

Australian Government



Radioactive Iodine-129 Capture in Mixed Cation Sodalites: *ab initio* Modelling

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Sodalites

- Large family of naturally occurring minerals
- Zeolite-type structures with prototype formula $Na_8(AlSiO_4)_6Cl_2$
- Known to be effective hosts of halogens: CI, I
- Natural analogues for waste materials
- Investigated experimentally for long-term containment of I-129
- Mixed cation sodalite $Na_{8-x}Ag_x(AlSiO_4)_6I_2$

Na-I Sodalite: β-Cage





I: purple; Na: yellow; Si: blue; AI: grey; O: red

Methodology I

- Compute energies and structures of various configurations
- ab initio Density Functional Theory (DFT) based
- VASP (Vienna Ab initio Simulation Package)
- 2 x 2 x 2 supercell: 8 x 46 = 368 atoms



Sodalite: M₄I Tetrahedra





I: purple; Na: yellow; Si: blue; AI: grey; O: red

Methodology II

- Mixed cation sodalite 2x2x2 supercell model: $8({\rm Na}_{8-x}{\rm Ag}_x({\rm AlSiO}_4)_6{\rm I}_2)$
- Solution energies:

$$E_{solution} = E - \frac{n_s^{\text{Na}}}{64} E_0^{\text{Na}} - \frac{n_s^{\text{Ag}}}{64} E_0^{\text{Ag}}, n_s^{\text{Na}} + n_s^{\text{Ag}} = 64$$

- Solution energy of a single solute: E_{s1}
- Binding energies:

$$E_{binding} = E_{solution} - n_s E_{s1}$$

Ag-I Sodalite: 1 and 2 Na Solutes



I: purple; Na: yellow; Ag: black; Si: blue; Al: grey; O: red

Na-I Sodalite: 2 Ag Solutes



I: purple; Na: yellow; Ag: black; Si: blue; AI: grey; O: red

Solution Energies: E_{solution} vs n_s



Binding Energies: E_{binding} vs n_s



Conclusions to Test! (I)

M = Na, Ag

 Dilute solid solutions should be possible from both ends of M₈(AlSiO₄)₆I₂:

$E_{solution} < 0$

• Expect higher concentrations to be energetically unfavourable:

 $E_{binding}$ >0 when 2 – 4 solutes sit in the same M_4 I tetrahedron

Conclusions to Test! (II)

- Dilute solid solutions of Ag in Na-I sodalite should have lower solution energies than corresponding dilute solid solutions of Na in Ag-I sodalite
- As concentrations increase, this should reverse, high concentration solutions of Ag in Na-I sodalite should have higher solution energies than corresponding solid solutions of Na in Ag-I sodalite

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- raijin: raijin.nci.org.au
- massive (Multi-modal Australian ScienceS Imaging and Visualisation Environment): <u>www.massive.org.au</u>

Reference Expt¹: Maddrell, E., Private Communications. 2015.