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# Calorimetric studies on the thermodynamic properties of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials

by

#### PINGHUI ZHANG DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

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### Abstract

Manganese oxides are abundant in the environment and are essential to various technologies. The four most common binary manganese oxides are  $MnO_2$  (pyrolusite),  $Mn_2O_3$  (bixbyite),  $Mn_3O_4$  (hausmannite) and MnO (manganosite). In 1965, Oswald *et al.* reported a new binary manganese oxide with the nominal stoichiometry  $Mn_5O_8$  or  $Mn(II)_2Mn(IV)_3O_8$ .  $Mn_5O_8$  exhibits a unique monoclinic layered crystal structure. Subsequent studies revealed that the divalent manganese ions in  $Mn_5O_8$  can be replaced by other divalent metal cations, including  $Ca^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  ions, which results in ternary oxides that bear the same crystal structure.

In this dissertation, samples of Mn<sub>5</sub>O<sub>8</sub>, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and a 50-50 solid solution of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> have been synthesized to study their thermodynamic properties. Their structures have been confirmed by X-ray diffraction and compositions by iodometric titration and/or electron microprobe analyses. High temperature oxide melt solution calorimetry has been carried out on all samples. Their formation enthalpies from binary oxide end members have been calculated from measured and literature data. The results are discussed in terms of stability, structure, bonding, and significance.

 $Mn_5O_8$  exhibits a slightly endothermic (< 6 kJ/mol) enthalpy of formation from an isochemical mixture of bixbyite and pyrolusite, suggesting that it is energetically metastable. Given that a solid-state reaction involving no gas species usually has very small change in entropy due to the small differences in heat capacities, the free energy of formation of  $Mn_5O_8$  from an isochemical mixture of bixbyite and pyrolusite is likely to

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be slightly endothermic or close to zero. Therefore, Mn<sub>5</sub>O<sub>8</sub> is probably a metastable phase not found on the equilibrium Mn - O phase diagram.

The energetic stabilities of the ternary M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> samples depend on the M<sup>2+</sup> cation (M = Ca, Cd, Cu) in the structure. The enthalpies of formation of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> from MO and MnO<sub>2</sub> are -133.25 ± 4.87 kJ/mol, -50.86 ± 3.52 kJ/mol and +35.42 ± 3.70 kJ/mol for M = Ca, Cd and Cu respectively, suggesting energetic stability decreases in the order Ca, Cd, Mn, and Cu. The same trend is observed in their thermal decomposition behavior, where Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is the most refractory and does not decompose until over 900 °C while Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> decomposes well below 500 °C. The 50-50 solid solution of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> or CaCdMn<sub>3</sub>O<sub>8</sub> has an enthalpy of formation from CaO, CdO and MnO<sub>2</sub> of -117.6 ± 4.75 kJ/mol. It is noticeably energetically more stable than a 1:1 mechanical mixture of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, whose enthalpy of formation from CaO, CdO and MnO<sub>2</sub> cdO and MnO<sub>2</sub> would be -96.09 ± 3.01 kJ/mol. The enthalpy of mixing for this solid solution is hence -22.14 ± 3.78 kJ/mol, indicating energetically favorable mixing, possibly related to some sort of short range ordering of cations.

The results of this dissertation work can aid in future computational and experimental studies on M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials. The quantitative study of thermodynamic properties can aid in assessing their stabilities in the environment which will be of interest to heavy/toxic metal immobilization. Also, the choice of materials for applications in areas such as electrochemical energy conversion and storage can directly benefit from these well documented thermodynamic data.

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## **Chapter 1** Introduction

#### 1.1 Background

Despite the efforts in recent years to extend the production and coverage of renewable energy sources, fossil fuels (mainly oil, coal and natural gas) still account for over 84 % of world's major energy consumption [1]. Renewable energy sources, although more promising in sustainability in the long term, are confronted by challenges in energy conversion and storage [2-5]. On the contrary, fossil fuels have physical forms that grant them convenient transportation and storage.

Pseudo-capacitors are promising candidates among the proposed conversion/storage devices. They are a type of electrochemical energy storage device that relies on oxidation-reduction (redox) reactions to store and utilize energy. Whilst in a conventional capacitor, no chemical reaction occurs between the electrodes and the charge carrying ions. When charged, a conventional capacitor stores energy in the static electric field that permeates the dielectric materials separating the two electrodes. The advantages of pseudo-capacitors include high power output and acceptable specific capacity [6-10]. The performance of a pseudo-capacitor depends strongly on the choice of its electrode material.

Manganese oxides and manganese-containing oxides have been widely studied [11-14] as potential candidate for such applications due to some desirable characteristics. First, manganese is by no means in short supply. Being one of the more abundant elements in the Earth's crust, it is often found in various oxides and other minerals.

Additionally, manganese has multiple oxidation states and readily forms complex oxides with other transition metal elements to facilitate the redox reactions needed to ensure the performance of pseudo-capacitors [13].

Manganese oxides can also act as catalysts for oxygen evolution reactions (OER), which are an essential part of water-splitting, to generate hydrogen and oxygen. Much effort have been made to find an efficient and cost-effective catalyst for OERs, among which, manganese oxide materials, especially layered manganese oxides, are of great interest to researchers for several reasons [15-20]. First, the layered structure provides ample space and potential active sites for the reaction to take place; second, manganese is a non-toxic element, especially compared to cobalt and nickel, which helps relieve environmental concerns if it is accepted into large scale manufacturing and application. Additionally, manganese often is found in mixed valences in these materials, which may aid in facilitating the necessary charge transfer during OER and thus accelerate the process. A few layered manganese oxide materials have been studied for catalyst for OERs, including birnessite and cryptomelane based materials [12, 21-24].

#### **1.2 Motivation and Objective**

The family of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials exhibit some very desirable qualities as mentioned above for applications in electrochemical energy storage/conversion as well as for catalysis of water splitting. In fact, some efforts have already been made in such areas [19, 20, 25, 26].

The synthesis of these materials and their stability in use is governed by their thermodynamic properties. Thus knowledge of such properties is essential from both fundamental and applied viewpoints. Quantitative thermodynamic study can help identify the materials that are energetically favorable and therefore more likely to be stable in long-term applications.

The main objective of this dissertation is to synthesize  $M_2Mn_3O_8$  materials (M = Mn, Ca, Cd, Cu) and study their thermodynamic properties. I wish to answer the fundamental question of whether they are thermodynamically favorable and thus, whether they are suitable candidates for various long-term applications.

The main challenges lie in the synthesis processes. Although M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials have similar crystal structures, their reported synthesis routes are drastically different. Some (M = Ca and Cd) can be synthesized relatively easily through a solid-state process, while others require methods such as hydrothermal synthesis that require days and even weeks. Additionally, efforts will be made to explore the possibility of forming solid solution among M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials with different divalent cations. Given their differences in synthesis routes, it may pose a significant challenge, perhaps kinetic rather than thermodynamic, for them to form a solid solution instead of mixed phases and/or undesirable secondary phases.

#### **1.3** High temperature oxide melt solution calorimetry

The primary method for investigating thermodynamic properties in this work is high temperature oxide melt solution calorimetry. This well-established method [27-29] obtains

the enthalpy of formation of refractory materials by measuring the enthalpy of solution of appropriate reactants and products in a molten oxide solvent.

The calorimetry experiments use custom-build Tian-Calvet type twin calorimeters (Figure 1.1). The calorimeters are held at 700 °C and small (5-10 mg) pellets of samples are dropped into molten solvent from room temperature via the drop tube. Oxygen flushing above the solvent and bubbling through it are maintained during the entire experiment to ensure that the samples dissolve efficiently and that all the manganese will be transformed to Mn<sup>3+</sup>, which is the most stable valence state under these conditions. This method allows one to accurately measure the drop solution enthalpy with only 5-10 mg of sample for each drop, with 5-10 experiments needed to obtain reproducibility and constrain uncertainties. The small size of each drop enables both sample characterization and multiple calorimetric drops for a relatively small amount (100 mg or so) of synthesized sample to obtain reliable data.



**Figure 1.1**: Schematic of the Tian-Calvet type twin calorimeter setup.[29] Measurements were carried out for all the synthesized samples, and, when necessary, the binary end member oxides to obtain their drop solution enthalpy values. Thermochemical cycles were constructed based on Hess's law, which states that regardless of the multiple steps and/or stages of a reaction, its total change of enthalpy is the sum of the changes of enthalpy of all steps/stages involved, allowing us to calculate the enthalpy of formation ( $\Delta H_{f,ox}$ ) of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> from binary end members at room temperature.

In the following chapters, Chapter 2 will discuss the synthesis, characterization, and thermodynamic properties of  $Mn_5O_8$ . Then in Chapter 3, the synthesis, characterization, and energetic stabilities of three  $M_2Mn_3O_8$  (M = Ca, Cd, Cu) materials will be discussed and compared. A preliminary study on the 50-50 solid solution between Ca<sub>2</sub>Mn<sub>3</sub>O8 and

Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> will be presented in Chapter 4. Finally, Chapter 5 will provide a summary to the thesis and some future perspectives.

