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THE DIFFERENTIAL THERMAL ANALYSIS OF GAUDEFROYITE

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ABSTRACT

Gaudefroyite, $Ca_8Mn^{3+}{}_6[(BO_3)_6(CO_3)_2O_6]$, from the Wessels mine in the Kalahari manganese field, South Africa, was studied using a Netzsch STA 409 EP/3/D simultaneous TG–DTA equipment. A finely powdered sample of gaudefroyite was heated from 20 to 1450°C at a rate of 5°C/min. The thermogravimetric (TG) and differential thermal analysis (DTA) results indicate that gaudefroyite possibly contains one polymorphic transition at a peak temperature of 1004°C. This transition is interpreted as the change from partial ordering to complete disordering of CO_3 groups. The loss of CO_2(g) occurs at a peak temperature of 1053°C. Similar changes take place in cancrinite; the disordering of CO_3 groups occurs at 868°C, and the loss of CO_2(g) occurs at a peak temperature of 949°C. The corresponding changes occur at higher temperatures in gaudefroyite than in cancrinite because the $(CO_3)^{2-}$ groups are surrounded by six Ca^{2+} cations, which results in strong bonds, whereas in cancrinite, they are surrounded by four Na^+ and two Ca^{2+} cations, resulting in weaker bonds. The TG–DTA results strongly indicate that the CO_3 groups in gaudefroyite are partially ordered and possibly give rise to a superstructure.

Keywords: gaudefroyite, order, CO_3 groups, superstructure, differential thermal analysis, thermogravimetric analysis.

SOMMAIRE

Nous avons étudié la gaudefroyite, $Ca_8Mn^{3+}{}_6[(BO_3)_6(CO_3)_2O_6]$, provenant de la mine Wessels, dans le camp minier manganifère de Wessels, en Afrique du Sud, en utilisant un appareil Netzsch STA 409 EP/3/D prévu pour analyses thermogravimétrique et thermique différentielle. Un échantillon finement broyé de gaudefroyite a été chauffé à un taux de 5°C/minute entre 20° et 1450°C. Les résultats montrent que la gaudefroyite subit possiblement une transformation polymorphique à une température de 1004°C. Cette transition serait due à une perte du degré d'ordre partiel des groupe CO_3. La perte de CO_2(g) a lieu à une température maximale de 1053°C. Des changements semblables affectent la cancrinite; dans ce cas, la perte du degré d'ordre des groupes CO_3 a lieu à 868°C, et la perte de CO_2(g), à 949°C. Les changements correspondants sont décalés vers des températures plus élevées dans la gaudefroyite par rapport à la cancrinite parce que les groupes $(CO_3)^{2-}$ sont entourés de six cations Ca^{2+}, ce qui assure des liaisons fortes, tandis que dans la cancrinite, ils sont entourés de quatre cations Na^+ et deux cations Ca^{2+}, dont les liaisons dans l'ensemble sont plus faibles. Nos résultats fournissent une indication claire que les groupes CO_3 sont partiellement ordonnés dans la gaudefroyite, et pourraient être à l'origine d'une surstructure.

(Traduit par la Rédaction)

Mots-clés: gaudefroyite, mise en ordre, groupes CO_3, surstructure, analyse thermique différentielle, analyse thermogravimétrique.

INTRODUCTION

Gaudefroyite, $Ca_8Mn^{3+}{}_6[(BO_3)_6(CO_3)_2O_6]$, space group $P6_3/m$, $Z = 1$, contains two types of anion groups: trivalent borate groups and divalent carbonate groups. Jouravsky & Permingeat (1964) first described gaudefroyite from the hydrothermal manganese deposits at Tachgagalt, Anti-Atlas Mountains, Morocco. Gaudefroyite was described from the Wessels and N'chwaning mines in the Kalahari manganese field, South Africa by Kleyenstüber (1985), Hochleitner (1986), and Beukes *et al.* (1993). In these deposits, black euhedral crystals of gaudefroyite occur either in vein fillings (associated with barite, calcite, manganite and hydrogrossular) or in massive ore (associated with manganite, bixbyite, braunite, hausmannite and hematite). The mineral associations indicate a high temperature and a low pressure of formation, the gaudefroyite and barite being deposited during an episode of boron metasomatism (Beukes *et al.* 1993). In general terms, the purpose of this study on gaudefroyite is to (1) determine if ordering of CO_3 groups is present, (2) determine tran-

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sition temperatures if polymorphs are present, and (3) determine the temperature where the loss of CO_2(g) occurs and measure this weight loss. The CO_2(g) is produced from the breakdown of the CO_3 groups.

