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Energetics of Formation and Oxidation of Microporous Calcium Aluminates: A New Class of Electrides and Ionic Conductors

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Microporous calcium aluminates with a common formula $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$, $(0 < \delta \leq 1)$, represent a new family of electrides with conducting extraframework electrons encaged within the framework. Their enthalpies of oxidation to eliminate these electrons and obtain a stoichiometric $Ca_{12}Al_{14}O_{33}$ compound, and formation enthalpies relative to the most stable annealed calcium aluminate $Ca_{12}Al_{14}O_{33.46}$ (which contains excess oxygen probably as O^- and O_2^- species), are studied by transposed temperature drop calorimetry and drop solution calorimetry in molten lead borate at 1080 K. The standard enthalpy of oxidation per O_2 consumed is -579.4 ± 9.4 kJ/mol (or -144.8 ± 9.4 kJ per encaged electron). The enthalpies obtained for samples with variable amounts of electrons (and less than 33 oxygens per formula unit) are compared to that for oxidation of a stoichiometric $Ca_{12}Al_{14}O_{33}$ sample to an oxygen-rich composition. The study supports the idea that the oxidation of the stoichiometric $Ca_{12}Al_{14}O_{33}$ sample results in formation of extraframework ions (O_2^- and O^-) with a standard enthalpy at 298 K of -161.9 ± 11.2 kJ per mol of O_2, which is in good agreement with previous data by Hayashi et al. (*J. Phys. Chem. B* **2004**, *108* (26), 8920) obtained for the same reaction at 898 K by electron paramagnetic resonance. The energetics of oxidation of electron-rich samples are discussed in terms of an electride model and "ionic" bonding of an encaged electron in the framework.

I. Introduction

Knowledge of thermodynamic properties of ionic conductors at high temperature is essential in construction of chemically and physically stable solid electrolytes for fuel cell applications.[1] The microporous calcium aluminate $12CaO{\cdot}7Al_2O_3$ (C12A7, with average pore size of ∼0.4 nm) constitutes a new class of ionic conductors that possess extraframework "free oxygens" as charge carriers.[2−4] In contrast to aluminosilicate zeolites,[5] where cationic species compensate for *negative* charge caused by the substitution of framework Si^{4+} by Al^{3+}, the extraframework *anions* (two oxide ions, O^{2-}, in the stoichiometric composition) randomly occupy 12 cages of the C12A7 unit cell to balance the +4 charge of the framework $[Ca_{24}Al_{28}O_{64}]^{4+}$ (Figure 1). Because the average distance between Ca^{2+} in the framework and the O^{2-} ion inside the pore is ∼50% longer than the Ca−O bond in CaO crystal, the extraframework O^{2-} oxygens are loosely bound and hence called "free oxide ions"[3].

Figure 1. Three crystallographic cages of $12CaO{\cdot}7Al_2O_3$ and encaged anion.

Several kinds of extrinsic anions, including halide (F^-, Cl^-), hydroxide (OH^-),[6] hydride (H^-),[7] superoxide (O_2^-), and oxygen anion (O^-),[4] selectively substitute for the free oxide ions by appropriate heat treatments. For example, annealing in a dry oxygen atmosphere results in the formation of oxygen anions (O_2^- and O^-) in cages[8,9] (Table 1, reaction 1). Their incorporation causes oxygen excess over the stoichiometric composition, $Ca_{12}Al_{14}O_{33+\epsilon}$.

When the extraframework O_2^- ions are fully replaced by electrons, the C12A7 becomes an "electride" with excess electrons confined within the cages.[10,11] This can be achieved

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Table 1. Enthalpies Δ*H* of Reactions Involving Various Oxygen Species

	reaction	Δ*H*, kJ/mol	reference
1	O^{2-}(cage) + $O_2 \rightarrow O_2^-$ (cage)+ O^- (cage)	−131	8
2	$O_2 + e^- \rightarrow O_2^-$	−42.5	28, 29
3	$O + e^- \rightarrow O^-$	−141	29−31
4	$O^- + e^- \rightarrow O^{2-}$	844	31
5	$O^{2-} + O_2 \rightarrow O_2^- + O^-$	−886.5	calculated from 2 and 4
6	$O^2 \rightarrow 2O$	504.5	32
7	$2e^- + 1.5O_2 \rightarrow O_2^- + O^-$	68.8	calculated from 2, 3, and 6

by reaction of parent C12A7 with Ca metal at high temperature, resulting in oxygen-deficient compositions, $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ (δ is 1/2[e^-]), up to ~2×10^{21} cm^{-3} concentration of electrons, which corresponds to $[Ca_{12}Al_{14}O_{32}]$ ($\delta = 1$) or $[e^-] = 2$. The small diameter (0.1 nm) of the connecting channels between framework cages makes the electrons inaccessible and the electride stable under ambient conditions.