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# **Chapter 2** Thermodynamic properties of Mn<sub>5</sub>O<sub>8</sub>

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#### 2.1 Abstract

Manganese oxides occur widely in nature and have technical applications in various areas. This study quantitatively evaluates the thermodynamic properties of Mn<sub>5</sub>O<sub>8</sub>, a binary manganese oxide that has a layered structure and contains coexisting divalent and tetravalent manganese. Three samples of the Mn<sub>5</sub>O<sub>8</sub> phase with slightly different manganese average oxidation states were synthesized using a wet chemical method and annealing. Synchrotron X-ray analysis revealed that the samples contain a small amount of a secondary MnO<sub>2</sub> phase that cannot be identified using laboratory X-ray diffraction. High temperature oxide melt solution calorimetry in molten sodium molybdate at 700 °C showed that all three samples are slightly higher in enthalpy than an isochemical mixture of bixbyite (Mn<sub>2</sub>O<sub>3</sub>) and pyrolusite (MnO<sub>2</sub>), probably rendering them metastable in free energy with respect to isochemical mixtures of bixbyite and pyrolusite. However, the energetic metastability (endothermic enthalpy) of Mn<sub>5</sub>O<sub>8</sub> is very small (< 6 kJ/mol) and does not depend significantly on the manganese average oxidation state. Thus, although Mn<sub>5</sub>O<sub>8</sub> probably does not appear on the equilibrium Mn-O phase diagram, its small metastability allows its synthesis by a variety of low temperature reactions.

#### 2.2 Introduction

Manganese oxides are abundant in the environment and are essential to various technologies. The four most common binary manganese oxides are MnO (manganosite) hausmannite (Mn<sub>3</sub>O<sub>4</sub>), bixbyite (Mn<sub>2</sub>O<sub>3</sub>) and pyrolusite (MnO<sub>2</sub>). In 1965, Oswald *et al.* synthesized and determined the crystal structure of a less common binary manganese oxide, Mn<sub>5</sub>O<sub>8</sub> [1].

The manganese – oxygen phase diagram shows four oxide phases: MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub>[2, 3]. An additional phase, Mn<sub>5</sub>O<sub>8</sub>, has been reported and exhibits interesting magnetic and electrochemical properties. It is antiferromagnetic with a magnetic transition temperature  $T_N = 128$  K, much higher than its isostructural counterparts including Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> ( $T_N = 60$  K) and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> ( $T_N = 10$  K) [4]. Mn<sub>5</sub>O<sub>8</sub> may have potential applications in electrochemical energy storage <sup>[5]</sup> and as a catalyst for oxygen evolution reactions [6].

Rask *et al.* investigated a mineral sample of pyrolusite  $MnO_2$  with transmission electron microscopy and detected a small amount of  $Mn_5O_8$  [7]. However, they were not certain whether the  $Mn_5O_8$  was originally present in their mineral sample or was a product of beam damage associated with electron microscopy. Azzoni *et al.* investigated the thermal stability of  $Mn_5O_8$  using Raman spectroscopy <sup>[8]</sup>. They concluded that  $Mn_5O_8$  was not stable at high temperature and would eventually transform to hausmannite,  $Mn_3O_4$ .

Although the above studies provide qualitative information about the occurrence and stability of Mn<sub>5</sub>O<sub>8</sub>, no quantitative thermodynamic study has been reported. A first order question is whether Mn<sub>5</sub>O<sub>8</sub> has a stability field in temperature - pressure - oxygen fugacity space or whether it is always metastable with respect to an isochemical mixture of MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> or Mn<sub>3</sub>O<sub>4</sub>. This is particularly important in considering whether Mn<sub>5</sub>O<sub>8</sub> can exist in geologic, planetary, and/or environmental settings and, in the latter case, if it could sequester toxic metals like copper and cadmium. In this chapter, we report the first quantitative experimental thermodynamic study, using high temperature oxide melt solution calorimetry of Mn<sub>5</sub>O<sub>8</sub> to address this question of stability versus metastability. In

this chapter, metastability refers to free energy (positive  $\Delta G$  relative to another phase assemblage, while energetic metastability refers to enthalpy (positive  $\Delta H$ ).

#### 2.3 Crystal Structure of Mn<sub>5</sub>O<sub>8</sub>

 $Mn_5O_8$  is isostructural with  $Cd_2Mn_3O_8$ , with a space group (S.G.) of C2/m (Figure 2.1). For the ideal composition, the  $Mn^{4+}$  cations are all octahedrally coordinated. The edge sharing [MnO<sub>6</sub>] octahedra form a [Mn<sub>3</sub>O<sub>8</sub>]<sup>4-</sup> layer. One fourth of the octahedral sites in this layer are vacant, and above and below each vacant site there is one  $Mn^{2+}$  cation surrounded by oxygen anions that form a trigonal prism. Therefore, this structure is comprised of [Mn<sub>3</sub>O<sub>8</sub>]<sup>4-</sup> layers, and in between two [Mn<sub>3</sub>O<sub>8</sub>]<sup>4-</sup> layers there is a  $Mn^{2+}$  layer. Although the manganese in  $Mn_5O_8$  has an average oxidation state (AOS) of 3.20 (i.e. between that of trivalent and tetravalent manganese), divalent and tetravalent manganese appear to coexist, with no evidence for trivalent manganese in the structure [5, 9]. This coexistence of  $Mn^{2+}$  and  $Mn^{4+}$  ions is also supported by the bond lengths obtained by theoretical [10] and experimental [5] methods. Even though  $Mn_5O_8$  is a layered manganese oxide, it shows no evidence of hydration or of intercalation of interlayer cations, making it different from the birnessite family of manganese oxide phases.



**Figure 2.1** Schematic representation of the crystal structure of  $Mn_5O_8$ . Purple:  $Mn^{4+}$ , blue:  $Mn^{2+}$ , red:  $O^{2-}$ .

#### 2.4 Experimental Methods

#### 2.4.1 Material synthesis

A previously reported synthesis method <sup>[12]</sup> was followed with modifications in the way the precipitates were treated. About 70 g manganese nitrate hydrate (Mn(NO<sub>3</sub>)<sub>2</sub> ·xH<sub>2</sub>O) was dissolved in 1.5 L Millipore water. Ammonium hydroxide (NH<sub>4</sub>OH) solution (pH ~ 10) was added dropwise until the desired dark brown color was achieved. The solution was boiled and magnetically stirred continuously while precipitates emerged. Then the system was kept under ambient conditions overnight to increase yield. The precipitates were left in the suspended state in a platinum crucible and heated in air through the following cycle to produce Mn<sub>5</sub>O<sub>8</sub>: 105 °C  $\rightarrow$  120 °C, hold for 3h  $\rightarrow$  380 °C, hold for 4h  $\rightarrow$  105 °C  $\rightarrow$  380 °C, hold for 4h  $\rightarrow$  105 °C. The heating/cooling rate was set at 10 °C/min. Also, in order to vary the manganese oxidation state, a portion of the as-synthesized sample was subjected to further annealing at a lower temperature, 250 °C, in air for up to 6 days.

#### 2.4.2 Powder X-ray diffraction

Laboratory X-ray diffraction patterns were collected at room temperature using a Bruker AXS D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) operated at 40 kV and 40 mA with a step size of 0.02 °/s. Synchrotron X-ray diffraction data were collected on the 11-BM beamline at the Advanced Photon Source (APS), Argonne National Laboratory with a wavelength of 0.414177 Å. X-ray pattern indexing and structure refinements were carried out using TOPAS academic version 6. [13] Two different phases are found in the as-prepared sample, with the major phase of Mn<sub>5</sub>O<sub>8</sub> (S.G. *C*2/m) and minor phase of pyrolusite-type MnO<sub>2</sub> (S.G. *P*4<sub>2</sub>/mnm). A phenomenological model of anisotropic peak broadening was implemented during Rietveld refinement of the structure of Mn<sub>5</sub>O<sub>8</sub>. <sup>[14]</sup>

#### 2.4.3 Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC)

In order to study behavior at elevated temperatures and identify possible phase transitions, thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was performed on the samples using a Netzsch STA 449C instrument. The sample was heated to 600 °C at 10 °C/min under a flow of argon at 40 mL/min as a protective gas.

#### 2.4.4 Iodometric titration

The manganese average oxidation states (Mn AOS) of the samples were determined by iodometric titration. This method has been developed and discussed in detail by Birkner elsewhere <sup>[15]</sup>. The following is a summary of the procedure used in this study. First, the sample was dissolved in excess sulfuric acid (2 M) and potassium iodide (KI). During dissolution, all the manganese was reduced by I<sup>-</sup> to Mn<sup>2+</sup> while the I<sup>-</sup> formed I<sup>-</sup><sub>3</sub>. Then the amount of triiodide was titrated by a standardized sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution (0.013 mol/L). The titration gives the result in the form of total oxidized equivalent, [OX], which is the number of moles of electrons transferred per gram of sample during the titration. Then the composition, MnO<sub>x</sub>, can be determined using the formula:

$$x = \frac{2+55[OX]}{2-16[OX]}$$

where x denotes the [O]/[Mn] molar ratio. Due to the variable Mn AOS of our samples, the formula MnO<sub>x</sub> will be used to denote the composition of all manganese oxides in our thermodynamic calculations. For example, bixbyite (Mn<sub>2</sub>O<sub>3</sub>) will be written as MnO<sub>1.5</sub>. Mn<sub>5</sub>O<sub>8</sub> will be used exclusively to refer to the structure and the phase.

#### 2.4.5 Calorimetry

High temperature oxide melt solution calorimetry was performed on all three samples. The details of the technique have been described previously [16-18]. Below is a brief description of a typical experiment. About 5 mg sample powder was pressed into a pellet and dropped from room temperature into molten sodium molybdate (3Na<sub>2</sub>O • 4MoO<sub>3</sub>) solvent maintained at 700 °C. During the entire experiment, oxygen was flushed through the calorimeter at 51.6 mL/min and bubbled through the solvent at 4 mL/min. Previous studies have confirmed that manganese exists in the form of Mn<sup>3+</sup> after the sample completely dissolves and reacts under the above conditions <sup>[19]</sup>.

