

Positron Annihilation Study of Cs-Deficient Pollucite

P Guagliardo¹, E R Vance², K Sudarshan¹, J Davis², J F Williams¹, C Ranganathaiah¹ and S Samarin¹

¹Centre for Antimatter-Matter Studies, School of Physics, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

²Institute for Materials Engineering, Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia

E-mail: paul.guagliardo@uwa.edu.au

Abstract. Positron annihilation has been applied to study a series of non-stoichiometric pollucite samples with the composition $\text{Cs}_{(1-x)}\text{Al}_{(1-x)}\text{Si}_{(2+x)}\text{O}_6$ for $x = 0.0-0.25$. Lifetime results showed a monotonic increase in the o-Ps lifetime and intensity as the Cs concentration was reduced. This is consistent with literature suppositions that vacancies are created as the Cs content is reduced.

1. Introduction

Pollucite is a caesium aluminosilicate with the composition $\text{CsAlSi}_2\text{O}_6$. Its structure is a rigid three-dimensional framework consisting of 48 corner-sharing (Si, Al) O_4 tetrahedra and 16 Cs^+ ions occupying its large 12-coordinate cavities [1-3]. The Cs-deficient form of pollucite has found utility in applications requiring high thermal stability, such as in gas turbine components, as its thermal expansion behaviour can be tuned by the amount of Cs^+ in the unit cell [4]. In addition, pollucite has been considered as a possible material for the immobilization of ^{137}Cs radioactive waste, owing to the fact that its structure can incorporate up to 40 wt% of Cs, which creates a highly dense wastefrom superior to glass-ceramic or zeolite alternatives [5, 6]. Kobayashi et al. [3] have shown by powder x-ray diffraction measurements that the lattice parameters of $\text{Cs}_{(1-x)}\text{Al}_{(1-x)}\text{Si}_{(2+x)}\text{O}_6$ showed a nearly linear decrease with a reduction in the amount of Cs^+ ions (increasing x), consistent with the replacement of Cs^+ ions with 12-fold vacancies in the structure. To investigate this we have used positron annihilation, x-ray diffraction and scanning electron microscopy to study a series of non-stoichiometric pollucite samples.

2. Experimental

X-ray diffraction (XRD) was performed with a Siemens D500 instrument, using Co $K\alpha$ radiation, as well as a PANalytical diffractometer, using Cu $K\alpha$ radiation. Scanning Electron Microscopy (SEM) was carried out on samples mounted in epoxy resin and polished to a 1-micron diamond finish. Approximately 50 Å of carbon was evaporated onto the surfaces under vacuum to prevent charging. The SEM was a Zeiss Ultra Plus instrument with an attached Oxford Instruments X-Max 80mm² SDD X-ray microanalysis system. The SEM was operated at an accelerating voltage of 15 kV.

The positron lifetime spectrometer was a fast-fast coincidence spectrometer, with detectors consisting of a BC418 plastic scintillator coupled to a Burle 8850 photomultiplier tube. A 30 μCi $^{22}\text{NaCl}$ source was used for collecting spectra; the source was encapsulated in 8 μm Kapton foil.



Experiments were carried out in the usual sandwich geometry between two identical samples. The time resolution of the instrument was determined to be 220 ps from spectra of a high-purity annealed nickel sample. Each spectrum had $3\text{-}4 \times 10^6$ counts and was analysed using PALSfit Version 1.64 [7]. For all samples, a three component analysis gave satisfactory fits (a variance close to unity). Measurements were conducted at room temperature and in air. Doppler broadening measurements were carried out with a HPGe detector with an energy resolution of approximately 1.5 keV at 511 keV.

Two series of Cs-deficient pollucite samples were produced by slightly varying methods, giving rise to differing levels of phase purity. The first series of samples with the composition $\text{Cs}_{(1-x)}\text{Al}_{(1-x)}\text{Si}_{(2+x)}\text{O}_6$ for $x = 0.0, 0.1, 0.2$ and 0.25 were made from mixed Al/Cs nitrate solutions and Ludox, a 40 wt% colloidal silica solution. The chemicals were accurately weighted, stir-dried, calcined, ball-milled in non-polar cyclohexane, and then sintered for 5 hours at 1200°C . Samples of $\text{CsAlSi}_5\text{O}_{12}$ and $\text{Cs}_{1.05}\text{Al}_{1.05}\text{Si}_{1.95}\text{O}_6$ were also produced by the same method. For the $\text{Cs}_{(1-x)}\text{Al}_{(1-x)}\text{Si}_{(2+x)}\text{O}_6$ samples, XRD showed major pollucite phase in all samples; however these samples contained a substantial contribution from $\text{CsAlSi}_5\text{O}_{12}$ (over 10%), with the amount increasing with x . The second series of samples ($\text{Cs}_{(1-x)}\text{Al}_{(1-x)}\text{Si}_{(2+x)}\text{O}_6$ for $x = 0, 0.1, 0.2$) was produced in a similar manner; however sintering was performed at a higher temperature of 1450°C . This gave rise to a higher degree of pollucite phase, as determined by XRD analysis. The $x = 0$ sample contained only a small amount of CsAlSiO_4 , with the strongest lines being only 2% of the intensity of the strongest pollucite line. The $x = 0.1$ sample exhibited only pollucite, insofar as any other X-ray lines were less than 1% of the intensity of the strongest pollucite line. The $x = 0.2$ sample did exhibit some $\text{CsAlSi}_5\text{O}_{12}$, but the strongest line was only 6% of the strongest pollucite line.