Conventional electrides are composed of alkali ions trapped within cages formed from one or two organic complexants such as crown ethers or cryptands.[12] Unfortunately, these organic electrides degrade rapidly upon exposure to air at room temperature, hampering their research and application.

The recent discovery[10] of the inorganic C12A7-based electride opens new avenues for development of thermally stable electrides and for studying the properties of electrons which behave as anions confined in three-dimensional micropore arrays. Indeed, extraframework electrons in C12A7 are not pinned to specific atoms or molecules but rather localized in anion sites that would otherwise be empty.[13,14] In contrast to organic electrides, C12A7 has excellent thermal stability even in air at room temperature and also exhibits high *electronic* conductivity[2] exceeding 100 S cm^{-1}. In addition, the C12A7 electride efficiently emits electrons in a vacuum by field emission at room temperature and thermoionic emission up to 513 K, making C12A7 useful as electron emitters.[15]

In this context, tackling the problem of energetics of substitution of excess electrons is very appealing from both fundamental and practical viewpoints. Thermochemical study of $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ samples should give deeper insight into energetics of electron-framework binding and, therefore, provide guidance in future theoretical studies of electride-type framework structures and in the search for new electrides.

In this study we employ drop solution and transposed temperature drop calorimetry at 1080 K to elucidate the formation and oxidation energetics of the C12A7 family of materials at 298 K. The formation enthalpies are compared to that of the annealed C12A7, which is most stable in an oxidizing atmosphere and has extra oxygen over the stoichiometric composition. For the first time, the enthalpies of the electron substitution for oxygen in microporous C12A7 of different electron concentration are measured, allowing comparison of energetics along the $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ series. In addition, thermogravimetric analysis, powder X-ray diffraction, and electron paramagnetic resonance are used to characterize the samples.

For further discussion the following notation for the samples studied is taken: $[Ca_{12}Al_{14}O_{32}]^{2+}(2e^-)$ = C12A7:2e⁻, $[Ca_{12}Al_{14}O_{32}]^{2+}(e^-)(0.5O^{2-})$ = C12A7:e⁻, $[Ca_{12}Al_{14}O_{32}]^{2+}(0.1e^-)(0.95O^{2-})$ = C12A7:0.1e⁻, and $[Ca_{12}Al_{14}O_{32}]^{2+}(0.01e^-)(0.995O^{2-})$ = C12A7:0.01e⁻; two stoichiometric samples $Ca_{12}Al_{14}O_{33}$ = C12A7:O^{2-}_1 and C12A7:O^{2-}_2, and $Ca_{12}Al_{14}O_{33.46}$ = C12A7:O^{2-}_a1 (C12A7:O^{2-}_1 annealed at 1173 K) and $Ca_{12}Al_{14}O_{33.44}$ = C12A7:O^{2-}_a2 (C12A7:O^{2-}_2 annealed at 1173 K). We use the chemical formulas above in the thermodynamic cycles. These represent standard nomenclature for the ceramic community. They correspond to (on a molar basis) half the content of a mole of unit cells and, therefore, half the structural formula unit recommended by IUPAC.[16]

II. Experimental Methods

Sample Synthesis. C12A7:O^{2-} single crystals (stoichiometric composition) grown by a floating zone method[17] were sliced into plates ~1 mm thick. To obtain electron-rich samples C12A7:2e⁻, C12A7:e⁻, C12A7:0.1e⁻, and C12A7:0.01e⁻, they were sealed in silica glass tubes under vacuum (~1 Pa) together with metallic calcium shot and annealed at 973 K for 12, 16, or 240 h. This treatment induces reaction of the extraframework oxygen ions, which are rather mobile at high temperatures, with Ca metal deposited at the sample surface. After annealing, the surfaces of samples were ground to remove the resulting CaO layers. Electron density of electron-rich samples was deduced from electrical conductivity measurements using the previously established relationships between electrical conductivity and electron concentration in single crystals.[10] For calorimetric experiments and further sample characterization the synthesis products were ground to micrometer-sized powder.

Powder XRD. Powder XRD experiments were carried out on an Inel X-ray diffractometer (XRG 3000) operated at 30 kV and 30 mA using Cu Kα radiation with a Ni filter. Data were collected in the 2θ range of 10°−120°.