#### 2.5 Results

The samples we synthesized exhibited different [O]/[Mn] ratios, i.e. different Mn AOS. The sample without any further annealing at low temperature was  $MnO_{1.58\pm 0.01}$  after correction for the secondary  $MnO_2$  phase. We also obtained two samples with different [O]/[Mn] ratios through further annealing at low temperature, namely  $MnO_{1.64\pm 0.01}$  and  $MnO_{1.66\pm 0.01}$  (after secondary phase correction). Therefore, it is possible to vary the Mn AOS of the  $Mn_5O_8$  phase at least to a limited extent by annealing at low temperature in air. The Mn AOS determinations are presented in Table 2.1.

[O]/[Mn] by titration	[O]/[Mn] by TGA	Average [O]/[Mn]	Corrected [O]/[Mn]
1.64 ± 0.01	1.64	1.64 ± 0.01	$1.58 \pm 0.01$
$1.69 \pm 0.01$	1.67	$1.69 \pm 0.01$	$1.64 \pm 0.01$
1.72 ± 0.01	1.70	1.71 ± 0.01	1.66 ± 0.01

**Table 2.1** Results of composition determination. Corrected [O]/[Mn] values are the [O]/[Mn] values of the Mn<sub>5</sub>O<sub>8</sub> component after accounting for the secondary MnO<sub>2</sub> phase.

A representative XRD pattern of the as-synthesized sample (without any further annealing at 250 °C) is presented in Figure 2.2(a). It was analyzed using JADE software and identified as  $Mn_5O_8$ . However, lab X-ray diffraction analysis was not able to discern the secondary pyrolusite phase consistently. Therefore, we relied on synchrotron X-ray analysis to quantitatively evaluate the secondary phase present in the samples.

A Le Bail fit (Figure 2.3) of the synchrotron data, involving unit cell parameters, peak width, and peak shape parameters, indicates the existence of two different phases in the as-prepared sample. The major phase is  $Mn_5O_8$  and pyrolusite  $MnO_2$  is identified as a minor phase. Figure 2.3(a) shows results of the quantitative Rietveld refinement with  $Mn_5O_8$  phase only, while Figure 2.3(b) displays the result obtained when  $MnO_2$  is included. Quantitative Rietveld refinement suggests the sample contains 84.2 % (mass ratio)  $Mn_5O_8$  and 15.8 %  $MnO_2$ . It is clear from misfits of specific diffraction intensities (for example, the very broad diffraction peak ( $11\overline{1}$ ) around  $2\theta = 6.5^{\circ}$ ) that anisotropic size effects, stacking disorder, or some combination of effects is present in the main phase. Significant size broadening is also noted in the case of  $MnO_2$ . It is even possible that  $Mn_5O_8$  has intergrowths of pyrolusite-like stacking but this has not been investigated. The R factor is relatively high in the refinement because the peaks are broad, reflecting the small particle size (nanophase character) of the material synthesized at low temperature.



**Figure 2.2** Powder XRD pattern of the Mn<sub>5</sub>O<sub>8</sub> (a) before and (b) after being heated to 600 °C. The structure is seen to transform to Mn<sub>2</sub>O<sub>3</sub> after heating.



**Figure 2.3** Rietveld refinement of  $Mn_5O_8$  and pyrolusite  $MnO_2$  using synchrotron XRD data ( $\lambda = 0.414177$  Å). Refinement in (a) is completed with the  $Mn_5O_8$  phase alone, while refinement in (b) incorporates both phases. Data are shown as black points, fits are shown as red lines, and a difference curve falls below the data and fits in blue. Reflection markers for  $Mn_5O_8$  and pyrolusite  $MnO_2$  are shown in green and pink, respectively, below the data and fit in (b). Notations:  $R_{wp}$  is weighted residual and Gof is goodness of fit.

The thermal analysis curves (Figure 2.4) show that, starting at 450 °C, there is a large weight loss associated with a DSC peak. It corresponds to a complete transformation of  $Mn_5O_8$  to  $Mn_2O_3$  as confirmed by subsequent XRD analysis (Figure 2.2 (b)). The decomposition temperature is slightly higher than that of  $MnO_2$ , which starts at 430 °C <sup>[20]</sup>.



**Figure 2.4** DTG and DSC curves of Mn<sub>5</sub>O<sub>8</sub> heated to 600 °C under a flow of argon.

The weight loss from reduction to  $Mn_2O_3$  was measured by microbalance for the three samples to be 2.9 %, 3.3 % and 3.9 % of the total initial sample weight, corresponding to initial [O]/[Mn] ratios of 1.64, 1.67 and 1.70. Iodometric titrations gave very similar results for manganese AOS. We use the average of three titrations and one TGA result as the composition of each sample. This means that our samples have higher Mn AOS than that

of the nominal composition  $Mn_5O_8$  ( $MnO_{1.60}$ ), Mn AOS = 3.20. After correction for pyrolusite secondary phase (assuming the same percentage of secondary phase in all three samples), the [O]/[Mn] ratios of the  $Mn_5O_8$  phase in these samples are  $1.58 \pm 0.01$ ,  $1.64 \pm 0.01$  and  $1.66 \pm 0.01$ . The sample without further annealing at 250 °C is very close to the nominal stoichiometric composition, while further annealing at lower temperature slightly oxidized the sample.

The results of high temperature oxide melt solution calorimetry are summarized in Table 2.2. To make comparison easier, the values for the same sample before and after secondary phase correction are listed in pairs. To demonstrate the correction process, we will use the sample with corrected [O]/[Mn] ratio of 1.58 as an example. Its overall [O]/[Mn] ratio is determined by titration and TGA to be 1.64. If we have 100 g of this sample, the weight of Mn is then 67.677 g and the weight of O is 32.323 g. Also, we know from synchrotron X-ray analysis that MnO<sub>2</sub> makes up for 15.8 wt% of the sample, accounting for 9.984 g Mn and 5.816 O. Subtracting these from the total weight of Mn and O in the sample, we have 57.693 g Mn and 26.507 g O that comes from the Mn<sub>5</sub>O<sub>8</sub> phase. The [O]/[Mn] molar ratio in the Mn<sub>5</sub>O<sub>8</sub> phase is hence 1.58. The compositions of all three samples are corrected by this process. The secondary phase corrections made the drop solution enthalpy values less endothermic, but the trend is preserved that higher Mn AOS samples have more endothermic values.

From these results, together with thermodynamic data in the literature <sup>[21, 22]</sup>, we were able to calculate the enthalpies of reactions among the Mn<sub>5</sub>O<sub>8</sub> samples and other manganese oxides at room temperature (Table 2.3). These calculated reaction enthalpy

values allow us to compare the thermodynamic property of Mn<sub>5</sub>O<sub>8</sub> relative to other manganese oxides.

**Table 2.2** Results of high temperature drop solution calorimetry before and after secondary phase correction. Numbers in parentheses are number of drops. Error is two standard deviations of the mean.

Correction for	Sample	$\Delta H_{ds}$ (J/g)	∆H <sub>ds</sub> (kJ/mol)
MnO <sub>2</sub> phase			
Before	$MnO_{1.64\pm0.01}$	1070.83 ± 3.71 (8)	86.93 ± 0.30 (8)
After	$MnO_{1.58\pm0.01}$	1002.40 ± 4.41 (8)	80.41 ± 0.35 (8)
Before	$MnO_{1.69\pm0.01}$	1112.25 ± 5.34 (8)	91.18 ± 0.44 (8)
After	$MnO_{1.64\pm0.01}$	1043.82 ± 6.34 (8)	84.73 ± 0.72 (8)
Before	$MnO_{1.71\pm0.01}$	1121.32 ± 7.10 (8)	92.17 ± 0.58 (8)
After	$MnO_{1.66\pm0.01}$	1060.70 ± 9.01 (8)	86.58 ± 0.73 (8)

The higher Mn AOS samples have more exothermic enthalpy of oxidation from bixbyite and less endothermic enthalpy of reduction from pyrolusite. The reaction enthalpies from an isochemical mixture of bixbyite and pyrolusite are slightly endothermic for all three samples and the differences are extremely small. It is worth noting that, although secondary phase correction resulted in less endothermic drop solution enthalpy values for all samples (Table 2.2), the above-mentioned trends in calculated reaction enthalpies (Table 2.3) were not affected. The enthalpy of formation of  $Mn_5O_8$  from elements are also
calculated and presented in Table 2.4. The thermochemical cycles used for the calculations above are provided in Table 2.5.

**Table 2.3** Calculated reaction enthalpies among the Mn5O8 samples and other manganese oxides at 25 °C. Enthalpy values per mole of oxygen are also tabulated for the reactions that involve consumption or production of oxygen. Calorimetric data with correction for MnO<sub>2</sub> impurity were used. Complete calorimetry data are provided in Table A1 in the appendix.