BACKGROUND INFORMATION

Granger & Protas (1965) first solved the structure of gaudefroyite from Tachgagalt in space group $P6_3$ and determined the topology of the structure. Yakubovich *et al.* (1975) also found evidence for the same space group. Subsequently, Hoffmann *et al.* (1997) refined the structure of gaudefroyite [a = 10.589(1), c = 5.891(1) Å] from the N'chwaning II mine, South Africa, in both space groups $P6_3$ and $P6_3/m$ and presented the structure in space group $P6_3/m$ as their preferred structural model. The structure of gaudefroyite contains infinite chains formed by *trans–trans*-connected edge-sharing [$Mn^{3+}O_6$] octahedra that are cross-linked by triangular $(BO_3)^{3-}$ groups, forming two different types of channels (Fig. 1; Hoffmann *et al.* 1997). The framework arrangement and the distribution of the Ca atoms in the structural channels obey the higher space-group symmetry $P6_3/m$. However, the $(CO_3)^{2-}$ groups situated in the center of

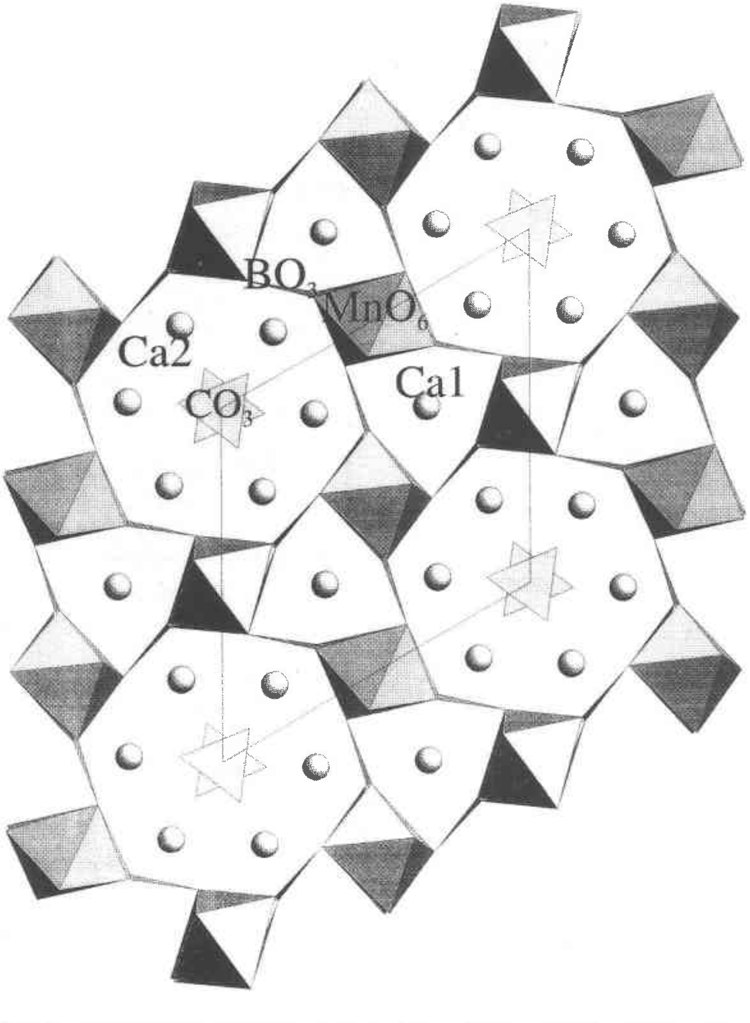

FIG. 1. The structure of gaudefroyite viewed down [001], with BO_3 triangles projected edge-wise and connecting the MnO_6 octahedra to build a porous framework. In the center of the large channels (*ca.* 10.8 Å in diameter) are the CO_3 groups, surrounded by Ca atoms on the *Ca*2 sites. The Ca atoms on the *Ca*1 sites reside in smaller channels *ca.* 3.6 Å in diameter; adapted from Hoffmann *et al.* (1997).

the wide structural channel locally violate the mirror-plane perpendicular to the *c* axis. Thus in the average structure, carbonate groups indicate positional disorder with respect to the centrosymmetry of the framework (Hoffmann *et al.* 1997). The structural framework of gaudefroyite and most of the channel-filling cations follow the higher symmetry, which is violated only by the arrangement of the CO_3 groups (Granger & Protas 1965, Hoffmann *et al.* 1997). As a result, a strong tendency for twinning or CO_3 disorder was predicted. Carbonate-group disorder was reported (Hoffmann *et al.* 1997), but no twinning.