Thermal Analysis. To measure water or other volatile content of as-received C12A7:2e⁻, C12A7:e⁻, C12A7:0.1e⁻, C12A7:0.01e⁻, and C12A7:O^{2-} samples, and also to examine their

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structural evolution and oxidation at elevated temperatures, thermogravimetry (TG) and differential scanning calorimetry (DSC) were conducted using a Netzsch simultaneous thermal analyzer, (STA 449), 30 mg pellets of powder were packed in a standard Pt crucible with a lid inside an Ar-filled glovebox. The loaded crucible was then placed in the DSC and heated to 1173 K at 10 K/min in an oxygen atmosphere. Baseline correction was done using an earlier scan of the empty Pt crucible under the same conditions. Buoyancy corrections were performed for all runs by allowing the sample to cool to room temperature and heating it back to 1173 K. DSC/TG runs consisting of heating and isothermal at 1080 K regimes were also done to mimic drop-solution and transposed temperature drop calorimetry experiments. Temperature had been calibrated against the melting point of several metal standards (In, Bi, Zn, Al, and Au), and sensitivity calibration had been done using the heat capacity of sapphire. Gases evolved during thermal analysis were analyzed by a Bruker EQUINOX 55 FTIR spectrometer, which is directly coupled with the TG/DSC by a heated transfer line kept at 423 K. FTIR spectra of evolved gases were collected from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. In addition, to identify and characterize the oxidized phase recovered from the TG/DSC scan, powder XRD was performed with a Scintag AD-V diffractometer using Cu Kα radiation.

High-Temperature Drop-Solution Calorimetry and Transposed Temperature Drop Calorimetry. Drop-solution calorimetry (DS) was performed using a Tian-Calvet microcalorimeter operating at 1080 K with molten lead borate ($2PbO \times B_2O_3$) as the solvent. The instrument and experimental procedure have been described in detail elsewhere.[18] The enthalpy measured includes the heat associated with heating the sample from room temperature to 1080 K (heat content) plus enthalpy of solution of the sample. To facilitate dissolution of the sample pellet and assist full oxidation, oxygen gas was bubbled through the solvent at 5 mL/min. In addition, gaseous oxygen was flowed through the calorimeter above the solvent at 80 mL/min. Transposed temperature drop (TTD) calorimetry was performed by dropping 5 mg pellets of samples into an empty Pt crucible using the same calorimeter and operating conditions. The calibration factors for the calorimeter (J/ mV) were obtained by dropping 5 and 15 mg pellets of alumina (Aldrich, 99.99%) stabilized in the corundum phase by heating overnight at 1773 K. The overall methodology is now standard and has been reported previously.[19]

III. Results and Discussion

In excellent agreement with previous studies by Hayashi et al.,[8] the stoichiometric C12A7:O^{2-} sample absorbs excess oxygen above 673 K as evidenced by DSC/TG analysis in oxygen (Figure 2).

Excess anions can go into an ionic crystal of the stoichiometric compound, resulting either in an equivalent number of cations being oxidized or the creation of vacancies to balance the charge. Examples include oxygen excess UO_{2+x} and metal deficit manganous $Mn_{1-x}O$ and ferrous oxides $Fe_{1-x}O$.[20] Unlike these examples, where the oxidation over the stoichiometric oxygen content leads to valence change of a metal, the extraframework oxygens in the present system are oxidized to O^- and O_2^-, as demonstrated by electron paramagnetic resonance[1] (Table 1), whereas the valence of the framework metal (calcium and aluminum) is unaffected. Note that 12 cages of the unit cell (6 per formula) are available to accommodate monovalant oxygen, although only four ions (two per formula) are needed to compensate the +4 framework charge.