Reaction	∆H (kJ/mol MnO <sub>x</sub> )	$\Delta H$ (kJ/mol O <sub>2</sub> )
$MnO_{1.5}(bixbyite) + 0.04 O_2 \rightarrow MnO_{1.58}(Mn_5O_8)$	-2.19 ± 0.61	-54.74 ± 15.26
$MnO_{1.5}(bixbyite) + 0.07 O_2 \rightarrow MnO_{1.64}$	-5.86 ± 0.71	-83.67 ± 10.20
$MnO_{1.5}(bixbyite) + 0.08 \ O_2 \rightarrow MnO_{1.66}(Mn_5O_8)$	-7.49 ± 0.88	-93.62 ± 11.06
$MnO_2 (pyrolusite) \rightarrow MnO_{1.58}(Mn_5O_8) + 0.21O_2$	+ 39.82 ± 1.09	+ 189.62 ± 5.18
$MnO_2 (pyrolusite) \rightarrow MnO_{1.64}(Mn_5O_8) + 0.18O_2$	+ 36.15 ± 1.15	+ 200.85 ± 6.39
$MnO_2(pyrolusite) \rightarrow MnO_{1.66}(Mn_5O_8) + 0.17 O_2$	+ 34.52 ± 1.26	+ 203.06 ± 7.43
$0.84MnO_{1.5}(bixbyite) + 0.16MnO_2(pyrolusite) \rightarrow MnO_{1.58}(Mn_5O_8)$	+ 4.53 ± 0.57	No O <sub>2</sub> involved
$0.72MnO_{1.5} (bixbyite) + 0.28MnO_2 (pyrolusite) \rightarrow MnO_{1.64} (Mn_5O_8)$	+ 5.91 ± 0.69	No O <sub>2</sub>
$0.68MnO_{1.5}(bixbyite) + 0.32MnO_2(pyrolusite) \rightarrow MnO_{1.66}(Mn_5O_8)$	+ 5.95 ± 0.87	No O <sub>2</sub> involved

**Table 2.4** Enthalpy of formation from elements ( $\Delta H_{f,ele}$ ) of Mn<sub>5</sub>O<sub>8</sub> samples at 25 °C.

Sample	$\Delta H_{f,ele}$ (kJ/mol MnO <sub>x</sub> )
MnO <sub>1.58</sub>	$-481.45 \pm 0.72$
MnO <sub>1.64</sub>	$\textbf{-484.93} \pm \textbf{0.80}$

MnO <sub>1.66</sub>	-486.51 ± 0.96

**Table 2.5** Thermochemical cycles used to calculate the enthalpy of reactions.

$MnO_{1.5}(s, 25 \text{ °C}) \rightarrow MnO_{1.5}(sln, 700 \text{ °C})$	$\Delta H_1 = 77.35 \pm 0.50 \ kJ/mol \ ^{[22]}$
$MnO_2 (s, 25 \text{ °C}) \rightarrow MnO_{1.5}(sln, 700 \text{ °C}) + 0.25 O_2 (g, 700 \text{ °C})$	$\Delta H_2 = 124.8 \pm 1.03 \ kJ/mol^{[22]}$
$MnO_{1.58}(s, 25 \text{ °C}) \rightarrow MnO_{1.5}(sln, 700 \text{ °C}) + 0.04 O_2(g, 700 \text{ °C})$	$\Delta H_3 = 80.41 \pm 0.35 \ kJ/mol$
$MnO_{1.64} (s, 25 \text{ °C}) \rightarrow MnO_{1.5} (sln, 700 \text{ °C}) + 0.07 O_2 (g, 700 \text{ °C})$	$\Delta H_4 = 84.73 \pm 0.72 kJ/mol$
$MnO_{1.66}(s, 25 \text{ °C}) \rightarrow MnO_{1.5}(sln, 700 \text{ °C}) + 0.08 O_2(g, 700 \text{ °C})$	$\Delta H_5 = 86.58 \pm 0.73 \; kJ/mol$
$O_2 (g, 25 \text{ °C}) \rightarrow O_2 (g, 700 \text{ °C})$	$\Delta H_6 = 21.76 \ kJ/mol^{[21]}$
$Mn (s, 25 \text{ °C}) + 0.750_2 \rightarrow MnO_{1.5}(s, 25 \text{ °C})$	$\Delta H_7 = -479.5 \pm 0.5 \ kJ/mol^{[21]}$
$Mn (s, 25 \text{ °C}) + O_2 \rightarrow MnO_2(s, 25 \text{ °C})$	$\Delta H_8 = -520.0 \pm 0.7 \ kJ/mol^{\ [21]}$
$MnO_{1.5}(s, 25 \text{ °C}) + 0.04 O_2(g, 25 \text{ °C}) \rightarrow MnO_{1.58}(s, 25 \text{ °C})$	$\Delta H_9 = \Delta H_1 - \Delta H_3 + 0.04 \Delta H_6$
$MnO_2 (s, 25 \text{ °C}) \rightarrow MnO_{1.58}(s, 25 \text{ °C}) + 0.21 O_2(g, 25 \text{ °C})$	$\Delta H_{10} = \Delta H_2 - \Delta H_3 - 0.21 \Delta H_6$
0.84 $MnO_{1.5}(s, 25 \text{ °C}) + 0.16 MnO_2(s, 25 \text{ °C}) → MnO_{1.58}(s, 25 \text{ °C})$	$\Delta H_{11} = 0.84 \Delta H_1 + 0.16 \Delta H_2 - \Delta H_3$
$Mn (s, 25 \text{ °C}) + 0.79 \ O_2 \rightarrow MnO_{1.58}(s, 25 \text{ °C})$	$\Delta H_{12} = \Delta H_{11} + 0.84 \Delta H_7 + 0.16 \Delta H_8$
$MnO_{1.5}(s, 25 \text{ °C}) + 0.07 O_2(g, 25 \text{ °C}) \rightarrow MnO_{1.64}(s, 25 \text{ °C})$	$\Delta H_{13} = \Delta H_1 - \Delta H_4 + 0.07 \Delta H_6$
$MnO_2 (s, 25 \text{ °C}) \rightarrow MnO_{1.64}(s, 25 \text{ °C}) + 0.18 O_2(g, 25 \text{ °C})$	$\Delta H_{14} = \Delta H_2 - \Delta H_4 - 0.18 \Delta H_6$
0.72 $MnO_{1.5}$ (s, 25 °C) + 0.28 $MnO_2$ (s, 25 °C) → $MnO_{1.64}$ (s, 25 °C)	$\Delta H_{15} = 0.72\Delta H_1 + 0.28\Delta H_2 - \Delta H_4$
$Mn (s, 25 \text{ °C}) + 0.82 \ O_2 \rightarrow MnO_{1.64}(s, 25 \text{ °C})$	$\Delta H_{16} = \Delta H_{15} + 0.72 \Delta H_7 + 0.28 \Delta H_8$
$MnO_{1.5}(s, 25 \text{ °C}) + 0.08 O_2(g, 25 \text{ °C}) \rightarrow MnO_{1.66}(s, 25 \text{ °C})$	$\Delta H_{17} = \Delta H_1 - \Delta H_5 + 0.08 \Delta H_6$
$MnO_2(s, 25 \text{ °C}) \rightarrow MnO_{1.66}(s, 25 \text{ °C}) + 0.17 O_2(g, 25 \text{ °C})$	$\Delta H_{18} = \Delta H_2 - \Delta H_5 - 0.17 \Delta H_6$
0.68 $MnO_{1.5}(s, 25 \text{ °C}) + 0.32 MnO_2(s, 25 \text{ °C}) → MnO_{1.66}(s, 25 \text{ °C})$	$\Delta H_{19} = 0.68\Delta H_1 + 0.32\Delta H_2 - \Delta H_5$
$Mn (s, 25 \text{ °C}) + 0.83 \ O_2 \rightarrow MnO_{1.66}(s, 25 \text{ °C})$	$\Delta H_{20} = \Delta H_{19} + 0.68 \Delta H_7 + 0.32 \Delta H_8$

#### 2.6 Discussion

The TGA and titration results indicate that the samples deviate from the nominal stoichiometric composition of  $Mn_5O_8$ . The same phenomenon was discussed by Oswald when he first reported this phase [1]. This deviation requires a charge balancing mechanism to maintain charge neutrality. Park *et al.* proposed one explanation when they were investigating materials that were isostructural to  $Mn_5O_8$  [23]. In their study on Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, where Ca<sup>2+</sup> and Cu<sup>2+</sup> replace Mn<sup>2+</sup> as the divalent cation between the [Mn<sub>3</sub>O<sub>8</sub>]<sup>4-</sup> layers, they found deviations from nominal composition in both materials. They proposed that there could be fewer vacant sites in the Mn<sup>4+</sup> layer, and hence fewer M<sup>2+</sup> (M = Mn, Cu or Ca) sites. As a result, the cation ratio will deviate from the nominal value [M<sup>2+</sup>]/[Mn<sup>4+</sup>] = 2:3, which then causes the change in the oxygen to cation ratio. When the divalent cation is Mn<sup>2+</sup>, the change in oxygen to cation ratio is reflected by the change in Mn AOS. However, there is no report on direct experimental evidence to validate this mechanism.

The oxidation from bixbyite is exothermic, with higher Mn AOS samples having slightly more exothermic oxidation enthalpy values (Table 2.3). The reduction from pyrolusite is endothermic, with the higher Mn AOS samples having slightly less endothermic reduction enthalpy values. However, if we compare the redox reaction enthalpy values per mole of oxygen, that is, writing the reaction such that it consumes or produces exactly one mole of oxygen, the enthalpy values display a weak association with the Mn AOS. The higher Mn AOS sample has more exothermic enthalpy of oxidation from bixbyite per mole of oxygen and slightly more endothermic enthalpy of reduction from pyrolusite per mole of oxygen.