SEM on the pollucite phases in the Cs-deficient samples also indicated Cs deficiencies corresponding approximately to the nominal sample stoichiometries.

3. Results and Analysis

Lifetime spectra could be successfully analysed in terms of three discrete components. The shorter component τ_1 is associated with p-Ps annihilation and positron annihilation in the bulk material; τ_2 can be attributed to positron annihilation in defects, and the nanosecond component τ_3 is indicative of o-Ps pick-off annihilation in structural open volume. Fitting results for these samples and the resulting pore sizes calculated from τ_3 using the Tao-Eldrup (TE) model [8] are given in table 1. The τ_3 lifetimes correspond to pores in the range of 0.33-0.38 nm; this is close to the ionic size of Cs (0.38 nm) [9].

Table 1. Fitting results and pore diameters calculated from the TE model for set 1 of the pollucite samples.

Composition	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	I_3 (%)	d (nm)
$\text{CsAlSi}_2\text{O}_6$	198 (10)	435 (9)	980 (20)	24 (2)	65 (1)	11 (1)	0.33
$\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$	192 (10)	447 (8)	1060 (10)	23 (2)	62 (1)	15.3 (0.7)	0.35
$\text{Cs}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$	168 (8)	453 (6)	1120 (9)	19 (1)	60 (1)	20.8 (0.5)	0.37
$\text{Cs}_{0.75}\text{Al}_{0.75}\text{Si}_{2.25}\text{O}_6$	153 (10)	440 (8)	1120 (11)	16 (1)	61 (1)	22.9 (0.6)	0.37
$\text{CsAlSi}_5\text{O}_{12}$	150 (10)	457 (7)	1170 (12)	13.8 (0.9)	63.4 (0.5)	22.7 (0.6)	0.38
$\text{Cs}_{1.05}\text{Al}_{1.05}\text{Si}_{1.95}\text{O}_6$	188 (8)	419 (6)	1045 (13)	24 (1)	64 (1)	12.0 (0.5)	0.35

It can be seen that as the Cs content decreased, both the lifetime and intensity of the o-Ps component increase monotonically. This could suggest an increase in the structural open volume initiated by Cs vacancy creation. However, as noted above, the amount of $\text{CsAlSi}_5\text{O}_{12}$ increases with x . Lifetime results for $\text{CsAlSi}_5\text{O}_{12}$ are also shown in table 1; it can be seen that this sample has the longest lifetime with high intensity. This is consistent with reports that $\text{CsAlSi}_5\text{O}_{12}$ can exhibit a substantial Cs-deficiency [10]. Thus, the monotonic increase in τ_3 and I_3 with x could simply be due to

the increasing concentration of $\text{CsAlSi}_5\text{O}_{12}$ in the samples. A sample with excess Cs was also produced, which gave rise to results closest to that of stoichiometric pollucite.

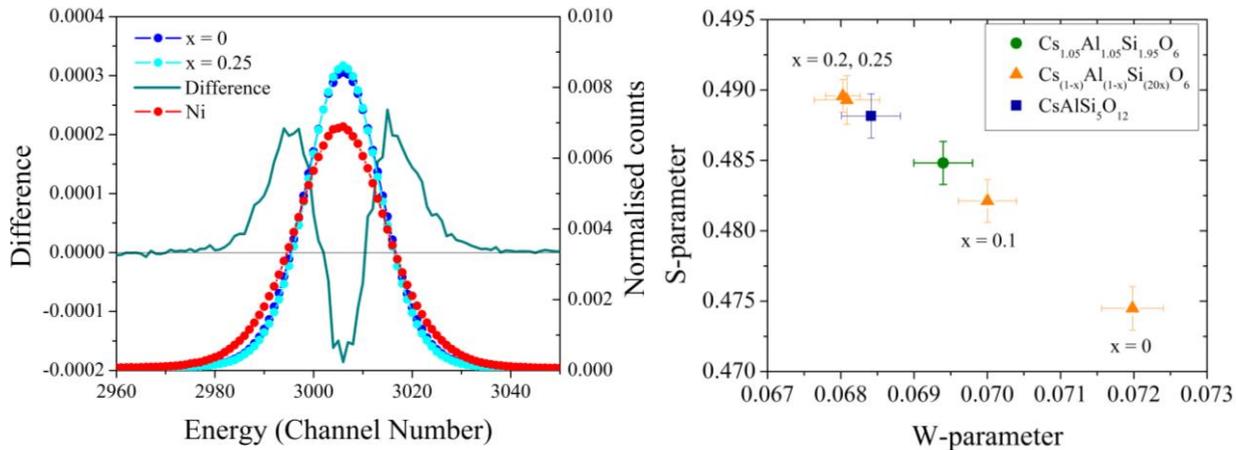


Figure 1. Left: 511 keV photo peak (taken with HPGe detector) for pollucites $x = 0.0$ and 0.25 , and nickel; the difference between the pollucite spectra is also shown; right: S- vs. W-parameter plot.