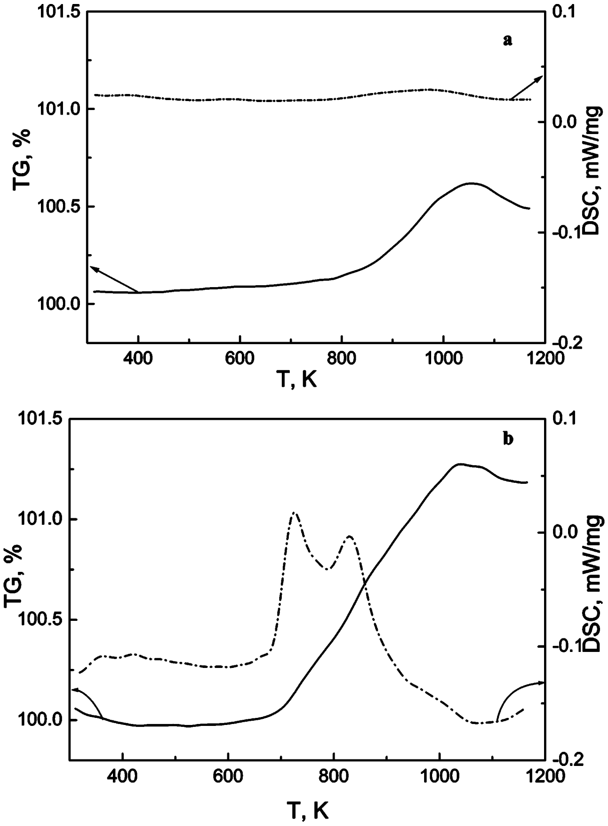

Figure 2. DSC/TG profiles of stoichiometric $[Ca_{12}Al_{14}O_{32}]^{2+}(O^{2-})$ (a) and electron-rich $[Ca_{12}Al_{14}O_{32}]^{2+}(2e^-)$ (b).

Indeed, the stoichiometric C12A7:O^{2-}_1 (Figure 2a) and C12A7:O^{2-}_2 samples show weight gains of 0.53% and 0.50% respectively (Table 2) which can be attributed to oxidation and formation of O^- and O_2^- anions at 1173 K.

On further heating, due to dynamic balance between ions inside the cages and oxygen gas at elevated temperature, the weight decreases and reaches a plateau in the temperature range 1123−1323 K. In the next cooling cycle a small weight gain of 0.05% is observed. In the second heating cycle a negligible weight gain of 0.01% is seen at 673−1073 K and the same negligible weight decrease at 1123−1173 K. Therefore, we will use the sample annealed at 1173 K as a reference, whose composition is fixed at the experimental temperature for DS and TTD calorimetry. Based on TG results, we assign the $Ca_{12}Al_{14}O_{33.46}$ stoichiometry for this annealed sample after DSC. The direct evidence of considerable oxidation (oxygen content above 33) for the initially stoichiometric C12A7:O^{2-} is an important finding of this report.

Figure 2b shows the DSC/TG curves for the C12A7:2e^- sample compared to C12A7:O^{2-} at 313−1173 K. On heating, the samples show broad exothermic peaks at 673−1073 K, corresponding to the weight gain observed in TG. The TG signals attain maxima at ~1000 K, suggesting that both

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Table 2. Measured Enthalpies and Calculated Heats of Reactions

sample	ΔH_{TTD} kJ/mol	no. of data points	ΔH_{ox} kJ/mol	$\Delta H_{f.ox}$ kJ/mol	ΔH_{ox}[b] per O_2/electron, kJ/mol	$\Delta H_{f.el}$ kJ/mol	weight gain %	$\epsilon/2$[c]
C12A7:O^{2-}_a1	1078.3 ± 8.2	10	0 ± 8.2	−79.4 ± 4.4	0 ± 8.2	−19268.0 ± 4.4	0	0
	842.9 ± 3.7[a]	9						
C12A7:O^{2-}_1	1039.0 ± 3.3	10	−33.4 ± 8.8	−46.0 ± 9.9	−145.2 ± 8.8	−19222.0 ± 9.9	0.53	0.23
C12A7:O^{2-}_2	1033.4 ± 1.8	8	−39.3 ± 8.4	−40.0 ± 9.5	−178.6 ± 8.4	−19228.0 ± 9.5	0.50	0.22
C12A7:O^{2-}_a2	1077.1 ± 8.1	7	−4.4 ± 11.5	−83.8 ± 12.3	−4.4 ± 11.5	−19184.2 ± 12.3	0	0
annealed at 1073 K	1096.5 ± 6.3	9	23.8 ± 10.3	−103.3 ± 11.2	−[d]	−19164.8 ± 11.2	−[d]	−
annealed at 973 K	1086.0 ± 8.5	8	13.3 ± 11.8	−92.7 ± 12.6	−	−19175.3 ± 12.6	−	−
C12A7:0.01e^-	1014.6 ± 1.9	9	−57.3 ± 8.4	−22.1 ± 9.5	−	−19245.9 ± 9.5	0.58	0.25
C12A7:0.1e^-	998.8 ± 1.0	8	−73.1 ± 8.3	−6.4 ± 9.4	−	−19261.6 ± 9.4	0.59	0.25
C12A7:e^-	869.2 ± 4.1	8	−199.2 ± 9.2	119.5 ± 10.2	−498.0/−124.5 ± 9.2	−19387.5 ± 10.2	0.92	0.40
C12A7:2e^-_1	712.0 ± 3.0	8	−351.5 ± 8.7	272.0 ± 9.8	−595.8/−148.9 ± 8.7	−19540.0 ± 9.8	1.35	0.59
C12A7:2e^-_2	701.8 ± 6.9	10	−360.3 ± 10.7	280.9 ± 11.6	−562.9/−140.7 ± 10.7	−19548.9 ± 11.3	1.47	0.64

[a] ΔH_{ds}, heat of drop solution in molten lead borate at 1080 K. [b] ΔH_{ox}, enthalpy of oxidation normalized to O_2 consumed or one electron. [c] $\epsilon/2$, total amount of O_2 consumed. [d] −, not measured/calculated.