The reaction enthalpies from an isochemical mixture of bixbyite and pyrolusite do not differ significantly among the three samples. They are all slightly endothermic, by 4 - 6kJ/mol. The change in entropy for a solid state reaction involving no gases is usually small because the heat capacities are not too different. For example, the entropy of the reaction at 25 °C MnO<sub>2</sub> + Mn<sub>3</sub>O<sub>4</sub> = 2Mn<sub>2</sub>O<sub>3</sub>, the change in entropy is  $\Delta S = 10.5 \text{ J/(mol·K)}$ .<sup>[21]</sup> Therefore, the T<sub>Δ</sub>S term at room temperature is also small (3.1 kJ/mol in the example above). Thus, the sign of the free energy change is likely to remain slightly positive for the formation of Mn<sub>5</sub>O<sub>8</sub> from an isochemical mixture of Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>. Therefore the Mn<sub>5</sub>O<sub>8</sub> phase is slightly metastable and would not appear on the equilibrium phase diagram between bixbyite and pyrolusite. Also, the degree of metastability does not appear to depend significantly on the Mn AOS in the slightly nonstoichiometric Mn<sub>5</sub>O<sub>8</sub> phase. This metastability is consistent with the lack of reports of its natural occurrence [2, <sup>3]</sup>. However, since the magnitude of its metastability is relatively small, it is possible to synthesize Mn<sub>5</sub>O<sub>8</sub> from aqueous solution by a variety of routes and it may be possible to transform other manganese oxides to Mn<sub>5</sub>O<sub>8</sub> under certain conditions. For example, Fritsch et al.<sup>[24]</sup> and Shan et al.<sup>[5]</sup> reported low temperature oxidation of hausmannite (Mn<sub>3</sub>O<sub>4</sub>) to Mn<sub>5</sub>O<sub>8</sub>. The slight metastability of Mn<sub>5</sub>O<sub>8</sub> is also consistent with the observation above that synthesis produced Mn<sub>5</sub>O<sub>8</sub> intergrown with a small amount of MnO<sub>2</sub>.

It is worth noting that although  $Mn_5O_8$  is evidently slightly metastable, its isostructural materials, such as  $Ca_2Mn_3O_8$ , may be stable. Indeed,  $Ca_2Mn_3O_8$  was shown to have a distinct stability field [25] and also has been successfully synthesized and studied by various groups [4, 23, 26, 27]. It is also possible that a small amount of substitution of

Mn<sup>2+</sup> by Ca<sup>2+</sup> may stabilize this phase along the Mn<sub>5</sub>O<sub>8</sub> - Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution series. It is thus interesting to evaluate which divalent cations can be accommodated in this structure and result in stabilization of the structure. Fundamental thermodynamic study of this family of materials should provide better understanding of this structure, suggest conditions under which it might form in nature, and potentially facilitate applications.

#### 2.7 Conclusion

Three samples of Mn<sub>5</sub>O<sub>8</sub> structure with different Mn AOS were synthesized and studied. Annealing at low temperature in air results in the slight oxidation of the manganese in the samples. All three samples are slightly energetically metastable with respect to an isochemical mixture of bixbyite and pyrolusite at room temperature. However, the energetic metastability is very small, explaining why Mn<sub>5</sub>O<sub>8</sub> can be synthesized relatively easily. The substitution of other divalent cations for Mn<sup>2+</sup> may also stabilize the structure and further synthetic and thermodynamic study is desirable.

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# Chapter 3 Calorimetry study on the thermodynamic properties of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials(M = Ca, Cd, Cu)

#### 3.1 Abstract

The family of isostructural  $M_2Mn_3O_8$  has interesting physical and chemical properties that are desirable for various applications. Samples of  $Ca_2Mn_3O_8$ ,  $Cd_2Mn_3O_8$  and  $Cu_2Mn_3O_8$  have been successfully synthesized. Oxide melt solution calorimetry has been carried out to study their energetic stability. The enthalpies of formation from binary oxides are -133.25 ± 4.87 kJ/mol, -50.86 ± 3.52 kJ/mol and +35.42 ± 3.70kJ/mol for M = Ca, Cd and Cu respectively, suggesting their energetic stability decreases in the order Ca, Cd, and Cu. A similar trend is observed in their thermal decomposition behavior, where  $Ca_2Mn_3O_8$  appears to be the most refractory of the three, while  $Cu_2Mn_3O_8$  decomposes at 450 °C, well below the synthetic temperatures of the other two.

#### 3.2 Introduction

Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> [1-5] all have the layered Mn<sub>5</sub>O<sub>8</sub> crystal structure introduced in Chapter 2. In short, this structure can be described as divalent cations filling in between  $[Mn_3O_8]^{4-}$  layers. The main distinction for each material is the divalent cation that occupy the octahedral sites in between the  $[Mn_3O_8]^{4-}$  layers. For Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, it is Ca<sup>2+</sup>, Cd<sup>2+</sup> for Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cu<sup>2+</sup> for Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. Since they are all isostructural to Mn<sub>5</sub>O<sub>8</sub>, they belong to the *C2/m* space group.

A visualization of the structures of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is provided in Figure 3.1 to better demonstrate the similarities among their structures. This unique layered structure is of interest for multiple reasons. Firstly, a layered structure containing transition metal elements is potentially useful for applications in energy conversion and storage. The variability of manganese oxidation state and the potential of intercalating other ions make it a potential candidate for electrode material for batteries or for catalytic applications in oxygen evolution reactions [6, 7]. In addition, manganese is a more benign and environmentally friendly element compared to some commonly used elements in such applications, such as cobalt, which is both highly toxic and more expensive. For such applications, the intrinsic energetic stability of the materials is crucial for evaluating the devices' reliability for long-term operation. Another important characteristic of this structure is its ability to accommodate heavy metal cations including cadmium and copper. Therefore, studying their thermodynamic properties can help to further the understanding of their behavior in an environmental setting along with other elements commonly found in soils, including manganese.



**Figure 3.1**: Schematic of the structures of (a) Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, (b) Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and (c) Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. Color code for elements: Oxygen: Red, Manganese: Purple, Calcium: Blue-grey; Cadmium: Blue, Copper: Green. Reproduced from structure information provided by the Materials Project. [8]

#### 3.3 Sample Preparation and characterization

#### 3.3.1 Sample preparation procedure

The preparation of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> follow similar procedures and are adapted with only small modifications from previously reported methods. [2, 3] First, a synthesis precursor is prepared by dissolving and mixing calcium nitrate or cadmium sulfate (Ca(NO<sub>3</sub>)<sub>2</sub> or Cd(NO<sub>3</sub>)<sub>2</sub>) with manganese nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) in deionized water so that the resulting Ca/Mn or Cd/Mn molar ratio is 2:3. Magnetic stirring is implemented to help dissolution. Then excessive potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) is added to the solution and white precipitates emerge immediately. When there are no more white precipitates emerging, magnetic stirring is stopped, allowing precipitates to settle. The acquired precipitates are separated and washed with deionized water by centrifugation at least three times before being vacuum dried at 60 °C overnight.

The dried precursor is then calcined under a flow of oxygen at different temperatures to yield the final product. For Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, the precursor is held at 650° C for 2 hours. For Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> the precursor is calcined at 700 °C for 2 hours. In order to eliminate the remaining carbonate in the sample, the Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> sample was again heated to 800°C for 2 hours under a flow of oxygen.

The preparation of  $Cu_2Mn_3O_8$  follows a previously published hydrothermal method. Details of the method can be found in literature [4, 6].

#### 3.3.2 Powder X-ray diffraction (PXRD)

To verify the phase of the as-synthesized samples, powder X-ray diffraction was implemented using a Bruker AXS D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) operated at 40 kV and 40 mA with a step size of 0.02 °/s. The collected pattern was analyzed using MDI JADE software.

#### 3.3.3 Cation Ratio by electron microprobe analysis

To verify the M/Mn (M = Ca, Cd, and Cu) ratios in the samples, electron microprobe analysis was implemented with a Cameca SX100 electron microprobe equipped with a wavelength dispersive spectrometer (WDS). It was operated at an accelerating voltage of 15 keV and a beam current of 20 nA to determine the amounts of Ca, Cd, Cu and Mn in each sample.

#### 3.4 Thermodynamic properties measurement

#### 3.4.1 Thermogravimetric analysis and differential Scanning calorimetry

Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was performed on all samples using a Netzsch STA 449C to study their behavior at elevated temperatures. Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> samples were heated to 1000 °C at 10 °C/min in a platinum crucible and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> sample was heated to 650 °C at 10 °C/min. A baseline scan with an empty crucible was performed ahead of each sample scan to account for the effect of the crucible itself.

#### 3.4.2 High temperature oxide melt solution calorimetry

Details of high temperature solution calorimetry can be found in previously published works [9-11]. In this study, typically, a sample pellet of ~5 mg was dropped into sodium molybdate maintained at 700 °C. During the entirety of the experiment oxygen was flushed through the calorimeter at 50 mL/min and bubbled through the solvent at 5 mL/min. A minimum of eight drops was performed on each sample.

#### 3.5 Results

The as synthesized samples all exhibit the expected Mn<sub>5</sub>O<sub>8</sub> structure as evidenced by their XRD patterns. The collected patterns match well with previously reports[6, 12]. Phase identification by MDI JADE software did not reveal any substantial secondary phase. The XRD patterns are presented in Figure 3.2.



Figure 3.2 XRD patterns of (a) Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, (b) Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and (c) Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>

The electron microprobe analyses reveal the M/Mn cation ratios are reasonably close to the nominal values. The complete sample cation ratios are presented in Table 3-1.

