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Thermodynamic, thermogravimetric and permittivity studies of hausmannite (Mn_3O_4) in air

R. K. Amankwah · C. A. Pickles

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Abstract Some manganese oxides are considered hyperactive under microwave irradiation because of their extremely high heating rates in air. In order to further understand this hyperactivity, thermodynamic calculations, thermogravimetric analysis and both real and imaginary permittivity determinations were performed for hausmannite (Mn_3O_4) as a function of temperature in an air atmosphere. The thermodynamic results demonstrated reasonable agreement with the thermogravimetric analysis data. A comparison of the derivative thermogravimetric analysis data with the derivative of both the real and the imaginary permittivities confirmed that the extremely high values of the permittivities were due to the conversion of the hausmannite to bixbyite (Mn_2O_3). The microwave hyperactivity of the manganese oxides in air is explained in terms of the high permittivities of bixbyite.

Keywords Hyperactivity · Microwaves · Thermodynamics · Permittivities · Manganese oxides · Thermogravimetric analysis · Derivative thermogravimetric analysis

R. K. Amankwah
Department of Mineral Engineering, University of Mines and Technology, PO Box 237, Tarkwa, Ghana
e-mail: rkamankwah@umat.edu.gh

C. A. Pickles (✉)
Department of Mining Engineering, Queen's University, Kingston, ON K7L 3N6, Canada
e-mail: pickles-c@mine.queensu.ca

Introduction

Manganese forms several oxides and the predominant oxide in a given sample generally depends on the temperature and the partial pressure of oxygen. The most common manganese oxide phases are: MnO_2 (pyrolusite), Mn_2O_3 (bixbyite), Mn_3O_4 (hausmannite) and $Mn_{1-x}O$ (manganosite). Both pyrolusite and bixbyite are believed to be stoichiometric compounds under normal conditions and according to Grundy et al. [1] there is no published research on the non-stoichiometry of these species. Differential scanning calorimetry studies have been performed on the phase transitions of manganese dioxide under reducing conditions [2]. Hausmannite has been described as being stoichiometric [3, 4] and also non-stoichiometric [5, 6] with the most recent research showing that the maximum homogeneity region of $Mn_{3-\delta}O_4$ was extremely small [7]. There is very little information in the literature on the interaction of microwaves with the various manganese oxides. However, it has been reported that some manganese oxides exhibit strong interactions with microwave radiation, in particular, MnO_2 has been referred to as being hyperactive [8], due to the extremely high heating rates and the maximum temperatures attained in air. Since the stability of the various manganese oxides depends upon the temperature and the oxygen potential, then an evaluation of both the phase changes and the interaction of microwaves with these phases is required, as a function of temperature in air.

For any given material, both the magnetic and the dielectric properties determine the interaction of an electric field with the material. If the material does not possess any substantial magnetic properties then the dielectric properties, i.e. the permittivities, determine the response, which can be described by the complex permittivity as follows:

$$\varepsilon = \varepsilon' - j\varepsilon'' \tag{1}$$

$$\varepsilon = \varepsilon_o(\varepsilon'_r - j\varepsilon''_r) \tag{2}$$

here ε is the complex permittivity, ε' is the real part of the permittivity and is also referred to as the dielectric constant; ε'' is the imaginary part of the permittivity and is also called the loss factor or the dielectric loss; j is the imaginary component and is equal to $(-1)^{1/2}$, ε_o is the permittivity of free space with a value of 8.86×10^{-12} F/m in vacuum; ε'_r and ε''_r are the relative real permittivity (or relative dielectric constant) and the relative imaginary permittivity (or relative dielectric loss), respectively. The penetration depth of the applied electric field is determined by the dielectric constant (ε'). The amount of microwave energy converted to heat energy in the material is controlled by the dielectric loss (ε''). The optimum microwave heating is achieved when the relative dielectric loss is high and the relative dielectric constant has an intermediate value. For convenience, these two factors are combined into the loss tangent ($\tan \delta$) as follows:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{3}$$

According to the Debye relations [9], both the real and the imaginary permittivities are inversely proportional to the square of the frequency.

