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The preparation, characterisation and structure of $Ca_8[AlO_2]_{12}Te_2$ and $Cd_8[AlO_2]_{12}Te_2$; two new members of the sodalite family

Sandra E. Dann*[a] **and Mark T. Weller**[b]

[a]*Department of Chemistry, Loughborough University, Loughborough, UK LE11 3TU*
[b]*Department of Chemistry, The University of Southampton, Highfield, Southampton, UK SO17 1BJ*

Two new aluminate sodalites containing the telluride ion have been synthesised for the first time. The structures of $Ca_8[AlO_2]_{12}Te_2$ and $Cd_8[AlO_2]_{12}Te_2$ have been determined using the Rietveld refinement of powder X-ray diffraction data. ^{125}Te and ^{27}Al MAS NMR and IR spectroscopy have been used to investigate the effect of the large occluded ion on the framework moiety.

Introduction

The sodalites are a well known class of anion-containing framework consisting of β-cages, formed from TO_4 tetrahedra, directly linked through the six-membered rings and containing a centrally placed anion coordinated to four cations (Fig. 1). The composition of the sodalite structure is very diverse[1–3] and many different cations and anions can be incorporated in the sodalite cage which has general formula $[M_8][TT'O_4]_6[X_y]$. Ions of different sizes and geometries such as SO_4^{2-} or Cl^- can be accommodated by tilting the tetrahedra out of their normal planes and by deviation from perfect tetrahedral geometry around T(T′). Guest–host interactions of the framework structure with the occluded species are exploited in pigments where the members of this class are the well known ultramarines which contain polysulfide radicals (S_2^-, S_3^-) and the corresponding selenium analogues. Although the S^{2-} and Se^{2-} species have been well studied, the Te^{2-} ion has received less attention.

The group of materials where $T = T' = Al$ are the aluminate sodalites with general formula $M_8[AlO_2]_{12}X_2$ [M = Ca, Cd, Sr; $X = SO_4$, WO_4, S^{2-}). Many of these materials have been extensively studied by Depmeier,[4–6] particularly with respect to the orientation of the tetrahedral anions located at the centre of the β-cage unit. These materials are also unusual as they disobey Lowenstein's rule of aluminium avoidance[7] and form a set of aluminium rich structures with bicchulite, $Ca_8[Al_2SiO_6]_4(OH)_8$.[8] The high aluminium content of these materials produces notably acidic frameworks which may have potential uses in catalysis and ion exchange. Recently the authors reported the first aluminate structures containing tellurium;[9] $Sr_8[AlO_2]_{12}(TeO_3)_2$ and $Sr_8[AlO_2]_{12}Te_2$, which was prepared by *in situ* reduction of the tellurite material. In this paper we report two new aluminate telluride sodalites prepared directly by solid state methods.

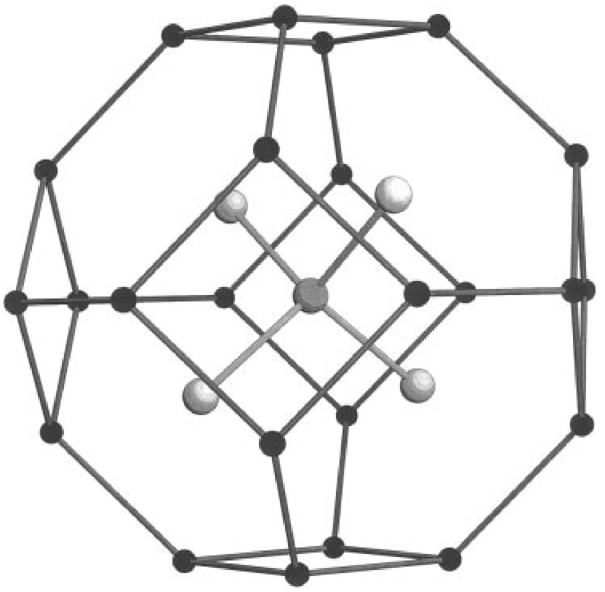

Fig. 1 Depiction of the sodalite structure showing the central Te anion (dark grey sphere) coordinated to four Cd cations (white spheres) occluded within the sodalite framework consisting of vertex linked AlO_4 tetrahedra

Experimental

The materials were prepared by solid-state synthesis at high temperatures as explored initially by Depmeier.[4] MO, MTe and Al_2O_3 (M = Cd,Ca) in the correct molar proportions were ground homogeneously using a pestle and mortar in a glove box. The reaction mixture was then sealed in a silica tube (to prevent volatisation of MTe which would occur below the reaction temperature of alumina) and heated to 1100 °C in a tube furnace for 48 h. The tube was then slow-cooled to room temperature. The products crystallised as fine white powders which were shown to be single cubic phases by powder X-ray diffraction with $a = 8.940(1)$ Å for $Cd_8[AlO_2]_{12}Te_2$ and $a = 9.154(1)$ Å for $Ca_8[AlO_2]_{12}Te_2$.