Nominal sample composition	Composition by microprobe
Ca <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub>	Ca1.93±0.04Mn3O7.93±0.04
Cd <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub>	Cd <sub>1.88±0.03</sub> Mn <sub>3</sub> O <sub>7.88±0.03</sub>
Cu <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub>	$Cu_{2.02\pm0.03}Mn_3O_{8.02\pm0.03}$

**Table 3.1** Sample composition by X-ray Microprobe Analysis

From the TGA-DSC results in Figure 3.3, all three samples decompose when heated to higher temperatures. However, the temperatures at which they decompose are quite different. For Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, the decomposition happens at over 900 °C, while the decomposition of Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> occurs at about 720 °C. Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is the least refractory of the three, and it decomposes below 500 °C. This result agrees with previous reports [6, 7].



Figure 3.3 TGA-DSC results (a) Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (b) Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and (c) Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>

The results of high temperature oxide melt solution calorimetry are summarized in Table 3-2 ( $\Delta H_{ds}$ ). In order to assess the samples energetic stability, their enthalpies of formation from respective binary oxide end members ( $\Delta H_{f,ox}$ ) at room temperature (25 °C) were calculated and are presented in Table 3-2 ( $\Delta H_{f,ox}$ ). The complete thermochemical cycle for computing the  $\Delta H_{f,ox}$  values is provided in Table 3-3 for reference. The drop solution enthalpy values for binary oxide end members and gas phases are acquired and/or calculated from previously published works [13, 14]. It is worth noting that, for both Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, their enthalpies of formation from oxides are fairly exothermic, while Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> exhibits a very endothermic  $\Delta H_{f,ox}$  value.

**Table 3.2** Results of high temperature oxide melt solution calorimetry. The numbers in parentheses are the number of drops. Complete calorimetry data are provided in Tables A2, A3 and A4 in the appendix.

Sample	ΔH <sub>ds</sub> (kJ/mol)	ΔH <sub>f,ox</sub> (kJ/mol)
Ca <sub>1.93</sub> Mn <sub>3</sub> O <sub>7.93</sub>	333.28 ± 1.43 (8)	-133.25 ± 4.87 (8)
Cd <sub>1.88</sub> Mn <sub>3</sub> O <sub>7.88</sub>	416.20 ± 1.61 (8)	- 50.86 ± 3.52 (8)
Cu <sub>2.02</sub> Mn <sub>3</sub> O <sub>8.02</sub>	423.62 ± 1.64 (8)	+ 35.42 ± 3.70 (8)

### Table 3.3 Thermochemical cycles for calculating the enthalpy of formation from binary

oxides at room temperature

Reaction	Enthalpy (kJ/mol)
$MnO_2(s, 25 \ \ C) \to 0.5 \ Mn_2O_3(sln, 700 \ C) + 0.25 \ O_2(g, 700 \ C)$	$\Delta H_1 = 124.8 \pm 1.03$
$CaO(s, 25 \ \ C) \rightarrow CaO(sln, 700 \ C)$	$\Delta H_2 = -90.3 \pm 1.8$
$CdO(s, 25 \ \ C) \rightarrow CaO(sln, 700 \ C)$	$\Delta H_3 = -4.82 \pm 0.28$
$CuO(s, 25 \ \ C) \rightarrow CaO(sln, 700 \ C)$	$\Delta H_4 = 41.9 \pm 0.6$
$Ca_{1.93}Mn_3O_{7.93}(s, 25 \ C)$	$\Delta H_5 = 333.28 \pm 1.43$
$ \rightarrow 1.93 \ CaO(sln, 700 \ \C) + 1.5 \ Mn_2O_3(sln, 700 \ \C) + 0.75 \ O_2 \ (g, 700 \ \C) \\ Cd_{1.88}Mn_3O_{7.93}(s, 25 \ \C) $	$\Delta H_6 = 416.20 \pm 1.61$
$ \rightarrow 1.88 \ CdO(sln, 700 \ C) + 1.5 \ Mn_2O_3(sln, 700 \ C) $ $Cu_{2.02}Mn_3O_{7.93}(s, 25 \ C) $	$\Delta H_7 = 423.62 \pm 1.64$
$ \rightarrow 1.88 \ CdO(sln, 700 \ C) + 1.5 \ Mn_2O_3(sln, 700 \ C) $ $ 1.93 \ CaO(s, 25 \ C) + 3 \ MnO_2(s, 25 \ C) \rightarrow Ca_{1.93}Mn_3O_{7.93}(s, 25 \ C) $	$\Delta H_8 = 3\Delta H_1 + 1.93 \Delta H_2 - \Delta H_5$
$1.88 \ CdO(s, 25 \ C) + 3 \ MnO_2(s, 25 \ C) \rightarrow Cd_{1.88} Mn_3O_{7.93}(s, 25 \ C)$	$\Delta H_9 = 3\Delta H_1 + 1.88 \Delta H_3 - \Delta H_6$
$2.02 \ CuO(s, 25 \ C) + 3 \ MnO_2(s, 25 \ C) \rightarrow Cu_{2.02} Mn_3 O_{8.02}(s, 25 \ C)$	$\Delta H_{10} = 3\Delta H_1 + 2.02 \Delta H_4 - \Delta H_7$

#### 3.6 Discussion

The electron microprobe analysis indicates that some of the samples deviate slightly from their nominal composition.  $Cu_2Mn_3O_8$  can be considered as stoichiometric within experimental error. Both  $Ca_2Mn_3O_8$  and  $Cd_2Mn_3O_8$  samples exhibit a slightly lower M/Mn (M = Ca, Cd) ratio. A similar observation was made by Park *et al.* [6] in their study on  $Ca_2Mn_3O_8$  and  $Cu_2Mn_3O_8$  as well as in our study of  $Mn_5O_8$  discussed in Chapter 2. The proposed explanation is that, in the ideal structure,  $M^{2+}$  sites only exist above and below vacant sites in the  $[Mn_3O_8]^{4-}$  layer. Thus, if there are fewer vacant sites in the  $[Mn_3O_8]^{4-}$ layer to begin with, then the number of  $M^{2+}$  sites would also be lower than the nominal value, the result of which would be a reduced M/Mn ratio. However more detailed structural study is needed to investigate this explanation.

In terms of energetic stability, both Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> show a considerably exothermic enthalpy of formation from binary oxide end members at room temperature. Since the entropy change in a solid-state reaction with no gas species is usually negligible, this indicates that Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> are thermodynamically favorable phases. In contrast, the enthalpy of formation from oxides for Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is substantially endothermic, suggesting it to be metastable. Our findings also support previously published phase equilibria in the Ca-Mn-O and Cu-Mn-O systems [15-18]. While Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is reported to have a distinct stability field up to around 850 - 900 °C, Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is not included in the reported equilibrium phase diagram of the Cu-Mn-O system. Although there is not conclusive thermodynamic assessment for the Cd-Mn-O system in the literature, given

its exothermic enthalpy of formation from binary oxides, it is reasonable to expect it to appear on the equilibrium phase diagram.

The trend of energetic stability also aligns with the trend in their thermal stability.  $Ca_2Mn_3O_8$ , which has the most exothermic enthalpy of formation from oxides, is also the most refractory when heated to elevated temperatures. While  $Cu_2Mn_3O_8$ , the only energetically metastable sample, decomposes at below 500 °C, far below the synthetic temperatures of both  $Ca_2Mn_3O_8$  and  $Cd_2Mn_3O_8$ . This can also explain why reports on the synthesis of  $Cu_2Mn_3O_8$  [4, 6] followed a time-consuming hydrothermal method instead of the solid-state method used to obtain  $Ca_2Mn_3O_8$  and  $Cd_2Mn_3O_8$ .

Another point worth noting here is that, since  $Ca_2Mn_3O_8$  and  $Cd_2Mn_3O_8$  can be obtained via the same procedures and at similar temperatures, they can potentially form a series of solid solutions that crystallize into the  $Mn_5O_8$  structure. A preliminary study on this topic is discussed in Chapter 4.

#### 3.7 Conclusion

Three samples of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (M=Ca, Cd, Cu) have been synthesized and studied. Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> are evidently thermodynamically favorable, due to their considerably exothermic enthalpy of formation from binary oxides at room temperature. In contrast, Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, which has an endothermic enthalpy of formation from binary oxides, is evidently metastable. A parallel trend is also observed in their thermal stability, where Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> decomposes at far lower temperature than the other two. Also, since the synthesis procedure are almost identical and synthesis temperature are close for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, there exists a possibility that a solid solution of the two can be obtained using the same procedure.

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## Chapter 4 Preliminary thermodynamic study on the solid solution of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>

#### 4.1 Abstract

A solid solution between Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> has been successfully synthesized. The 1:1 Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution composition is energetically stable evidenced by its very exothermic enthalpy of formation from binary oxides. The enthalpy of mixing from end members is also found to be substantially exothermic, indicating energetically favorable mixing of Ca<sup>2+</sup> and Cd<sup>2+</sup>, possibly due to some short range ordering.