In this research, firstly, thermodynamic calculations were performed using HSC Chemistry® 5.1 to determine the phases present during the heating of hausmannite in air. Secondly, thermogravimetric analysis was used to establish the actual phases and these were compared to the equilibrium calculations. Thirdly, both the real and the imaginary permittivities were measured as a function of temperature and related to the phase changes.

Thermodynamic considerations

The temperature and the oxygen potential primarily determine the thermodynamic stability of the various manganese oxides. In this regard, the predominance area diagram for the Mn–O–N system was calculated as a function of temperature at $pN_{2(g)} = 0.79$ bar. This diagram was determined using the Tpp Diagram module of Outokumpu HSC Chemistry® 5.1 Chemical Reaction and Equilibrium software [10]. The changes in the phase composition as a function of temperature and partial pressure of oxygen are shown in Fig. 1. Higher temperatures and lower oxygen partial pressures favor manganese oxide phases with higher manganese to oxygen ratios, according to the following sequence; $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow Mn_{1-x}O$. The reaction path for heating in air is shown by the horizontal dotted line at $pO_{2(g)} = 0.21$ bar From room temperature up to about 730 K the predominant phase would be MnO_2 and then Mn_2O_3 up to about 1100 K. Subsequently, Mn_3O_4 would become stable until about 1850 K and then finally $Mn_{1-x}O$ would be produced.

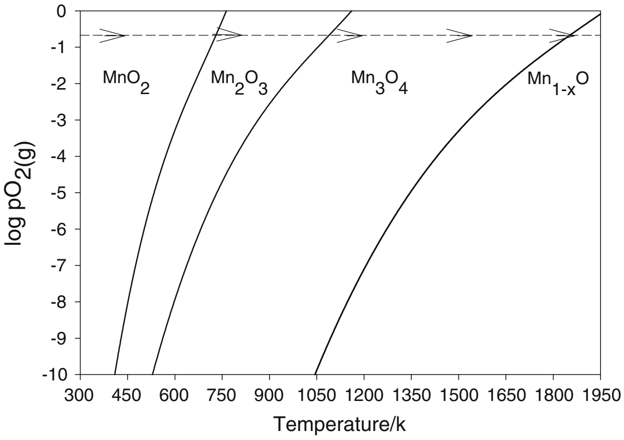

Fig. 1 Predominance area diagram for the Mn–O–N system at $pN_{2(g)} =$ 0.79 bar

Additionally, the equilibrium composition of the phases in the Mn–O–N system was calculated as a function of temperature using the GIBBS solver of HSC Chemistry® 5.1. This technique uses the Gibbs free energy minimization method. One mole of manganese and one hundred moles of excess air, consisting of 79 mole of N_2 and 21 mole of O_2, were utilized as the input data. The results are shown in Fig. 2 and are consistent with Fig. 1, however, in contrast to the predominance area diagram, it can be seen that under a given set of conditions there is an equilibrium mixture of the various manganese oxides. From room temperature, the amount of MnO_2 continuously decreases, with a rapid decrease starting at about 600 K and above about 1200 K, MnO_2 is present only in small amounts. On

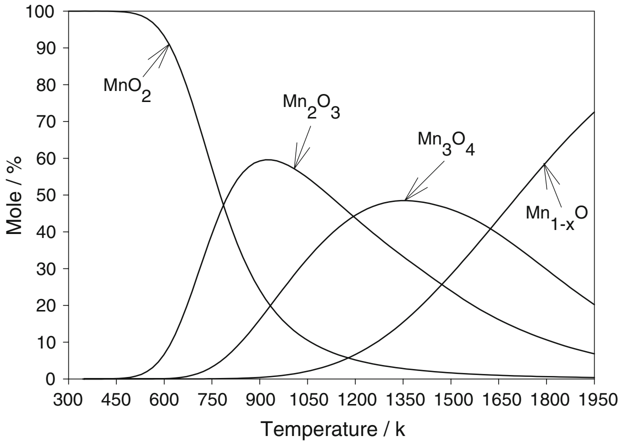

Fig. 2 Equilibrium composition in the Mn–O–N system for one mole of manganese and one hundred moles of excess air, consisting of 79 mole of N_2 and 21 mole of O_2

