Structural Studies of Hollandite-Based Radioactive Waste Forms

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ABSTRACT

Hollandites with compositions $Ba_{1,2-x}Cs_xMg_{1,2-x/2}Ti_{6.8+x/2}O_{16}$, and $Ba_{1,2-x}Cs_xAl_{2,4-x}Ti_{5.6+x}O_{16}$ (x=0, 0.1, 0.25) have been synthesised using a modified alkoxide/acetate precursor route. The samples have been sintered using two procedures; hot isostatic pressing and sintering at ambient pressure. X-ray powder diffraction has shown samples from both systems to form tetragonal hollandites, with little change when pressed by both methods. Cs-133 MAS NMR spectra have been recorded showing the chemical shift in Al containing samples to be ~250ppm, and in Mg hollandites ~175ppm and 200ppm, with little change when prepared by both methods.

INTRODUCTION

In the field of nuclear waste immobilisation the safe storage of active Cs-135 and Cs-137 is essential, as the Cs⁺ tends to be soluble under most conditions [1]. Systems based on hollandite, $A_x B_8 O_{16}$, have been selected as the 'wasteform of choice' and are part of the Synroc assemblage [1,2].

The hollandite type structure is based on octahedra, in these samples Ti-O, which share edges and corners forming tunnels. The A cation (Ba,Cs) is located within the tunnels, (Figure 1). The structure can either be monoclinic[3], e.g. $Ba_{1.2}Mg_{1.2}Ti_{6.8}O_{16}$, or tetragonal[4] in nature e.g. $Ba_{1.121}Al_{2.24}Ti_{5.76}O_{16}$, essentially the difference is due to variations in A/B cations radius ration, causing a shear-type collapse of the tunnel and a reduction in symmetry (I4/m \rightarrow C2/m)

The hollandite structure can accommodate a variety of atoms on both the A and B sites, e.g. on the A site Ba, Na, and K; on the B site it is possible to mix cations such as Mg, Ti, Al, and Zr. In the area of nuclear waste immobilization it is routine to base the hollandite on Ti[1,5-8], e.g.Ba_{1.2}Mg_{1.2}Ti_{6.8}O₁₆. The use of Ti is important because, as Cs⁺ undergoes β -decay forming Ba²⁺ a charge imbalance results, in order to compensate for this a Ti⁴⁺ cation in the lattice undergoes reduction to Ti³⁺ conserving charge balance.

 Cs^+ can be immobilized in hollandites that contain Al^{3+} and $Mg^{2+}[9]$, in these systems the Al^{3+} and Mg^{2+} are present to ensure charge balance is maintained during formation, preventing the premature formation of Ti³⁺. Such components are also used as they modify the tunnel size allowing larger atoms to be accommodated e.g. $Cs^+ \sim 1.7$ Å and Ba ~ 1.4 Å – both ions are in 8-fold co-ordination[10].

Although there is a broad understanding of tunnel site ordering for individual elements (e.g. K, Cs or Ba) within in the hollandite structure it is unknown how mixed large cations (e.g. Cs^+ and Ba^{2+}) order within the tunnels and how their location is related to the atomic constituents on the B-site, e.g. Mg, Al, and Ti. The aim of this work is to study such ordering and see whether it contributes to the stability of Cs-containing hollandites under leaching conditions.



Figure 1 - Image of Ba-Hollandite crystal structure, showing the tunnels and Ba^{2+} ions large spheres, located within – view looking down the b-axis.

EXPERIMENTAL

Stoichiometric mixtures, shown in Table 1, of barium acetate (Aldrich, 99.5%), caesium nitrate (Aldrich, 99.99%), aluminium nitrate (Aldrich, 99%), and magnesium nitrate (Aldrich, 99%) were dissolved in 250-300ml of deionised water. To the resultant solution a stoichiometric amount of titanium isopropoxide (Aldrich, 98+%) in acetone was added. A small excess of Mg/Al (0.1M) and Ti (0.5M) was added to prevent the formation of Ti³⁺. The resultant flocculent mixture was then homogenised, and stirred while heating until dryness.

The resultant powder was then heated at 750° C for 4 hours to completely remove any remaining nitrate and acetate contaminants. The resultant white powder was then ground until the average particle size was less then 75 μ m. The powder was then sintered in one of two manners:

- i) Cold Uniaxial Pressing (CUP) Portions of the sample were cold pressed into pellets ~ 10mm in diameter and then sintered at 1300°C for 2hours.
- ii) Hot Isostatic Pressing (HIP) Sample pressed at 1300°C and ~200MPa in nickel cans for 2hours.

Barium	Caesium	Magnesium	Aluminium	Titanium
1.2	0.0	1.2 (0.1)		6.8 (0.5)
1.1	0.1	1.15 (0.1)		6.85 (0.5)
0.95	0.25	1.075 (0.1)		6.925 (0.5)
1.2	0.0		2.4 (0.1)	5.6 (0.5)
1.1	0.1		2.3 (0.1)	5.7 (0.5)
0.95	0.25		2.15 (0.1)	5.85 (0.5)

Table 1 - Stoichiometric values used in preparation of samples, figures in brackets indicate extra addition to ensure minimum Ti^{3+} formation.