#### 4.2 Introduction and motivation

It has been established in Chapters 2 and 3 that the M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> structure is capable of accommodating different divalent metal cations at the M<sup>2+</sup> site, which are located between [Mn<sub>3</sub>O<sub>8</sub>]<sup>4-</sup> layers. The variety of the M<sup>2+</sup> (M=Mn, Ca, Cd, Cu) cations presents a potential for forming a series of solid solutions containing two or more of the abovementioned cations. These materials have already attracted attention due to their potential for applications in electrochemical energy conversion and storage[1-3], mostly due to its layered structure which presents an opportunity for intercalation of other ions such as lithium. It is of interest to investigate whether their energetic stability as well as other physical and chemical properties can be tuned by tailoring their composition, especially through forming solid solutions among them. Moreover, knowledge of thermodynamic properties of their solid solutions could aid in the design and engineering of these materials, balancing their performance and long-term stability.

Due to the profound similarities in their structures, one would intuitively think that it is possible to form solid solution between or among different M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials. However, the variability in their energetic stability, available synthetic methods are potential obstacles to the formation of a solid solution.

Nonetheless, one promising pair does exist for forming a solid solution, namely Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. Both can be synthesized by calcining a carbonate precursor. And the synthetic temperatures are also reasonably close, which is 800°C for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and 700°C for Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. Thus, if one manages to synthesize a carbonate precursor with both calcium and cadmium, it is very likely that calcination in the proximity of 700-800°C would yield the desired solid solution.

#### 4.3 Sample preparation

Sample preparation follows the same procedure for synthesizing  $Ca_2Mn_3O_8$  and  $Cd_2Mn_3O_8$ , discussed in Chapter 3. Calcium nitrate, cadmium sulfate and manganese nitrate tetrahydrate are dissolved and mixed in deionized water. The cation ratio is Ca:Cd:Mn = 1:1:3. Magnetic stirring is continued for 5 mins after complete dissolution to facilitate mixing. Excessive potassium carbonate is then added, and white precipitates

emerge immediately with continued stirring for 5 mins. The precipitates are allowed to settle and are then separated and washed by centrifugation in deionized water. Finally, the acquired precipitates are dried at 60 °C overnight under vacuum.

Calcination of the precursor is implemented in a tube furnace and oxygen flow is maintained throughout the process. The precursors are held at 750 °C for 2 hours.

#### 4.4 Sample characterization

#### 4.4.1 Powder X-ray diffraction (XRD)

To verify the phase(s) of the as-synthesized sample, powder X-ray diffraction was implemented using Bruker AXS D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) operated at 40 kV and 40 mA with a step size of 0.02 °/s. The collected pattern was analyzed using MDI JADE software.

#### 4.4.2 Thermogravimetric analysis and differential scanning calorimetry

To study the behavior of the as-synthesized sample, coupled thermogravimetric analysis and differential scanning calorimetry was performed using a Netzsch STA 449C instrument. The sample was heated to 1000 °C at 10° C/min under a flow of argon at 40 mL/min. A baseline scan was performed on the empty crucible before the sample scan.

#### 4.5 High temperature oxide melt solution calorimetry

For high temperature oxide melt solution calorimetry, ~5 mg of sample is pressed into a pallet and dropped from room temperature into the solvent maintained at 700°C. In this case, the solvent is sodium molybdate (3Na<sub>2</sub>O • 4MoO<sub>3</sub>). Oxygen is flashed through the calorimeter and bubbled through the solvent during the entire experiment. A total of eight drops were performed.

#### 4.6 Results

The XRD pattern of the as synthesized solid solution sample show a pattern that has a similar profile to that of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. The difference in peak positions are subtle and therefore, zoom-in images for selected 2θ ranges in contrast with patterns of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O8 are provided in Figure 4.2 along with the full range scan in Figure 4.1. For simplicity, the sample will be referred to as CaCdMn<sub>3</sub>O<sub>8</sub>. From the zoomed-in images in Figure 4.2 (a) and (b), no major peak splitting can be observed which indicates that the sample is a solid solution instead of a simple mechanical mixture.



**Figure 4.1** Powder XRD pattern of CaCdMn<sub>3</sub>O<sub>8</sub> in contrast with patterns of Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>.



**Figure 4.2** Zoom in of XRD pattern of CaCdMn<sub>3</sub>O<sub>8</sub> in contrast with profiles of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> :(a)  $2\theta = 25-40^{\circ}$  (b)  $2\theta = 50-60^{\circ}$ 



Figure 4.3 TG-DSC of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution

The DSC-TG data are presented in Figure 4.3. Upon heating to elevated temperatures, the  $Ca_2Mn_3O_8$ -Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution will undergo a series of decomposition and phase transition. The onset of the first transition is observed at 730 °C.

The result of high temperature oxide melt solution calorimetry ( $\Delta H_{ds}$ ) is included in Table 4.1, along with the calculated enthalpy of formation from binary oxides ( $\Delta H_{f,ox}$ ) and enthalpy of mixing from the end members. The thermochemical cycles used to compute  $\Delta H_{f,ox}$  is provided in Table 4.2. Drop solution enthalpies for binary end members and gas species involved are acquired from or calculated based on literature results [4-7].

**Table 4.1** High temperature oxide melt solution calorimetry result for one sample having composition CaCdMn<sub>3</sub>O<sub>8</sub> in the Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution. Complete calorimetry data are provided in table A5 in the appendix.

ΔH <sub>ds</sub> (J/g)	ΔH <sub>ds</sub> (kJ/mol)	$\Delta H_{f,ox}$ (kJ/mol)	$\Delta H_{f,mix}(kJ/mol)$
891.87± 6.99	396.88 ± 3.11	-117.6 ± 4.75	-22.14± 3.78

**Table 4.2** Thermochemical cycle for computing enthalpy of formation from binary oxidesfor Ca2Mn3O8-Cd2Mn3O8 solid solution

Reaction	Enthalpy (kJ/mol)
$MnO_2(s, 25 \ \ \mathcal{C}) \to 0.5 \ Mn_2O_3(sln, 700 \ \ \mathcal{C}) + 0.25 \ O_2(g, 700 \ \ \mathcal{C})$	$\Delta H_1 = 124.8 \pm 1.03$

$CaO(s, 25 \ \ C) \rightarrow CaO(sln, 700 \ C)$	$\Delta H_2 = -90.3 \pm 1.8$
$CdO(s, 25 \ C) \rightarrow CaO(sln, 700 \ C)$	$\Delta H_3 = -4.82 \pm 0.28$
$CaCdMn_{3}O_{8}(s, 25 \ C)$ → CaO(sln, 700 C) + CdO(sln, 700 C) + 1.5 Mn_{2}O_{3}(sln, 700 C) + 0.75 O_{2} (g, 700 C)	$\Delta H_4 = 396.88 \pm 3.11$
$CaO(s, 25 \ \mathcal{C}) + CdO(s, 25 \ \mathcal{C}) + 3 MnO_2(s, 25 \ \mathcal{C}) \rightarrow CaCdMn_3O_8(s, 25 \ \mathcal{C})$	$\Delta H_5 = 3\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$

#### 4.7 Discussion

The X-ray diffraction pattern (Figure 4.1) confirms that the as-synthesized sample crystalizes in the  $Mn_5O_8$  structure. The zoomed-in view reveals no substantial peak splitting, indicating the successful formation of a solid solution between Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>.

The synthesis follows the same procedure which yielded the two end members. Therefore, by adjusting the Ca/Cd ratio in the precursor, it is possible to obtain a series of solid solution between Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>.

The decomposition of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution appears to be complex. The decomposition starts at 730 °C, while the entire process covers a temperature range of 730 - 900° C. This range coincides well with the decomposition temperatures of the two end members, which is 720 °C for Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and 920°C for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. Evident from the shoulders on the DSC peak corresponding to sample decomposition, it is very likely that the Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> solid solution will transform into multiple different phases. Due to the multiple phases present in the sample after thermal decomposition, it is not feasible to reliably identify and quantify the phases present using only lab X-ray diffraction.

The enthalpy of formation from binary oxides for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>-Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is exothermic, with a value of -117.6  $\pm$  4.75 kJ/mol. The strongly exothermic enthalpy of formation suggests that the solid solution itself is energetically stable. Additionally, its value is notably different from what a 1:1 mechanical mixture of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> would exhibit, which is -96.09  $\pm$  3.01 kJ/mol, resulting in an enthalpy of mixing of -22.14 $\pm$  3.78kJ/mol.

It should be noted here that, due to the lack of exactly stoichiometric samples for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>, the drop solution enthalpies of Ca<sub>1.93</sub>Mn<sub>3</sub>O<sub>7.93</sub> and Cd<sub>1.88</sub>Mn<sub>3</sub>O<sub>7.88</sub> were used as an approximation to the exactly stoichiometric sample. However, it is unlikely that the minor discrepancies could result in a drastic change in the value of the calculated enthalpy of mixing that would render it endothermic.

Thus, the substantially exothermic enthalpy of mixing indicates that the mixing of Ca<sup>2+</sup> and Cd<sup>2+</sup> cations in the structure is energetically favored. This could be due to some short range ordering of the M<sup>2+</sup> cations (namely Ca<sup>2+</sup> and Cd<sup>2+</sup>). Similar behaviors have also been observed in solid solutions of other complex oxide materials [8, 9].

Although to fully understand the thermodynamic properties for this solid solution series, it would require the synthesis and characterization of more samples with different Ca/Cd ratios. In addition, structural characterization is needed to investigate the possibility of cation ordering at the M<sup>2+</sup> sites.

#### 4.8 Conclusion

One sample of 1:1 solid solution between  $Ca_2Mn_3O_8$ - $Cd_2Mn_3O_8$  has been synthesized and studied. The sample exhibits an exothermic enthalpy of formation from binary oxides and an exothermic enthalpy of mixing from the end members. This indicates an energetically favorable mixing at the M<sup>2+</sup> (M = Ca, Cd) site, which is possibly due to some range ordering among the M<sup>2+</sup> cations.