the other hand, Mn_2O_3 begins to form at about 480 K and reaches a maximum value of about 60 mol% at about 930 K. The formation of Mn_3O_4 starts at about 620 K and afterward the equilibrium amount increases with temperature and eventually levels off at about 50 mol% at about 1380 K. The formation of $Mn_{1-x}O$ is initiated at about 850 K and then the equilibrium amount continuously increases with increasing temperature. It should be noted that in an actual heating process, particularly in a microwave heating process, equilibrium may likely not be achieved and therefore the actual phase composition will also depend on kinetic factors, such as surface area and processing time.

Experimental

Materials characterization

Analytical grade hausmannite (Mn_3O_4) from Noah Inc., Texas, was utilized as the raw material in the experiments. The hausmannite had a purity of 99% and a particle size of minus 325 mesh. The phases present in the as-received sample and also after microwave processing were determined by X-ray diffraction (XRD) using a Philips X'Pert Pro MPD diffractometer. Thermogravimetric analysis (TGA) of the ore was performed on a Netzsch STA-409 high temperature (1848 K) DTA up to about 1273 K. The samples, weighing a few hundred milligrams, were placed in an alumina crucible and the heating rate was 3 K/min in air. The Derivative Thermogravimetric (DTG) analysis data were calculated from the TG analysis results and 1%/K corresponds to 3.0%/min.

The real and the imaginary permittivities of the hausmannite were determined using the cavity perturbation technique, which has been described previously by Hutcheon et al. [11]. About 0.5 g of the material was compacted into a briquette. The heating rate, the maximum temperature and the atmospheric conditions were the same as those employed in the TG analysis study. The tests were performed at two frequencies of 915 and 2450 MHz.

Results and discussion

Thermogravimetric analysis of hausmannite

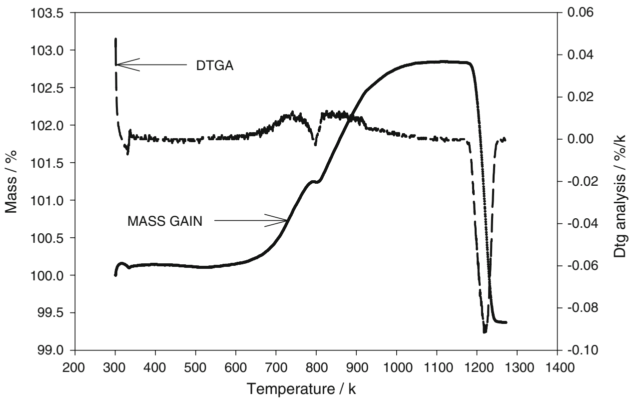

Fig. 3 Thermogravimetric analysis and derivative thermogravimetric analysis of hausmannite in air

Figure 3 shows both the TG analysis and the DTG analysis results for the hausmannite sample. From about room temperature, there is initially a rapid increase in mass, a slight decrease and then a slow but rapidly increasing mass up to about 800 K where there is a peak in the DTG analysis curve. After the peak there is a decrease in the rate of mass increase and the mass remains relatively constant. According to the equilibrium predictions as described previously, the initial increase in mass would be due to the oxidation of some of the Mn_3O_4 to MnO_2 and then at about 800 K this MnO_2 would convert to Mn_2O_3. These relatively low temperatures and short reaction times limit the amount of Mn_3O_4 that can be oxidized. However, as the temperature increases above about 800 K, the kinetics are accelerated and any previously unreacted Mn_3O_4 is oxidized to Mn_2O_3 so that by about 1050 K the mass has achieved a constant value. At about 1100 K the mass begins to decrease slowly and then more rapidly as the Mn_2O_3 reverts back to Mn_3O_4. The maximum rate occurs at about 1220 K and by about 1250 K the reaction is essentially complete. The total mass loss is about 3.45%, which is in excellent agreement with the stoichiometric amount of 3.49% for the reversion reaction as follows;

$$6Mn_2O_3 = 4Mn_3O_4 + O_{2(g)} \tag{4}$$

An X-ray diffraction pattern of a sample heated in air at 1200 K is shown in Fig. 4 and confirms that the major phases present are bixbyite and hausmannite.