Table 3. Thermochemical Cycles

Enthalpies of Oxidation due to Substitution of Electrons by Oxygen Ion at 298 K for $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$, Using TTD Data	
$[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ (s.298) + $0.5\epsilon O_2$ (g.1080 K) → $Ca_{12}Al_{14}O_{33-\delta+\epsilon}$(s.1080 K)	ΔH_1
$Ca_{12}Al_{14}O_{33-\delta+\epsilon}$ (s.1080 K) → $Ca_{12}Al_{14}O_{33-\delta+\epsilon}$ (s.298 K)	ΔH_2
$0.5\epsilon O_2$ (g. 298) → $0.5\epsilon O_2$ (g.1080 K)	$0.5\epsilon \cdot \Delta H_3$
$[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ (s.298) + $0.5\epsilon O_2$ (g.298 K) → $Ca_{12}Al_{14}O_{33-\delta+\epsilon}$ (s.298 K)	ΔH_{ox}
$\Delta H_1 + \Delta H_2 + 0.5\epsilon \cdot \Delta H_3 = \Delta H_{ox}$	
Standard Enthalpies of Formation of $Ca_{12}Al_{14}O_{33.46}$ from the Oxides at 298 K, Using DS Data	
12CaO (s.298 K) → 12CaO (soln.1080 K)	ΔH_4
$7Al_2O_3$ (s.298 K) → $7Al_2O_3$ (soln.1080 K)	ΔH_5
$0.23O_2$ (g.298 K) → $0.23O_2$ (g.1080 K)	$0.23 \cdot \Delta H_3$
12CaO (soln.1080 K) + $7Al_2O_3$ (soln.1080 K) + $0.23O_2$(g.1080 K) → $Ca_{12}Al_{14}O_{33.46}$ (s.298 K)	ΔH_{ds}
12CaO (s.298 K) +$7Al_2O_3$ (s.298 K) +$0.23O_2$ (g.298 K) → $Ca_{12}Al_{14}O_{33.46}$ (s.298 K)	$\Delta H_{f.ox}$
$\Delta H_4 + \Delta H_5 + 0.23 \cdot \Delta H_3 + \Delta H_{ds} = \Delta H_{f.ox}$	
Standard Enthalpies of Formation of $Ca_{12}Al_{14}O_{33.46}$ from the Elements at 298 K, Using DS Data	
12Ca (s.298 K) → $6O_2$ (g.298 K) → 12CaO (s.298 K)	ΔH_7
14Al (s.298 K) + $10.5O_2$ (g.298 K) → $7Al_2O_3$ (s.298 K)	ΔH_8
$0.23O_2$ (g.298 K) → $0.23O_2$ (g.1080 K)	$0.23 \cdot \Delta H_3$
12CaO (s.298 K) + $7Al_2O_3$ (s.298 K) + $0.23O_2$ (g.298 K) → $Ca_{12}Al_{14}O_{33.46}$ (s.298 K)	$\Delta H_{f.ox}$
12Ca (s.298) + $16.73O_2$ (g.298) + 14Al (s.298) → $Ca_{12}Al_{14}O_{33.46}$ (s.298)	$\Delta H_{f.el}$
$\Delta H_7 + \Delta H_8 + 0.23 \cdot \Delta H_3 + \Delta H_{f.ox} = \Delta H_{f.el}$	
Standard Enthalpies of Formation of $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ from the Oxides at 298 K, Using TTD Data	
$Ca_{12}Al_{14}O_{33-\delta+\epsilon}$ (s.298 K) → $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ (s.298) + $0.5\epsilon O_2$ (g.298 K)	ΔH_8
12CaO (s.298 K) + $7Al_2O_3$ (s.298 K) + $0.23O_2$ (g.298 K) → $Ca_{12}Al_{14}O_{33.46}$ (s.298 K)	ΔH_9
12CaO (s.298 K) + $7Al_2O_3$ (s.298 K) + $(0.23-0.5\epsilon)O_2$ (g. 298 K) → $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ (s.298 K)	$\Delta H_{f.ox}$
$\Delta H_9 - \Delta H_8 = \Delta H_{f.ox}$	

C12A7:$2e^-$ and C12A7:O^{2-} oxidize in this temperature range.