#### 4.9 References

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### Chapter 5 Summary and future perspective

#### 5.1 Summary

In conclusion, a total of four samples of  $M_2Mn_3O_8$  (M = Mn, Ca, Cd, Ca) materials and one solid solution composition have been synthesized and studied.

As evidenced from their enthalpy of formation from isochemical mixture of binary oxides, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> ( $\Delta$ H<sub>f,ox</sub> = -133.25 ± 4.87 kJ/mol), Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> ( $\Delta$ H<sub>f,ox</sub> = -50.86 ± 3.52 kJ/mol) and the 1:1 solid solution composition between them, CaCdMn<sub>3</sub>O<sub>8</sub> ( $\Delta$ H<sub>f,ox</sub> = -21.51± 5.62 kJ/mol), are energetically stable phases. Mn<sub>5</sub>O<sub>8</sub> ( $\Delta$ H<sub>f,ox</sub> ~ 5 kJ/mol) is slightly metastable and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> ( $\Delta$ H<sub>f,ox</sub> = 35.42 ± 3.70 kJ/mol) is the least energetically favorable .

This suggests that Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is potentially a good candidate for long-term applications, given its outstanding energetic stability. In contrast others, due to either toxicity and/or relatively poor energetic stability, may not be as promising. However, it is also shown that the solid solution between Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> is in fact energetically stable and that the mixing of Ca and Cd is also energetically favorable. Therefore, it is possible that through the formation of solid solutions, one might be able to tune the energetic stability as well as chemical properties of M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> at the same time. Thus, even metastable phases could be of interest for applications by tuning the composition.

#### 5.2 Exploration of more iso-structural M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials

The  $M^{2+}$  site in  $M_2Mn_3O_8$  have the potential to host a variety of divalent cations. For example, in a computational study,  $Mg_2Mn_3O_8$  was proposed to exhibit the  $M_2Mn_3O_8$ structure, although computational studies by various groups proposed different structures that it possibly exhibits [1, 2]. Similarly,  $Zn_2Mn_3O_8$ , in some literature was claimed to have the  $M_2Mn_3O_8$  structure, but other studies supported an orthorhombic structure rather than a monoclinic one [3, 4].

Nevertheless, since magnesium is in the same column of the periodic table as calcium, and likewise for zinc and cadmium, it is reasonable to explore the possibility that magnesium and zinc could occupy the M<sup>2+</sup> site in M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and form energetically favorable phases. Careful structural study is needed to first confirm their structure, should the synthesis be successful.

Additionally, contradictions in the literature [3, 4] point to a possibility that the  $M_2Mn_3O_8$  stoichiometry can exist in different structures based on the species of the  $M^{2+}$  cation. In other words, it is entirely possible to find another family of isostructural  $M_2Mn_3O_8$  materials, in a different crystal structure.

# 5.3 Exploration of possible solid solutions amongst isostructural M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials

As discussed in Chapter 4, it is very possible that energetically stable phases can form solid solutions, CaCdMn<sub>3</sub>O<sub>8</sub> being an example. It would also be interesting to explore whether a solid solution could form between an energetically stable structure and a

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metastable one, for example, between Ca<sub>2</sub>Mn<sub>3</sub>O8 and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. However, the difficulty would inevitably lie with synthesis, since Ca<sub>2</sub>Mn<sub>3</sub>O8 and Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> are rather drastically different in their energetic and thermal stability. They also do not share common synthetic routes.

#### 5.4 Exploration of possible applications

One major interest for layered materials arises from the fact that they are potentially useful as electrode materials for devices such as Li-ion batteries or as catalysts for oxygen evolution reactions.

The space between layers is naturally suitable for intercalation of small ions, such as the Li<sup>+</sup> cation, while still maintaining structural integrity. Therefore, it would be interesting to explore whether the energetically stable M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> phases, including the solid solutions between them, are suitable for such applications, Mg-ion batteries could also be a potential field of application for M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials, since the M<sup>2+</sup> sites readily accommodate divalent cations. Whether Mg<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> exists as an energetically stable and electrochemically active phase for such applications requires further experimental investigation.

Besides applications as battery materials, other layered manganese oxides, such as birnessite and cryptomelane, have found potential applications in pseudo-capacitors, owning to the layered structure as well as the variable oxidation state of manganese. Since M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials also possess such characteristics, it is interesting to explore their capabilities for being a pseudo-capacitor.

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In addition, the space between layers also provides a high active area necessary for catalytic events. The mixed and/or variable valences in  $M_2Mn_3O_8$  can facilitate redox reactions like those that occur during water splitting. In  $Mn_5O_8$ , the mixed valence states of Mn provide some flexibility and therefore it exhibits decent catalytic capability. However, for other  $M_2Mn_3O_8$  materials where M is not manganese, such flexibility cannot be achieved in the same way. Thus, a  $M^{2+}$  cation with variable oxidation state is required if it is to provide flexibility for manganese to change its oxidation state. Therefore, a transition metal element is desirable as  $M^{2+}$  in this scenario. As such, it may be of interest to explore whether other transition metal cations with variable valence states can be incorporated into the  $M_2Mn_3O_8$  structure.

#### 5.5 Final remarks

In conclusion, the study of the M<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> materials can be extended to cover a wider range of materials, not necessarily bearing the Mn<sub>5</sub>O<sub>8</sub> structure. In short, we may extend the scope of the current study to explore possibilities of more than one family of iso-structural materials. The quantitative thermodynamic study of these materials together in a systematic fashion will form a much clearer picture of the relationships among their energetics, composition, and structure.

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#### 5.6 References

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## Appendix

#### High temperature oxide melt solution calorimetry Data

Table A.1 Drop solution enthalpy data for  $Mn_5O_8$ . The errors are two standard deviations of the mean.

Composition	Weight	$\Delta H_{ds}$	$\Delta H_{ds}$	Average	Error
	(mg)	(J/g)	(kJ/mol)	(kJ/Mol)	(kJ/mol)
	5.02	1067.70	86.68		
	5.22	1069.53	86.82		
	4.39	1070.97	86.94		
	5.11	1066.21	86.55		
MnO <sub>1.64</sub>	3.69	1074.04	87.19	86.93	0.30
	4.74	1074.21	87.20		
	4.46	1063.74	86.35		
	4.66	1080.23	87.69		
		Chap	ter 1		
	8.24	1105.46	90.63		
	5.50	1116.94	91.57		
	4.62	1112.63	91.21		
	4.76	1097.43	89.97		

MnO <sub>1.69</sub>	6.96	1120.98	91.90	91.18	0.44
	5.59	1117.15	91.58		
	5.31	1111.90	91.15		
	4.77	1115.52	91.45		
	5.24	1116.14	91.86		
	5.67	1134.23	93.35		
	5.19	1114.01	91.68		
	5.17	1123.17	92.52		
MnO1.71	5.51	1123.38	92.45	92.17	1121.32
	5.40	1141.34	93.11		
	4.93	1105.99	91.02		
	5.64	1110.60	91.36		
1	1			1	

Table A.2 Drop solution enthalpy data for Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. The error is two standard deviations of the mean.

Pellet weight	$\Delta H_{ds}$	$\Delta H_{ds}$	Average	Error
(mg)	(J/g)	(kJ/mol)	(kJ/mol)	(kJ/mol)
6.67	901.51	332.70		
6.56	905.88	334.31		
5.40	907.30	334.84		
8.63	907.57	334.94		
6.20	893.74	329.84	333.28	1.43
6.79	910.20	335.91		
6.59	899.42	331.93		
7.07	903.49	333.43		

Pellet weight	$\Delta H_{ds}$	$\Delta H_{ds}$	Average	Error	-
(mg)	(J/g)	(kJ/mol)	(kJ/mol)	(kJ/mol)	
10.04	829.29	416.50			
8.35	828.12	415.91			
6.48	834.30	419.01			
6.03	831.49	417.60			
4.07	824.16	413.92	416.20	1.61	
9.18	821.05	412.35			
5.73	827.66	415.68			
5.60	833.54	418.63			

Table A.3 Drop solution enthalpy data for Cd<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. The error is two standard deviations of the mean.

Pellet weight	$\Delta H_{ds}$	$\Delta H_{ds}$	Average	Error	-
(mg)	(J/g)	(kJ/mol)	(kJ/mol)	(kJ/mol)	
6.92	1002.98	422.74			
5.60	1009.82	425.63			
5.77	1012.85	426.91			
5.27	996.71	420.10			
5.44	1000.24	421.59	423.62	1.64	
5.13	1001.60	422.17			
6.75	1008.77	425.19			
5.74	1007.38	424.60			

Table A.4 Drop solution enthalpy data for Cu<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>. The error is two standard deviations of the mean.

Pellet weight	$\Delta H_{ds}$	$\Delta H_{ds}$	Average	Error
(mg)	(J/g)	(kJ/mol)	(kJ/mol)	(kJ/mol)
8.81	878.70	391.02		
5.27	905.03	402.74		
4.59	882.38	392.66		
6.07	887.60	394.98		
5.46	897.28	399.29	396.88	3.12
6.12	900.55	400.74		
5.79	899.69	400.36		
7.71	883.74	393.27		

Table A.5 Drop solution enthalpy data for a sample with the composition  $CaCdMn_3O_8$  of the  $Ca_2Mn_3O_8$ - $Cd_2Mn_3O_8$  solid solution. The error is two standard deviations of the mean.