Gaudefroyite is both structurally and compositionally somewhat similar to cancrinite with regards to the CO_3 groups and its surroundings. The chemical formula for cancrinite is $Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_{1.57}\cdot 1.75H_2O$, space group $P6_3$, $Z = 1$, with parameters of the hexagonal subcell *a* 12.590, *c* 5.117 Å (Grundy & Hassan 1982, Hassan & Buseck 1992). Figure 2 shows the structure of cancrinite for comparison with that of gaudefroyite. The carbonate groups occupy the large channels in both structures. The Ca2 and Ca1 sites in gaudefroyite are similar to the Na2 and Na1 sites in cancrinite. In cancrinite, the CO_3 groups are ordered and produce a superstructure (Hassan & Buseck 1992), but in gaudefroyite, the CO_3 groups are disordered, and no superstructure was observed in X-ray-diffraction studies (*e.g.*, Hoffmann *et al.* 1997). In cancrinite, disordering of the CO_3 groups occurs at 868°C, at which point the superstructure is destroyed, and the loss of CO_2(g) occurs at a peak temperature at 949°C (Hassan 1996). The melting point of cancrinite appears at about 1200°C. Therefore, it would be of interest to test for similar features in gaudefroyite and compare results with those for cancrinite, as the chemical surrounding is very similar in the two minerals.

This study on gaudefroyite was carried out to: (1) determine if ordering of CO_3 groups is present, (2) determine transition temperatures if polymorphs are present, (3) determine the temperature where the loss of CO_2(g) occurs and measure this weight loss, and (4) compare the results for gaudefroyite with those for cancrinite.

EXPERIMENTAL

The gaudefroyite sample used in this study is from the Wessels mine, Kalahari manganese field, South Africa. Well-developed crystals of gaudefroyite occur in association with barite, calcite, manganite, and hydrogrossular. The cell parameters for gaudefroyite were obtained by X-ray powder diffraction using a Siemens D5000 diffractometer, and the refined unit-cell

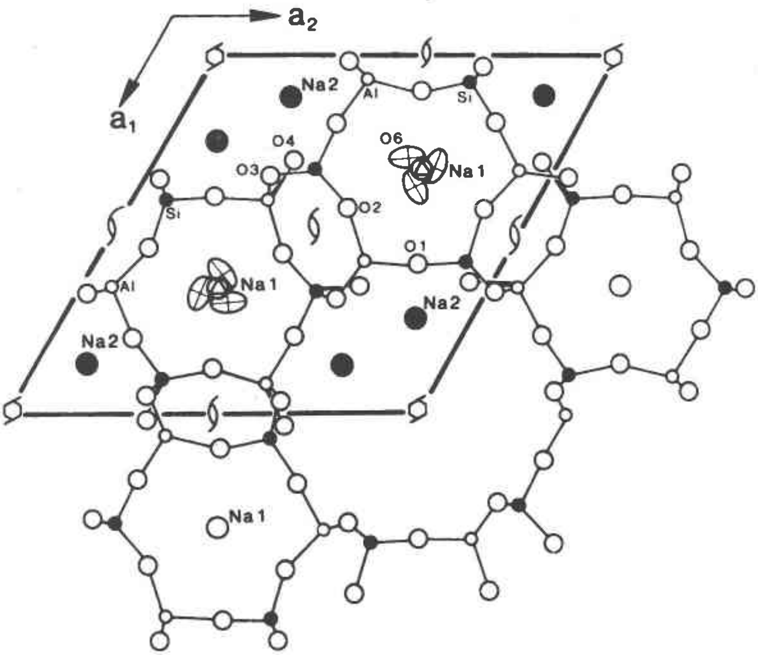

FIG. 2. The structure of cancrinite viewed down [001] showing the framework of large twelve-member-ringed channels that contain CO_3 groups at the center of these channels, surrounded by *Na*2 sites shared by Na and Ca atoms. The smaller six-member-ringed channels contain the *Na*1 sites, only occupied by Na atoms (after Grundy & Hassan 1982).

parameters were obtained by the program WIN-METRIC: *a* 10.606(1), *c* 5.896(1) Å, *V* 574.3(2) Å^3. These parameters are similar to those already reported (*e.g.*, Beukes *et al.* 1993, Hoffmann *et al.* 1997).