In contrast to conventional DSC, transposed temperature drop (TTD) calorimetry (no solvent present) provides instant heating of the sample from room temperature to the calorimeter temperature in flowing gas and, therefore, allows one to extract the heat of reaction eliminating complications of the preheating history. The enthalpy measured by TTD calorimetry (ΔH_{TTD}) includes the heat content plus heat of oxidation. ΔH_{TTD} data for all samples studied and C12A7:O^{2-} annealed at 973, 1073, and 1173 K are given in Table 2. ΔH_{TTD} of the C12A7:O^{2-}_a1 sample 1078.3 ± 8.2 kJ/mol is in very good agreement with the literature value[21] 1078.5 ± 13.0 kJ/mol for the heat content of conventional $12CaO \cdot 7Al_2O_3$, therefore providing further support for the use of annealed sample ($Ca_{12}Al_{14}O_{33.46}$) as a reference. However, variations in enthalpy for stoichiometric C12A7 samples annealed at different temperatures are insignificant compared to experimental errors, precluding further analysis.

Utilizing TTD data (Table 2) and a thermodynamic cycle (Table 3), we calculate the enthalpies of oxidation at 298 K (Table 2). The average enthalpies needed to oxidize an electron are −148.9 ± 8.7 kJ/mol for C12A7:$2e^-$_1 and −140.7 ± 10.7 kJ/mol for C12A7:$2e^-$_2 sample. The errors represent only 0.1−0.8% of the large measured heat effects. The two values are the same within the experimental error and we use an average of all data, −144.8 ± 9.4 kJ/mol, in further discussion.

The enthalpies of oxidation are plotted in Figure 3 with respect to the oxygen loss (derived from the weight gain), which is a measure of the composition change. The data can be formally divided into two groups: oxygen-deficient and oxygen-excess samples.

The data points for oxygen-deficient samples lie on a straight (solid) line, suggesting a common mechanism of oxidation along the $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ series. The slope of this line is −583.2 ± 20.0 kJ/mol, giving an enthalpy of oxidation per mole of O_2 incorporated (or per 4 electrons removed).

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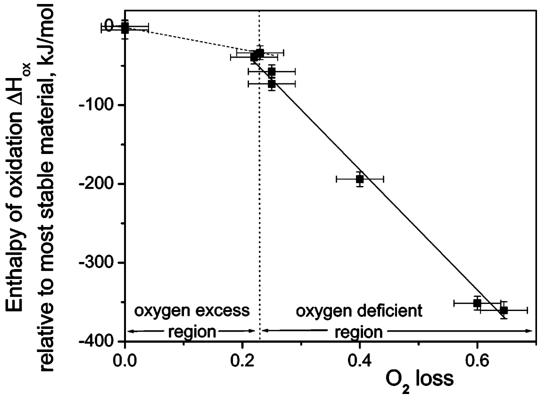

Figure 3. Enthalpies of oxidation of oxygen-deficient $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$, ($0 < \delta \leq 1$), stoichiometric $[Ca_{12}Al_{14}O_{32}]^{2+}(O^{2-})$, and excess oxygen $Ca_{12}Al_{14}O_{33+\epsilon}$ samples vs oxygen loss. The solid line is a linear fit with the slope of −583.2 ± 20.0 kJ/mol for oxygen-deficient samples. The dashed line is a linear fit with the slope of −141.5 ± 5.0 kJ/mol for oxygen-excess samples.

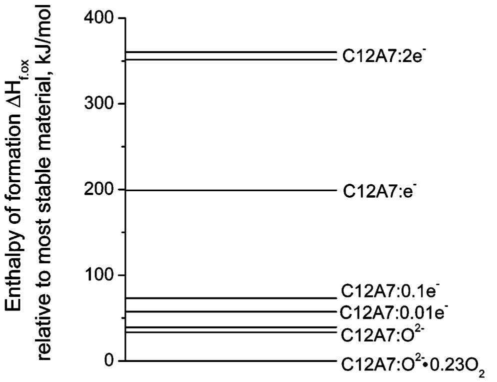

Figure 4. Enthalpies of formation $\Delta H_{f.ox}$ relative to most stable $Ca_{12}Al_{14}O_{33.46}$ annealed at 1173 K. Sample codes are indicated on the plot.