Attempts to oxidise the occluded species to tellurite failed in both cases. The cadmium analogue showed good heat stability to 600 °C before decomposition to cadmium silicate, alumina and cadmium tellurite whereas the calcium analogue was considerably more stable with notable decomposition only above 800 °C. Attempts to make the tellurite materials directly using $MTeO_3$ instead of MTe also failed in both cases.

IR spectra were obtained for both compounds using a Perkin Elmer FTIR 1710 spectrometer with a 3600 data station on pressed KBr discs. The four characteristic IR active bands expected for aluminate sodalites are observed between 1000 and 400 cm^{-1}; $Ca_8[AlO_2]_{12}Te_2$ $\nu_{as} = 840\ cm^{-1}$, $\nu_{s1} = 685\ cm^{-1}$, $\nu_{s2} = 645\ cm^{-1}$ and $\delta = 415\ cm^{-1}$ and for $Cd_8[AlO_2]_{12}Te_2$ $\nu_{as} = 825\ cm^{-1}$, $\nu_{s1} = 705\ cm^{-1}$, $\nu_{s2} = 662\ cm^{-1}$ and $\delta = 423\ cm^{-1}$.

The composition of the materials were examined using SEM. The morphology of the crystals can be described as polyhedral with a typical particle size of between 50 and 100 μm. The samples appeared single phase in both cases with no crystals of markedly different morphology. EDX analysis on the crystals gave mass percentages of Ca:Al:Te of 25:25:20 for $Ca_8[AlO_2]_{12}Te_2$ and of 53:16:12 for Cd:Al:Te in $Cd_8[AlO_2]_{12}Te_2$ in good agreement with the theoretical formulations; the calculated mass percentages are 25:25:20 and 54:15:12 for $Ca_8[AlO_2]_{12}Te_2$ and $Cd_8[AlO_2]_{12}Te_2$ respectively.

UV–VIS spectra were recorded on a Perkin-Elmer Lambda-19 Spectrophotometer on undiluted samples. The spectra were automatically absorption corrected using the Kulbelka–Munk function.

^{125}Te and ^{27}Al MAS NMR spectra were collected at room temperature referenced to dimethyltellurium and 1 mol dm^{-3} $AlCl_3$ solution respectively on a Bruker AM300 spectrometer fitted with a 7 mm probe. ^{27}Al NMR spectra were recorded using a field of 78.158 MHz and a 1 µs pulse corresponding to a 10° pulse in the reference solution of 1 mol dm^{-3} $AlCl_3$ over 2000 repetitions at spinning rates of 4.5 kHz and 7 kHz with a relaxation delay of 1 s. ^{125}Te NMR spectra were recorded using a field of 94.45 MHz with a 1 µs pulse with a relaxation delay of 30 s and a spinning rate of 4.5 kHz. Typically 1000 scans were performed to give good signal to noise.

The ^{125}Te NMR and ^{27}Al NMR spectra obtained were very simple; a sharp ^{125}Te resonance is observed at −1340 (CaTe) and −1318 ppm (CdTe) which is characteristic of the Te^{2-} anion and similar to that observed for $Sr_8[AlO_2]_{12}Te_2$,[9] whilst the ^{27}Al NMR spectra show the characteristic line shapes expected for a quadrupolar nucleus in a slightly distorted environment with incomplete averaging of quadrupolar coupling. Since the distortion of the tetrahedral geometry in the aluminate sodalites is relatively small, the isotropic chemical shift could be obtained by fitting the spectrum for various quadrupolar coupling constants.[10] Simulation of the experimental spectra allowed calculation of the isotropic chemical shift, giving values of 77.7 ppm ($C_q = 3.9$ MHz) and 79.8 ppm ($C_q = 2.7$ MHz) respectively for the calcium and cadmium materials.