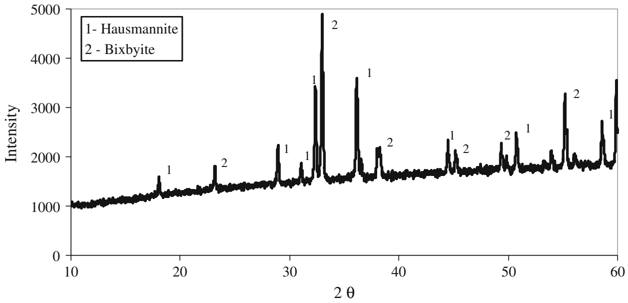

Fig. 4 X-ray diffraction (XRD) pattern of hausmannite heated in air to 1200 K

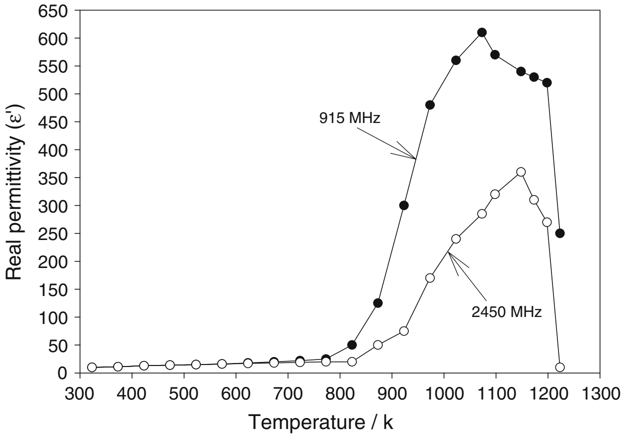

Fig. 5 Real permittivities of hausmannite as a function of temperature at the two frequencies of 915 and 2450 MHz

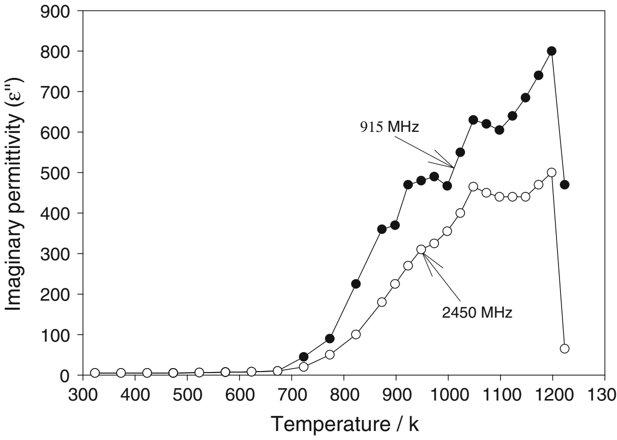

Fig. 6 Imaginary permittivities of hausmannite as a function of temperature at the two frequencies of 915 and 2450 MHz

Real and imaginary permittivities of hausmannite

The real and the imaginary permittivities of hausmannite as a function of temperature at the two frequencies of 915 and 2450 MHz are shown in Fig. 5. At a frequency of 915 MHz, the real permittivity increased slowly up to about 775 K and then more rapidly to a maximum value of 625 at about 1075 K. Subsequently, the real permittivity decreased slowly to 1200 K and then dropped precipitously to a value of 250 at 1225 K. At 2450 MHz the trends in the behaviour were similar to those observed at 915 MHz. Up to about 675 K, the real permittivity values at the two frequencies were similar and then at higher temperatures, the permittivities at 2450 MHz became lower than at 915 MHz. In addition, the temperature at which the maximum permittivity was attained, i.e. 1150 K, was about 75 K higher than at 915 MHz. Beyond 1150 K, the real permittivity decreased slowly and then, as observed previously at 915 MHz, dropped rapidly at 1200 K to a value of 10 at 1225 K. As discussed previously, the real permittivity decreased with increasing frequency and therefore the real permittivity values at 915 MHz would be expected to be higher than those at 2450 MHz. The real permittivity values reported here would be considered as being extremely high for a metal oxide.