After sintering the samples were split into chips and finely ground powder, these were then analysed by the following techniques.

X-ray diffraction measurements were carried using a modified Bede D1 X-ray diffractometer running in reflexion geometry, using weighted Cu K_{α} radiation and a graphite monochromator. Patterns were recorded over an angular range of 10-80°, with an average step size of 0.02°.

MAS NMR spectra were acquired on a Varian Infinity Plus 500 spectrometer equipped with an 11.7 T wide-bore magnet, operating at 65.6 MHz. Samples were packed inside 7.5 mm or 2.5 mm MAS rotors and rotated at speeds of 7 kHz and 20 kHz, respectively. The recorded spectra are referenced to CsCl (aq).

RESULTS AND DISCUSSION

X-ray powder diffraction

Ba_{1.2-x}Cs_xMg_{1.2-x/2}Ti_{6.8+x/2}O₁₆Samples

The X-ray diffraction patterns recorded for samples prepared by CUP show the presence of a predominantly tetragonal based 'hollandite' structure. There is no evidence in the recorded data for a monoclinic structure as predicted by Fanchon et al[3]. This observation however, maybe due to many effects the least of which is poor crystallinity obscuring the monoclinic splitting in these samples. A second cause for the absence of a visible monoclinic splitting could be due to the mixed incident radiation used in these studies. If monochromatic Cu K_{α 1} radiation was used it maybe visible, further examinations are currently being carried out. The samples prepared by HIP show a much greater degree of crystallinity than those pressed and sintered separately. They still however, show a structure tetragonal in nature. Both sets of samples show no measurable change unit-cell size with the addition of Cs.

Ba_{1.2-x}Cs_xAl_{2.4-x}Ti_{5.6+x}O₁₆ Samples

The data recorded for these systems when prepared by CUP show the system has adopted the expected tetragonal lattice from Cheary [4]. When prepared by HIP the samples show increased crystallinity.

There was no direct evidence of a phase containing Cs, when prepared by both techniques, however this it be expected as Cs^+ and Ba^{2+} have closely matched scattering magnitudes in X-ray diffraction.



Figure 2 - X-ray diffraction patterns from pure and doped barium aluminium hollandites.



Figure 3 - Figure showing example patterns from cold pressed and hot pressed samples of $Ba_{1.2}Al_{2.4}Ti_{5.6}O_{16}$.

Magic Angle-Spinning Nuclear Magnetic Resonance

MAS NMR is a valuable technique in the study of Cs containing samples as it can provide additional local information not provided by other techniques. Example spectra are shown in Figures 4 & 5.

Ba_{1.2-x}Cs_xMg_{1.2-x/2}Ti_{6.8+x/2} Samples

The spectra recorded for these samples show a peak that contains two sub peaks, at chemical shifts of 200ppm and 175ppm. The positions of these peaks are coincidental for both samples prepared by CUP. There is a difference in intensity, between samples prepared by different techniques, which is due to the change in relative amounts of nuclei under investigation. When the samples are prepared by HIP a similar chemical shift is found, at 198 ±1 ppm and 174 ±1 ppm.



Figure 4 – Cs-133 MAS NMR spectrum recorded for Ba_{0.95}Cs_{0.25}Mg_{1.075}Ti_{6.925}O₁₆



Figure 5 - Comparison plot of MAS NMR spectra recorded for Cs-133 nuclei in a variety of hollandites

Ba_{1.2-x}Cs_xAl_{2.4-x}Ti_{5.6+x}O₁₆ Samples

The spectra recorded from these samples again show a single peak with a chemical shift of 250 ± 1 ppm, with again both samples being coincidental when prepared by CUP. When prepared by HIP the chemical shift is found to be 252 ± 1 ppm.

The data outlined above are indicative of Cs^+ being located in the tunnels within the structure. The chemical shifts are close to those previously reported that give a chemical shift of 245ppm for Cs^+ located in hollandite tunnels with no Ti^{3+} present[2]. The observed small difference in these samples with respect to those previously published can be explained by a slight change in chemical composition, in the reference data the formulation used was $BaCs_{0.1}Al_{2.1}Ti_{5.9}O_{16}$ [2]. The observation that the Mg-containing samples show two peaks can be explained if the different effects that Mg^{2+} and Ti^{4+} have on the Cs^+ are different when they are located as next-nearest neighbours i.e Cs-O-Mg would be different to Cs-O-Ti. The lack of visible difference in spectra recorded for Al-containing samples is probably due to very similar effects from Al³⁺ and Ti⁴⁺.

CONCLUSIONS

The data recorded so far show that the Cs is located within the channels in the structure, with no evidence of secondary phases. Secondly, there has been a change in crystal type for samples containing Mg from the expected monoclinic to a tetragonal type. Although this change is observed structurally it is likely to have little or no effect on the overall structural stability. The stability of samples under leaching conditions is currently being investigated.

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