Structure determination

Powder X-ray diffraction data were collected on a Siemens D5000 diffractometer fitted with primary monochromator using Cu-Kα_1 radiation, in the 2θ range 20–120° over a period of 12 h with a 0.02 step. Both patterns could be indexed on a body-centred cubic structure with systematic absences consistent with the space group $I\bar{4}3m$ as expected for a sodalite with a single tetrahedral framework species. Rietveld refinement analysis was performed in this space group using the program GSAS.[11]

Starting models were taken from Dann and Weller[9] and used as the basis for both refinements with Te on the 2a site (000) Ca, Cd on 8c (x,x,x) $x = 0.24$, aluminium on 12d (¼, ½, 0) and the cage oxygen on the 24g site (x,x,z) $x = 0.38$ and $z = 0.47$. Initial stages of the refinement proceeded well in both cases including scale factor, cell constant and polynomial background. All variable atomic positions and peak shape parameters were varied smoothly and finally the isotropic factors were added. In the case of the calcium telluride sodalite a very small amount of a second phase was observed which was identified as mayenite[12] $Ca_{12}Al_{14}O_{33}$, which was included in the refinement. Since the proportion of the impurity phase was so small (<3%) the atomic positions and temperature factors of mayenite were kept constant as determined in the reported crystal structure determination; a slight improvement to the fit was obtained. Final refined parameters are given in Tables 1 and 2 respectively for the $Cd_8[AlO_2]_{12}Te_2$ and $Ca_8[AlO_2]_{12}Te_2$. The profile fits to $Cd_8[AlO_2]_{12}Te_2$ and $Ca_8[AlO_2]_{12}Te_2$ are shown in Fig. 2 and 3.

Table 1 Refined atomic parameters for $Cd_8[AlO_2]_{12}Te_2$

atom	site	x	y	z	B_{iso}/Å^2
Cd	8c	0.1794(1)	0.1794(1)	0.1794(1)	1.79(7)
Al	12d	¼	½	0	1.7(2)
O	24g	0.1428(10)	0.1428(10)	0.4209(12)	1.2(4)
Te	2a	0	0	0	1.7(1)

$a = 8.9398(1)$ Å, $\chi^2 = 12.37$, space group $= I\bar{4}3m$.

Table 2 Refined atomic parameters for $Ca_8[AlO_2]_{12}Te_2$

atom	site	x	y	z	B_{iso}/Å^2
Ca	8c	0.1975(3)	0.1975(3)	0.1975(3)	2.7(1)
Al	12d	¼	½	0	1.9(1)
O	24g	0.1519(7)	0.1519(7)	0.4378(8)	1.9(3)
Te	2a	0	0	0	1.8(1)

$a = 9.1543(1)$ Å, $\chi^2 = 8.37$, space group $= I\bar{4}3m$.

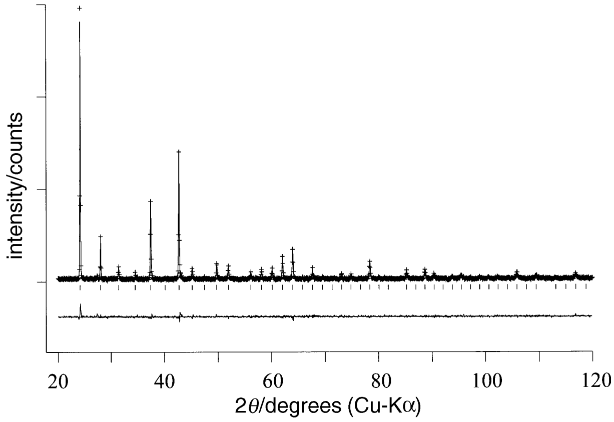

Fig. 2 Final profile fit to the X-ray diffraction data for $Cd_8[AlO_2]_{12}Te_2$. The crosses represent the experimental data points and the upper continuous line the calculated pattern. The lower continuous line represents the difference. Tick marks indicate the calculated reflections positions.

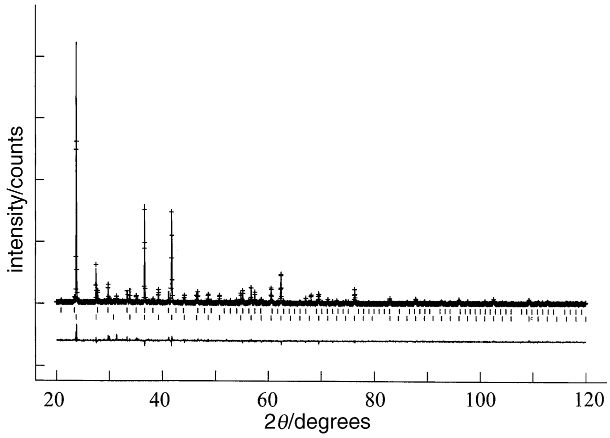

Fig. 3 Final profile fit to the X-ray diffraction data for $Ca_8[AlO_2]_{12}Te_2$. The crosses represent the experimental data points and the upper continuous line the calculated pattern. The lower continuous line represents the difference. The upper tick marks indicate the calculated reflections positions for the minor impurity phase $Ca_{12}Al_{14}O_{33}$ and the lower tick marks the calculated reflection positions of $Ca_8[AlO_2]_{12}Te_2$.