The line drawn for stoichiometric and annealed (oxygen excess) samples reflects another regime of less exothermic oxidation as indicated by a smaller enthalpy for the slope −141.5 ± 5.0 kJ per mol of O_2.

Recently, Hayashi et al.[8] estimated the enthalpy of oxidation of extraframework O^{2-} to form oxygen ions O_2^- and O^- at 898 K to be −131 ± 10 kJ/mol (reaction 1 in Table 1), on the basis of electronic paramagnetic resonance measurements. This enthalpy compares well with the oxidation enthalpy of −145.2 ± 8.8 kJ/mol at 298 K normalized to 1 mol of O_2 from data for the stoichiometric sample. The calculated value from the slope in Figure 3 (regime with excess oxygen) is −141.5 ± 5.0 kJ per mol of O_2. This again indicates that the oxygen anion-incorporated state is more stable than the stoichiometric state, and the free O^{2-} ion is easily oxidized by molecular oxygen. These results require further analysis (see discussion below).

Figure 4 represents the energetic stability of all the samples studied with respect to the most stable C12A7:O^{2-}_a1 (i.e., C12A7:O^{2-}_1 annealed at 1173 K). The enthalpy of formation ($\Delta H_{f.ox}$) from oxides for the annealed sample is −79.4 ± 4.4 kJ/mol (Table 2), which is 33.4 ± 10.8 kJ/mol more exothermic than the enthalpy of stoichiometric C12A7:O^{2-} (−46.0 ± 9.9 kJ/mol). The less favorable enthalpy for C12A7:O^{2-}_1 is consistent with the observed weight gain due to oxidation above 800 K. Electron-rich C12A7:2e^-_1 is less stable by −351.4 ± 10.7 kJ/mol than C12A7:O^{2-}_a1.

Table 4. Enthalpies of Drop Solution in Lead Borate at 1080 K and Enthalpies of Formation from the Elements at 298 K of the Oxides Used in Formation Enthalpy Calculations

oxide	ΔH_{ds} kJ/mol	$\Delta H_{f.el}$ kJ/mol
CaO	−7.1 ± 2.3[a]	−635.1[b]
Al_2O_3	120.4 ± 0.5[c]	−1675.7[b]
O_2	25.5[b,d]	0

[a] Reference 23. [b] Reference 24. [c] Reference 22. [d] ΔH_{ds} of O_2 is the heat content of O_2 gas.

To study the stability relations between the sample with electrons and totally oxidized samples, drop-solution calorimetry in molten lead borate at 1080 K was also attempted on C12A7:O^{2-}_a1 and C12A7:2e^- (only ΔH_{ds} for the annealed sample is shown in Table 2). With use of DS data, the enthalpies of solution[22,23] and the enthalpies of formation from the elements[24] for Al_2O_3 and CaO (Table 4), and the corresponding thermochemical cycles (Table 3), we calculated the standard molar enthalpies of formation for all the samples from constituent oxides ($\Delta H_{f.ox}$) and from the elements ($\Delta H_{f.el}$) at 298 K (Table 2). The enthalpy of oxidation (ΔH_{ox}) at 298 K is also computed. We found a systematic difference of about 35 kJ/mol between enthalpies of oxidation obtained by DS experiments and TTD for all electron-rich samples. We suspect that a parasitic reaction with lead oxide may take place in the molten lead borate (we observed black discoloration on the Pt calorimetry crucible after the experiment, which could be an indication of Pb precipitation) due to high electron activity and fast oxidation. Therefore, the DS results for electron-containing samples cannot be used to calculate heat of formation. However, the enthalpy of formation −79.4 ± 1.6 kJ/mol (normalized to stoichiometry) of $12CaO{\cdot}7Al_2O_3$ obtained by an earlier acid solution calorimetry study elsewhere[25] is the same as our data for the most stable annealed sample C12A7:O^{2-}_a1, −79.4 ± 4.4 kJ/mol. The amount of excess oxygen in the earlier sample is unknown.

Since TTD calorimetry provides the heat of oxidation of the electron-rich samples to the fully oxidized form and these data are more reliable than the DS data for electron-rich samples, a combination of the enthalpy of formation ($\Delta H_{f.ox}$ and $\Delta H_{f.el}$) for fully oxidized sample (C12A7:O^{2-}_a1) by DS and the enthalpy of oxidation of electrons for oxide ions (ΔH_{ox}) by TTD, summarized in Table 2, is used to obtain the standard enthalpies of formation from the oxides and the elements for all electron-containing samples using thermochemical cycles in Table 3.