Some of the same gaudefroyite sample that was crushed to a fine powder with an agate mortar and pestle was used for thermal analyses. The powdered sample was placed into an Al_2O_3 crucible for differential thermal analyses (DTA), and the measurements were made with a fully computerized Netzsch STA 409 EP/3/D simultaneous TG–DTA instrument. The sample was heated using a microprocessor-controlled program and a 414/0 data-acquisition unit consisting of a high-current transformer. The heating thermocouple stage is similar to a two-prong fork. The empty reference Al_2O_3 crucible was placed on one prong, and the weighed amount (90.8 mg) of finely powdered sample was placed in a similar Al_2O_3 crucible on the other prong. The thermocouples are made of Pt10%Rh–Pt (type S). A furnace was placed over the sample and reference crucibles, and they were heated together in a controlled manner. The unit was programmed to collect a continuous scan from 20 to 1450°C at a heating rate of 5°C/min. The sample was run in a static air environment. The thermal data were analyzed using Netzsch software programs supplied with the instrument.

The thermogravimetric (TG) curve, which shows the measured mass as a function of temperature (T), was corrected for the buoyancy effect. The differential thermal analysis (DTA) curve, which shows the temperature difference between a substance and a reference material as a function of T, was corrected for the baseline effect. Corrections for buoyancy and baseline effects were obtained in a blank run using empty crucibles that were later used to run the sample in a second run, but the two experimental runs were made under identical conditions. The relationship between change in enthalpy and peak area in the DTA curve was determined by calibration using different standard materials.

DTA–TG RESULTS

Figure 3 shows the TG and DTA curves and their corresponding derivative curves (DTG and DDTA, respectively) for gaudefroyite. These curves are obtained from the raw TG and DTA data, respectively, using a narrow window for filtering the measured data. The differentiation was done by a modified Golay–Savitzky algorithm of second order. Data for gaudefroyite obtained from these curves are summarized in Table 1.

The DTA curve gives the peak temperature as well as extrapolated onset and end temperatures for each peak (Figs. 3a, c, Table 1). By definition, an exothermic change is considered positive [(+)ve]. For each DTA peak, the DDTA curve also gives the onset and end temperatures (Fig. 3c, Table 1). Five peaks are observed in the DTA and DDTA curves; peaks 1, 2, 3, and 4 are well defined. Peak 5 is partially shown in the DTA curve but is clearly seen in the DDTA curve (Figs. 3a, c). At 1004°C, a discontinuity occurs in the DTA trace (peak 1) where the loss in weight in the TG curve just started; peak 1 probably represents a polymorphic transition in gaudefroyite, because peak 2 corresponds to the proper weight-loss peak. There is some overlap between peaks 1 and 2 (Fig. 3). Peak 3 shows a small loss in weight (0.2 wt.%) and is attributed to some unknown minor constituent within gaudefroyite, as the X-ray-diffraction trace does not indicate the presence of any other impurity phase. Peak 3 occurs at too high a temperature to represent the loss of H_2O or OH, if in fact, these constituents do occur in our sample of gaudefroyite; OH and H_2O are indicated by Beukes *et al.* (1993) to occur