As shown in Fig. 6, the imaginary permittivity values at the two frequencies followed trends similar to those observed for the real permittivities (Fig. 5). At 915 MHz, the imaginary permittivity increased slowly up to 675 K and then more rapidly up to about 1200 K. Beyond this temperature, it decreased sharply to 1225 K. The imaginary permittivity at 2450 MHz exhibited a comparable behaviour. Again, as for the real permittivities, the imaginary permittivities were significantly higher than the corresponding values reported for typical metal oxides. Furthermore, below about 675 K the imaginary permittivities were lower than the real permittivities, which is the generally observed behaviour. However, above this temperature the imaginary permittivities became higher than the real permittivities. Again the imaginary permittivities would be considered as being extremely high for a metal oxide.

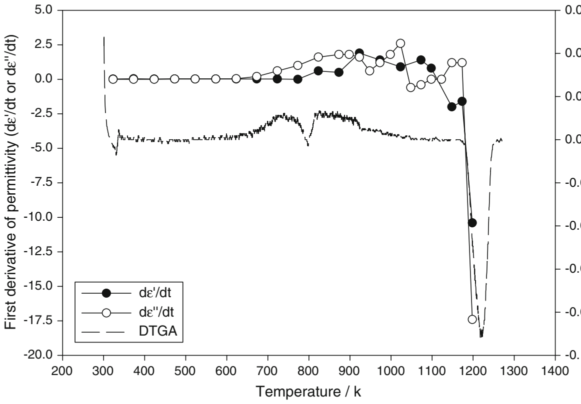

Fig. 7 Comparison of the derivative thermogravimetric analysis curve and the real and imaginary permittivities at 2450 MHz as a function of temperature for hausmannite

Figure 7 compares the DTG analysis curve with the first derivative curves of both the real and the imaginary permittivities with respect to temperature ($d\varepsilon'/dT$ and $d\varepsilon''/dT$) at 2450 MHz. It can be seen that there is a direct relationship between the DTG analysis curve and the derivative of the permittivities with respect to temperature. Therefore, the increases in the permittivities up to about 1200 K are due to the oxidation of hausmannite to bixbyite. On the other hand, the decrease in the permittivities beyond 1200 K could be attributed to the reversion of bixbyite to hausmannite. Additionally, the values of the real permittivity and usually the imaginary permittivity are related to the amount of material. Consequently, as the hausmannite oxidizes, the sample mass increases and this also contributes to the increased permittivities. Conversely, as the bixbyite reverts back to hausmannite, then the mass decreases and this adds to the decrease in the values of the permittivities beyond about 1200 K. The good correlation between the DTG analysis results and the permittivities demonstrates that with further refinement, permittivity measurements could be utilized to characterize phase changes in materials. Furthermore, the microwave hyperactivity observed when heating manganese oxides in air is likely due to the high permittivities of bixbyite.

Conclusions

The phase changes and the permittivities of hausmannite were studied as a function of temperature in an air atmosphere. Firstly, the Outokumpu HSC Chemistry® 5.1 Chemical Reaction and Equilibrium software was utilized to predict the equilibrium phase composition in the Mn–O–N system. On heating from ambient temperature in air, the Mn_3O_4 would be oxidized to MnO_2, and then the MnO_2 would be converted to Mn_2O_3. Subsequently above about 1200 K the Mn_2O_3 would revert back to Mn_3O_4. In general, the thermogravimetric analysis data agreed with the thermodynamic predictions with only a small amount of MnO_2 being formed because of kinetic limitations. Both the real and the imaginary permittivities increased rapidly above about 675 K and attained extremely high values before decreasing sharply at about 1200 K. These changes corresponded to the oxidation of hausmannite to bixbyite with increasing temperature and then the decomposition of bixbyite to hausmannite and oxygen at about 1200 K. There was good agreement between the thermodynamic predictions, the DTG analysis results and the temperature dependencies of the permittivities. It is postulated that the microwave hyperactivity exhibited by some manganese oxides, when heated in air, is due to the high permittivities of bixbyite.

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