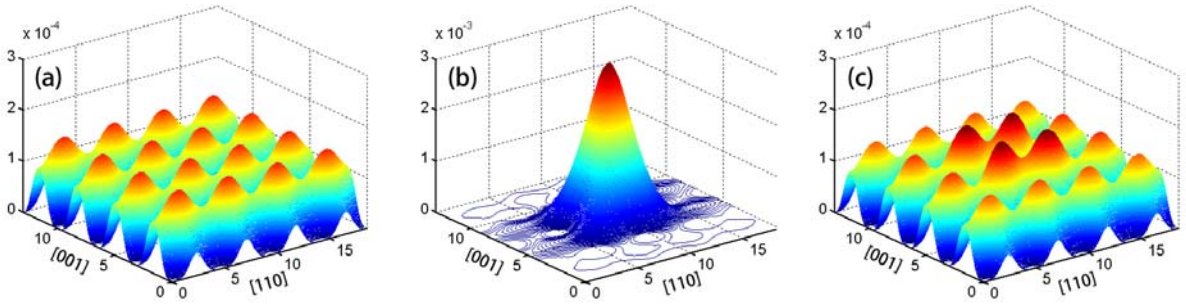

Figure 1. Positron density in PbTe [110] direction (Å): (a) defect-free; (b) with mono-vacancy V_{Pb} and (c) Na atom substituting on Pb site.

As for the comparison of theoretical calculations with experimental data, the two lattice parameters are adopted respectively for positron annihilation calculations and the experimental positron lifetimes in rocksalt structure PbTe were also listed in table 2. We can find that the calculated results are in agreement with those previous calculations and experimental values within the allowable limits of error [9, 10]. The positron lifetime of 258 ps, which correspond to positron annihilation at Na atom substituting on Pb site, is slightly higher than that assigned to annihilation at defect-free PbTe. It illustrates that positrons can distinguish mono-vacancies but not the corresponding substituted defects. Furthermore, if the dislocations exist in crystalline PbTe, owing to the similar positron lifetime values, only using positron lifetime technique to identification the defect structures would cause disturbance. Recently, the positron annihilation lifetimes of He-ion-irradiated Fe samples were measured by a pulsed positron beam technique and meet the similar situation and difficulties [11].

Table 2. Calculated positron annihilation lifetime in bulk (τ_b), in mono-vacancy Pb (τ_{Pb}) and Te (τ_{Te}) of PbTe, and at Na atom substituting on Pb site (Na_{Pb}) respectively

a0(Å)	6.552	6.462	
τ_b (ps)	252	244	244[a]
τ_{Pb} (ps)	335	329	331[a]
τ_{Te}(ps)	320	314	
τ_{NaPb}(ps)	258	246	

[a] corresponding experimental results within reference 10.

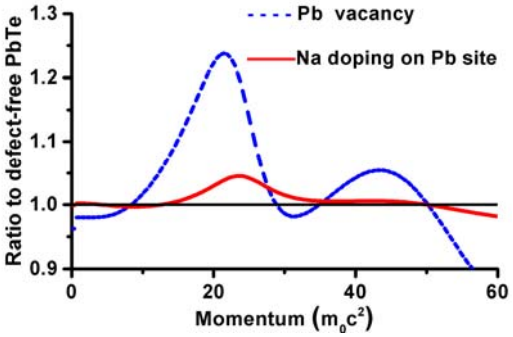

Figure 2. Calculated the ratio momentum spectrum of Na atom doping on Pb site in PbTe.

The reconstructed positron annihilation probability density spectra are shown in figure 2. Comparing with defect-free PbTe, the positron annihilation probability density for PbTe with V_{Pb} is varying greatly. The calculated positron binding energy to the Na_{Pb} substitutional defect is 0.011eV lower than it for the defect-free system. As can be seen in figure 1(c), the Na_{Pb} defects can also trap positrons, which may be called shallow positron traps, and compete with vacancies at very low temperatures. The advent of Na atom substituting on Pb site plays an important role in the relative positron annihilation probability density change at low momentum. In contrast to the positron density distributions, we may draw conclusion that the calculated positron annihilation momentum distributions show the remarkable effect of the presence of the substitutional Na impurities.

4. Conclusion

The positron lifetimes and positron annihilation momentum distributions in defect-free PbTe and with Na substitution are calculated and the comparison of different defect structures yields distinct differences in the positron probability distributions. The results show that the relative lifetime difference between Na_{Pb} substitutional structure and the defect-free PbTe is small. A comparison of positron annihilation momentum distributions spectra of the two structures demonstrates the strong affection with the existence of different positron traps. And the differences are mainly attributed to the existence of Na atom substituting on Pb site.

Acknowledgements

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