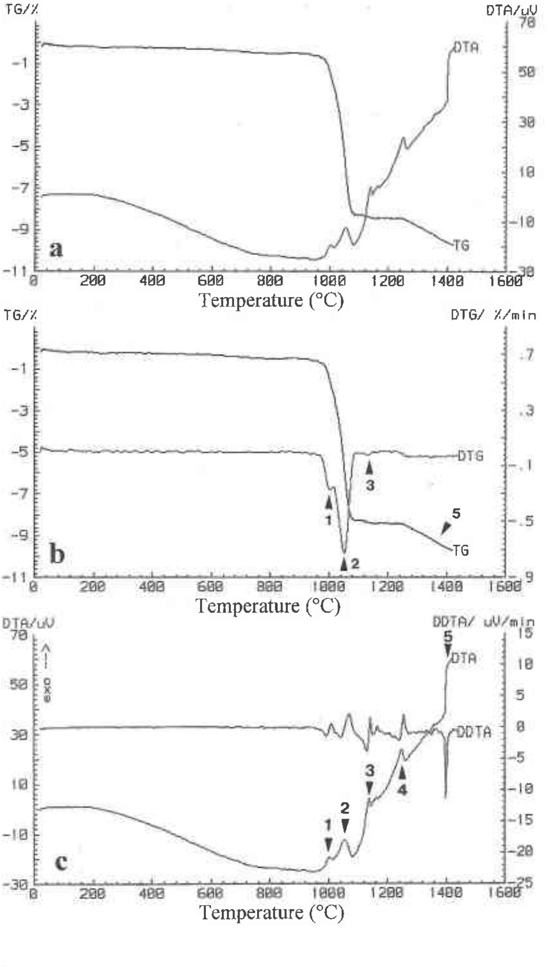

FIG. 3. TG, DTG, DTA, and DDTA curves for gaudefroyite: (a) TG and DTA curves, (b) TG–DTG curves, and (c) DTA–DDTA curves. Corresponding peaks at a particular temperature are given the same number and are labeled on the DTA and TG curves in (c) and (b), respectively.

TABLE 1. DATA DERIVED FROM THE TG–DTG–DTA–DDTA ANALYSES OF GAUDEFROYITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1	Onset-T(°C)	981.6	971.0		993.0	
	Peak-T (°C)	----	1001.0	1004.0		Disordering of
(+)ve‡	End-T (°C)	?	1016.0		1009.0	CO_3 groups
	% Wt. Loss	?				
	Enthalpy (J/g)			29.7		
Peak 2	Onset-T (°C)	?	1016.0		1040.2	
	Peak-T(°C)	----	1050.0	1053.1		Loss of
(+)ve	End-T (°C)	1069.8	1151.0		1069.0	CO_2 (g)
(1 & 2)	% Wt. Loss	–7.7				
	Enthalpy (J/g)			194.4		
Peak 3	Onset-T (°C)	1111.3	1115.0		1131.0	
	Peak-T(°C)	----	1128.3	1138.0		Loss of minor
(+)ve	End-T (°C)	1146.1	1151.0		1141.0	constituents
	% Wt. Loss	–0.2				
	Enthalpy (J/g)			51.1		
Peak 4	Onset-T (°C)	----	----		1239.0	
	Peak-T(°C)	----	----	1246.0		Melting
(+)ve	End-T (°C)	----	----		1255.0	point
	% Wt. Loss	0.0				
	Enthalpy (J/g)			27.6		
Peak 5	Onset-T (°C)	1248.1	----			
	Peak-T(°C)	----	----	~1400	1399.4	
(+)ve	End-T (°C)	>1400	----			
	% Wt. Loss	–1.2				

‡ (+)ve = exothermic, (–)ve = endothermic. Total % wt. loss for peaks 1, 2, 3, and 4 = –7.9. Melt was visible in the crucible at the end of the run. Crucible fused (reacted) with thermocouple (this accounts for peak 5, see text).

in their samples of gaudefroyite. Evidence of a melt was observed in the sample crucible after the experimental run, and this melting may be assigned to peak 4. Peak 4 corresponds to no weight loss and is the only peak (except peak 1) that can possibly be interpreted as a phase transition that corresponds to melting. Peak 1 can be ruled out as being due to melting because it occurs at the lowest temperature among the peaks. The melting temperature of gaudefroyite is 1246°C, compared to about 1200°C for cancrinite.

Peak 5 is not observed in the DTG curve but is seen as continuous weight-loss in the TG curve, and occurs as peaks in the DTA and DDTA curves. Peak 5 occurs close to the end of the experiment, where the maximum temperature allowed by the instrument (1450°C) was reached. Therefore, the corresponding weight-loss for peak 5 may not represent the true value because the experiment was stopped before complete observation of peak 5 was finished. At the end of the experimental run, we observed that the sample crucible has reacted (or fused) with the thermocouple, thereby making the thermocouple useless. Therefore, peak 5 seems to arise from the above reaction, and the subsequent continuous loss in weight is from the leaking of the melt from the crucible. A weight loss of 1.2 wt.% corresponds to peak 5, as indicated by the TG curve. Because the thermocouples are expensive, this experiment was not repeated.