The calculated enthalpy of oxidation of oxide ion in the gas phase (reaction 5 in Table 1), analogous to the process in C12A7, has a large negative value −886.5 kJ/ mol at 0 K. The free oxide ion is very unstable in the gas phase. This stresses the essential role of the framework in stabilization. This can be easily understood if one remembers that the second electron affinity of oxygen is positive (reaction 4 in Table 1). That implies that oxide ion is an unstable species

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relative to the O^- anion and one has to supply energy to attach another electron to O^- and make the O^{2-} ion. The O^{2-} ion needs positive ions around it to attain a stable state, as in calcium oxide, which is a stable salt because the Ca^{2+} and O^{2-} stabilize each other. In the C12A7 the extraframework O^{2-} is loosely bound due to the ~50% longer Ca−O distance than in CaO crystal. This makes the stabilization effect of the framework weaker compared to that in CaO crystal, and the O^{2-} ions tend to oxidize forming oxygen anions O_2^- and O^-. Consequently, the free O^{2-} ion is in an intermediate state between the unstable O^{2-} ion in the gas phase and the stable one in an ordinary metal oxide lattice.

The reaction of oxidation of two electrons to oxygen anions, analogous to oxidation of C12A7:2e$^-$ (reaction 7 in Table 1), has a positive enthalpy 68.8 kJ/mol in the gaseous state, calculated from enthalpies of electron attachment ("affinities") to molecular and atomic oxygen. On the other hand, the enthalpy of oxidation for C12A7:2e$^-$ is negative (-144.8 ± 9.4 kJ per electron), indicating that formation of extraframework O_2^- and O^- is energetically favorable. This further implies that behavior of encaged electrons is different from that of free electrons due to confinement within the framework.

Recent theoretical studies[13,14,26] show contradictory results regarding the bond character of the excess electrons. The pioneering theoretical work by Sushko et al.[14] supports the electride model, characterized by electrons localized within cages. Later work by Medvedeva and Freeman[26] favors highly delocalized electrons similar to that of the shared electron cloud in metals. Recent topological analysis by Li et al.,[13,14,26,27] based on use of electron-delocalization basis functions, has provided support for the electride model with ionic type bonding between electrons and the framework.

As far as oxidation is concerned, the electrons are usually not regarded as ions because they act as a part of atoms and molecules. Here extraframework electrons are not attached to specific atoms but rather occupy anionic sites within the cages. In this context, it is interesting to compare the energetics of oxidation normalized to one ion/electron in the cage (Table 2). Surprisingly, the enthalpy of oxidation for the stoichiometric sample -145.2 ± 8.8 kJ per mol of oxygen is comparable to the oxidation enthalpy (-144.8 ± 9.4 kJ/mol) of the C12A7:2e$^-$ normalized to one electron. Calorimetry cannot provide direct evidence to favor one model of electronic structure over another. Nevertheless, it is remarkable that these enthalpies are similar.

The C12A7 framework has a unique structure that is able to stabilize both oxygen ions and electrons in cages at room temperature and, at the same time, provide the environment for ion and electron conductivity. The latter is strongly related to framework-ion vacancy geometry and ion-framework bonding, which is reflected in oxidation energetics in the oxidizing atmosphere. One can speculate that if C12A7cages were smaller, the monovalent anions such as O_2^- and O^- could no longer be stabilized. Larger cages would result in a shallower energetic landscape of encaged anions and a weaker stabilization effect of confined geometry. It is also suggestive to note that the inner diameter of the cage in C12A7 is close to that of the cavity space in which an electron is trapped in a conventional organic electride composed of cyclic ether molecules such as crown-ether.[12]

IV. Conclusions

Drop-solution and transposed temperature drop calorimetry allow us to compare energetics along the $[Ca_{12}Al_{14}O_{33-\delta}]^{2\delta+}(2\delta e^-)$ series ($0 \leq \delta \leq 1$) and, for the first time, to calculate the standard enthalpy of oxidation of two electrons by an oxide ion in the electride ($\delta = 1$).

The thermochemical data presented not only provide deeper insight into energetics of electron-framework interactions but also set up the stage for future theoretical studies of electride-type structures and search for new electrides. From a thermodynamic standpoint, the promising electride oxide has a microporous structure capable of confining electrons, characterized by small interconnecting channels, inaccessible to other ions under ambient conditions. These electrons, loosely bound to the framework, behave like extraframework anions. This can be achieved through the formation of an anionic site within an energy landscape which can be tuned by the framework-anion site bond distance. Future research should focus on tuning the size of the cage, to see what distance is optimal, and investigating the effect of other cations compatible with the reducing conditions needed to generate electrides.

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