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 Cs\(_{1-x}\)Al\(_{1-x}\)Si\(_{2+x}\)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 CsAlSi\(_2\)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 wasteform 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 Cs\(_{1-x}\)Al\(_{1-x}\)Si\(_{2+x}\)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\(_{α}\) radiation, as well as a PANalytical diffractometer, using Cu K\(_{α}\) 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 80mm\(^2\) 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 \(^{22}\)NaCl source was used for collecting spectra; the source was encapsulated in 8 µm Kapton foil.

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

16th International Conference on Positron Annihilation (ICPA-16) IOP Publishing
Journal of Physics: Conference Series 443 (2013) 012015 doi:10.1088/1742-6596/443/1/012015
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 3.4x10^6 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 Cs(1-x)Al(1-x)Si(2+x)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 CsAlSiO(6) and Cs(1.05)Al(1.05)Si(1.95)O(6) were also produced by the same method. For the Cs(1-x)Al(1-x)Si(2+x)O(6) samples, XRD showed major pollucite phase in all samples; however these samples contained a substantial contribution from CsAlSiO(6) (over 10%), with the amount increasing with x. The second series of samples (Cs(1-x)Al(1-x)Si(2+x)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(6), 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 CsAlSiO(6), 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.

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

| Composition         | τ₁ (ps) | τ₂ (ps) | τ₃ (ps) | I₁ (%) | I₂ (%) | I₃ (%) | d (nm) |
|---------------------|---------|---------|---------|--------|--------|--------|--------|
| CsAlSiO₆             | 198 (10)| 435 (9) | 980 (20)| 24 (2) | 65 (1) | 11 (1) | 0.33   |
| Cs₀.₉Al₀.₁Si₂.₀O₆    | 192 (10)| 447 (8) | 1060 (10)| 23 (2) | 62 (1) | 15.3 (0.7)| 0.35  |
| Cs₀.₈Al₀.₂Si₂.₀O₆    | 168 (8) | 453 (6) | 1120 (9)| 19 (1) | 60 (1) | 20.8 (0.5)| 0.37  |
| Cs₀.₇₅Al₀.₂₅Si₂.₀O₆  | 153 (10)| 440 (8) | 1120 (11)| 16 (1) | 61 (1) | 22.9 (0.6)| 0.37  |
| CsAlSiO₆             | 150 (10)| 457 (7) | 1170 (12)| 13.8 (0.9)| 63.4 (0.5)| 22.7 (0.6)| 0.38  |
| Cs₀.₉₅Al₀.₀₅Si₁.₉₅O₆ | 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 CsAlSiO(6) increases with x. Lifetime results for CsAlSiO(6) 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 CsAlSiO(6) can exhibit a substantial Cs-deficiency [10]. Thus, the monotonic increase in τ₃ and I₃ with x could simply be due to...
the increasing concentration of CsAlSi$_5$O$_{12}$ in the samples. A sample with excess Cs was also produced, which gave rise to results closest to that of stoichiometric pollucite.

In figure 1, Doppler broadening spectra are shown for the stoichiometric pollucite CsAlSi$_2$O$_6$ and for Cs$_{0.75}$Al$_{0.25}$Si$_{2.25}$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 CsAlSi$_5$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 $\tau_1$ and $I_1$ with decreasing Cs content. As the content of CsAlSi$_5$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 $\tau_3$ 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   | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (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. \( \tau_3 \) 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.

References
[1] Beger R M 1969 Z. Kristallogr. 129 280
[2] Hirao K, Soga N and Kunugi M 1976 J. Phys. Chem. 80 1612
[3] Kobayashi H, Sumino S, Tamai S and Yanase I 2006 J. Am. Ceram. Soc. 89 3157
[4] MacLaren I, Cirre J and Ponton C B 1999 J. Am. Ceram. Soc. 82 3242
[5] Komarneni S and Roy R 1983 J. Am. Ceram. Soc. 66 471
[6] Hess N J, Espinosa F J, Conradson S D and Weber W J 2000 J. Nucl. Mater. 281 22
[7] Olsen J V, Kirkegaard P, Pedersen N J and Eldrup M 2007 Phys. Status Solidi (c) 4 4004
[8] Tao S J 1972 J. Chem. Phys. 56 4754
[9] Shannon R 1976 Acta Crystallogr. Sec. D 32 751
[10] Gatta G D, Rotiroti N, Fisch M, Kadiyski M and Armbruster T 2008 Phys. Chem. Minerals 35 521