In figure 1, Doppler broadening spectra are shown for the stoichiometric pollucite $\text{CsAlSi}_2\text{O}_6$ and for $\text{Cs}_{0.75}\text{Al}_{0.75}\text{Si}_{2.25}\text{O}_6$ (annealed Ni is also shown as a reference). For the Cs-deficient sample there is an increase in the peak intensity relative to the stoichiometric pollucite, which is apparent in the difference spectra (also shown in figure 1). An S vs. W plot is shown in figure 1 where the line shape parameters for all samples are plotted; it can be seen that there is an increase in the S-parameter with increasing x . Again, this could indicate an increase in structural open volume (i.e. increased annihilation with low momentum electrons), or an increase in the concentration of $\text{CsAlSi}_5\text{O}_{12}$, which displays similar line shape parameters to the $x = 0.2$ and 0.25 cases.

PALS fitting results for the samples with a higher degree of phase purity are given in table 2. For these samples there is a monotonic increase in τ_3 and I_3 with decreasing Cs content. As the content of $\text{CsAlSi}_5\text{O}_{12}$ does not increase monotonically for these samples then this provides an indication that it is Cs vacancy creation, rather than the development of a second phase, that is giving rise to the observed increase. This is consistent with the results of Kobayashi et al. [3]. The o-Ps lifetimes and intensities for both sets of samples are compared in figure 2. The variation in τ_3 is significantly reduced for sample set 2, which displayed higher phase purity; however, the variation in I_3 with doping is comparable for both sets of samples.

Table 2. PALS fitting results and pore diameters calculated from the TE model for the final set of pollucite samples.

x	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	I_3 (%)	d (nm)
0	188 (8)	465 (5)	1081 (13)	17 (1)	69.7 (0.6)	13.4 (0.5)	0.358
0.1	182 (7)	467 (5)	1108 (12)	18.3 (0.9)	66.6 (0.6)	15.2 (0.5)	0.366
0.2	180 (8)	464 (5)	1108 (8)	15.7 (0.9)	63.0 (0.5)	21.3 (0.5)	0.366

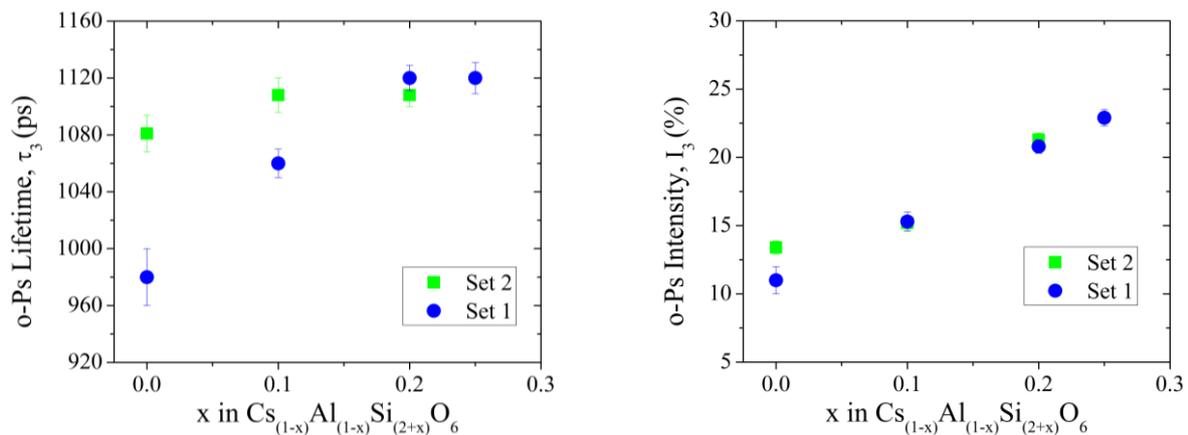


Figure 2. τ_3 and I_3 vs. x for both sets of pollucite samples; for sample set 1 there is an increase in the amount of $\text{CsAlSi}_5\text{O}_{12}$; set 2 is closer to single phase pollucite.

4. Conclusion

Two sets of Cs-deficient pollucite samples were studied with differing degrees of phase purity. Both sets of samples showed a monotonic increase in the o-Ps lifetime and intensity as the Cs concentration was reduced. This is consistent with literature suppositions that vacancies are created as the Cs content is reduced. However, in all samples there was a contribution from non-pollucite phases which could influence the positron annihilation parameters. In the future we will attempt to produce single phase pollucite so as to remove any ambiguity in the data.

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