From the TG curve, extrapolated onset and end temperatures and the percentage (wt.%) loss of weight are obtained for each weight-loss segment (Table 1, Fig. 3b). The DTG trace gives the temperature where the maximum weight-loss occurs; there are three DTG peaks (1, 2, and 3; Fig. 3b). A continuous loss of weight occurs over peaks 1 and 2 (Figs. 3a, b) and corresponds to a net loss in weight of about 7.7 wt.%. The weight loss (0.2 wt.%) shown by the TG curve for peak 3 can be attributed to the escape of a minor constituent of unknown composition from gaudefroyite, or peak 3 may be an experimental artifact.

DISCUSSION

Jouravsky & Permingeat (1964) reported $Ca_8Mn^{3+}_{6-x}[(BO_3)_6(CO_3)_2(O,OH)_6]$ with $x = 0.34$ as the chemical formula for gaudefroyite. They further suggested that in fresh gaudefroyite, x may be zero and no OH is present, and thus the ideal chemical formula is obtained. Beukes *et al.* (1993) chemically analyzed several samples of gaudefroyite. They calculated the B_2O_3 and CO_2 contents by assuming Ca = 8, B = 6, and C = 2 atoms per unit cell ($Z = 1$), and an amount of H_2O^+ was calculated for charge balance. Analyses were then made for Mn^{3+} and several other cations (see Beukes *et al.* 1993). Their results indicate that x varies from 0.38 to 0.64 among their samples, with corresponding OH contents from 1.16 to 1.94 per formula unit. Garvie & Craven (1994) used high-resolution parallel electron energy-loss spectroscopy to study the Mn $L_{2,3}$-edges in inorganic manganese compounds, and found that the oxidation state of manganese is trivalent Mn^{3+} in gaudefroyite. The present results indicate no loss of OH or H_2O from gaudefroyite; these constituents thus are absent in our sample.

The present study indicates that gaudefroyite hosts trivalent Mn. The incorporation of divalent Mn^{2+} in the structure would be detected in the DTA–TG experiments as an increase in weight in the TG curve that corresponds to the oxidation of divalent Mn^{2+} to Mn^{3+}, as we observed in the mineral helvite (unpubl. data). According to Figures 3a and b, this increase was not observed; therefore divalent manganese is absent in gaudefroyite. Similarly, evidence of oxidation of Mn^{3+} to Mn^{4+} was not observed during the experiment.

From the ideal chemical formula of gaudefroyite, $Ca_8Mn^{3+}_6[(BO_3)_6(CO_3)_2O_6]$, the calculated wt.% oxides are: Mn_2O_3 38.85, CaO 36.80, B_2O_3 17.13, and CO_2 7.22. The TG results gave 7.7 wt.% CO_2 compared to 7.22 wt.% for the ideal chemical formula. The excess amount of CO_2, 0.48 wt.%, may arise from experimental errors, because the gaudefroyite structure cannot accommodate more than two CO_3 groups per cell. Therefore, the proportion of CO_3 is essentially stoichiometric at 2.0 groups per unit cell. If $(OH)^-$ is an essential constituent of gaudefroyite, as indicated by the analytical data of Beukes *et al.* (1993), who documented about 1 wt.% H_2O^+, the loss of these constituents is not observed in our experiment. Moreover, it should be noted that Hoffmann *et al.* (1997) modeled the structure of gaudefroyite on the basis of the ideal chemical formula.

The DTA–TG study indicates that gaudefroyite possibly contains one polymorphic transition, which occurs at a peak temperature of 1004°C. This transition is interpreted as the change from partial order to complete disorder among the CO_3 groups. The DTA–TG results strongly indicate that the CO_3 groups in gaudefroyite are partially ordered. This partial order could give rise to a superstructure, as was found in cancrinite (*e.g.*, Grundy & Hassan 1982). Partial order of the CO_3 groups in gaudefroyite has been recently confirmed by transmission electron microscopy (Hassan 2000). The loss of CO_2(g) occurs at a peak temperature of 1053°C. Similar changes take place in cancrinite, in which the disordering of CO_3 groups occurs at 868°C and the loss of CO_2(g) occurs at a peak temperature of 949°C (Hassan 1996). However, the corresponding changes in gaudefroyite occur at higher temperatures than in cancrinite because the $(CO_3)^{2-}$ groups are surrounded by six Ca^{2+} cations, which result in strong bonds, whereas in cancrinite, they are surrounded by four Na^+ and two Ca^{2+} cations, and give rise to weaker bonds.

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