Results and Discussion

Bond distances and angles calculated from the refined atomic positions are given in Table 3. The telluride ion is tetrahedrally coordinated to four calcium/cadmium ions. The bond distances of 2.77 Å for the CdTe material and 3.13 Å for the CaTe material are in excellent agreement with the bond lengths observed in the bulk materials of 2.81 Å (zinc blende structure) and 3.18 Å (rock salt structure) respectively. The slight shorten-

Table 3 Derived important bond distances (Å) and angles (°)

parameter	$Cd_8[AlO_2]_{12}Te_2$	$Ca_8[AlO_2]_{12}Te_2$
Al—O	1.746(5)	1.750(4)
M—O × 3	2.21(1)	2.278(9)
M—O × 3	3.22(1)	3.075(7)
M—Te	2.777(3)	3.131(5)
Al—O—Al, γ	129.7(7)	135.2(6)
O—Al—O, α	113.4(8)	118.2(6)
O—Al—O, α'	107.5(4)	105.3(3)
tilt, ϕ	29.0(4)	22.3(4)

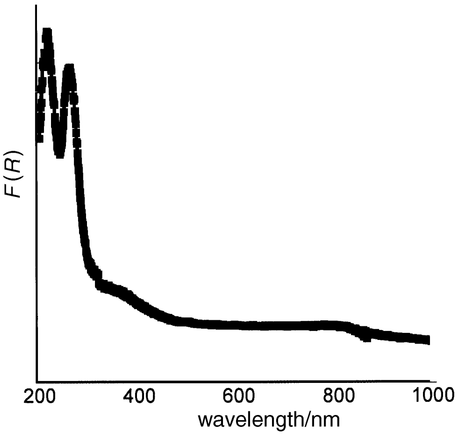

Fig. 4 Kulbelka–Munk corrected diffuse reflectance UV–VIS spectrum of $Cd_8[AlO_2]_{12}Te_2$

ing of the bond lengths of the occluded metal chalcogenide moieties is presumably related to the smaller ionic radius of the anion in pseudo four-fold coordination, as opposed to the more normal six-fold coordination. The metal coordination consists of three short and three long interactions with the oxygens in the six-ring and one interaction to the central tellurium. The 3 + 3 coordination to the ring is facilitated by partial collapse of the cage around the occluded anion; in cases where the occluded cation is small the longer interactions are effectively non-bonding and the coordination of the cation is tetrahedral. Calcium and cadmium have much smaller ionic radii, *ca.* 1 Å, in comparison to strontium, *ca.* 1.25 Å. Smaller ions cause more prominent collapse of the six-ring and hence a larger differential between the two different bonding interactions with the six-ring oxygens. In $Sr_8[AlO_2]_{12}Te_2$ the difference is only 0.3 Å whereas in these materials the difference is 0.8–1 Å and the longer interaction is effectively non-bonding.

The cell collapse is almost totally performed by variations in the Al—O—Al bond angle which can take values between 120 and 160°. Larger bond angles are typically observed for the aluminates in comparison to the aluminosilicates where the bond ionicities are lower. The extent of collapse can be described by several values as investigated by Depmeier.[13] Of importance are α and α' which are tetrahedral distortion angles for the O—Al—O angles in the AlO_4 tetrahedron, which can distort considerably from the perfect 109.48°. The more important term in defining cell collapse is the tilt angle, ϕ, which describes how much the tetrahedra are tilted out of their -4 axis. ϕ can hold values between 0 and 35° for the aluminate sodalites, where 0 equates to a fully expanded centrosymmetric sodalite with symmetry *Im*3*m*. The large tilt angles observed for these two materials of 29.0° and 22.3° suggest that oxidation from telluride to tellurite could be achieved as the framework is far from fully expanded. However, experiments to facilitate oxidation of the telluride have failed in both these materials despite the stability of $CaTeO_3$ and $CdTeO_3$.

UV–VIS data recorded for the CdTe analogue are shown in Fig. 4. The absorption is dramatically blue-shifted from that of bulk cadmium telluride. This spectrum is indicative of isolated, rather than electronically communicating, units. The ^{125}Te spectra are also consistent with this hypothesis as the resonances are shifted upfield by 500 ppm relative to bulk CdTe. This effect has been observed for other frameworks containing cadmium chalcogenides including the beryllosilicates[14] and borates.[15]

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