Journal of Thermal Analysis, Vol. 48 (1997) 145-154

Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

THERMAL BEHAVIOUR OF MECHANICALLY AMORPHIZED COLEMANITE
I. Thermal decomposition of ground colemanite

I. Waclawska

University of Mining and Metallurgy, 30–059 Cracow, Poland

Abstract

The effect of mechanical treatment on the thermal decomposition of calcium borate, colemanite – $Ca_2B_6O_8(OH)_6 \cdot 2H_2O$ was studied by means of XRD, FTIR, SEM and thermal analysis methods. Grinding of colemanite causes the solid-state amorphization of this mineral, as a result of the destruction of its structure along the cleavage plane. The decrease in the particle size of the original material and the increase in its internal structural disorder affect the temperatures and the magnitudes of the thermal effects accompanying the processes of dehydration and dehydroxylation. The diminishing values of the enthalpies of these processes may be a quantitative measure of the degree of amorphization of colemanite.

Keywords: colemanite, dehydration, dehydroxylation, solid-state mechanical amorphization, thermal decomposition

Introduction

The conventional method of preparation of amorphous substances consists in a rapid solidification of alloys. Recently several studies have appeared on the possibilities of preparing amorphous substances, amorphous alloys in particular, by solid state amorphization reactions [1]. The formation of an amorphous substance then occurs through disordering of the lattice of a crystalline solid. Such phenomena take place in naturally occurring and in crystalline minerals (gadolinite, thorite, zircon) which, in the course of geological times, assumed the properties of an amorphous material. This phenomenon called the process of metamictization is the result of the destruction of the crystalline structure of minerals by irradiation. During the last 20 years irradiation-induced amorphization was intensively investigated in a wide variety of materials using high-energy ion accelerators [2].

Formation of amorphous materials may also occur in the course of heat treatment of crystalline, inorganic polymers such as silicates, phosphates and borates [3, 4].

The disordering of a crystalline lattice may also be attained by mechanical grinding (wet or dry). Using this method, one can obtain powder materials of controlled microstructure and chemical reactivity.

0368–4466/97/ $ 5.00

John Wiley & Sons, Limited
Chichester

Many authors have investigated the processes accompanying the grinding of layered silicates such as kaolinite [5], montmorillonite [6, 7], illite [8] or pyrophyllite [9, 10]. On the other hand, there are not data available on the mechanical treatment of such substances as borates which have also a polymerized structural framework.

This paper presents the results of investigations of the effect of mechanical treatment on the processes of internal thermal dehydration and dehydroxylation and the accompanying structural changes of the chain structure of calcium borate, colemanite – $Ca_2B_6O_8(OH)_6{\cdot}2H_2O$.

Experimental

Selected, coarse-crystalline samples of colemanite from Turkey occurring in montmorillonized volcanic tuffs were studied. The mineral compositions of colemanite samples were determined by means of X-ray diffraction and FTIR methods. The samples proved to be pure colemanite.

Dry grinding was carried out in a laboratory vibration mill using different times of grinding from 1 to 90 h. The progress of amorphization of colemanite was followed by X-ray diffraction, FTIR spectroscopy and thermal examinations. X-ray diffraction powder patterns were obtained with a Dron-3 diffractometer, using CuK_α radiation. FTIR spectra were recorded by means of Bio-Rad Win-IR spectrometer and the samples were prepared as KBr discs.

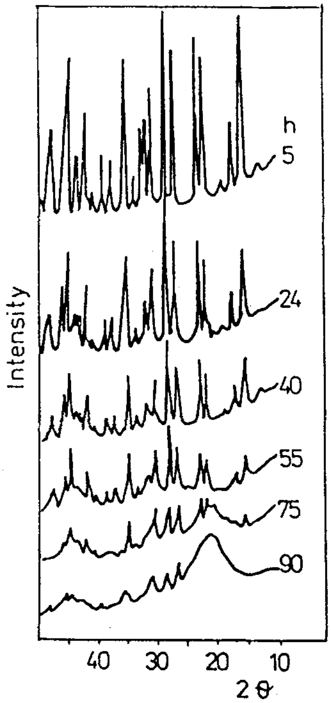

Fig. 1 Comparison of X-ray diffraction patterns of colemanite after different times of grinding

Thermogravimetric (TG and DTG) measurements were carried out with a microcomputer-controlled derivatograph C (Hungarian Optical Works) using 30 mg samples, platinum crucibles, static air atmosphere and a heating rate of 10°C min^{-1}.

Differential thermal analysis measurements were made with a Perkin-Elmer DTA-7 apparatus with both DTA and DSC modes of operation. The temperature and heat calibrations of the instrument were performed using the melting temperature and melting enthalpy of high purity aluminium and gold. The samples of colemanite (30 mg), placed in platinum crucibles and dry nitrogen atmosphere were heated at a rate of 10°C min^{-1}.

Scanning electron microscopy examinations were carried out to study the changes in the morphology of colemanite powder particles during grinding.

Results and discussion

Structure and morphology of mechanically amorphized colemanite

The structure of colemanite contains infinite boron-oxygen chains parallel to the 'a' axis. The chain elements consist of two BO_4 tetrahedra and a ring of the composition $[B_3O_4(OH)_2]^2$. The chains are laterally joined to each other by ionic bonds through Ca^{2+} ions to form sheets extending parallel to (010). A system of hydrogen bonds comprising the hydroxyl groups in the chain and the water molecules ties the sheets together [11].

In order to examine the time dependence of the structural changes during grinding, colemanite samples were analysed by X-ray diffraction after various milling times. Figure 1 shows the X-ray diffraction patterns of the colemanite powders milled for 5, 24, 40, 55, 75 and 90 h. It was found that with increasing milling time the intensities of the crystalline colemanite lines are reduced and a broad diffuse diffraction band appears independently. It is obvious that mechanical treatment increases the structural disorder of this borate, effecting gradual, but very slow destruction of the crystal structure. After 90 h of grinding the crystal structure almost completely disappears and the X-ray diffraction pattern shows a diffuse band which is characteristic of an amorphous phase.

When analyzing the disappearance rate of the X-ray reflections of various (*hkl*) series with increasing milling time (Fig. 2) it can be found that (010) reflections are strongly degraded in comparison to the other ones, e.g. (011). The structure of colemanite comprises infinite boron-oxygen chains joined by Ca^{2+} cations to form planes parallel to (010). Accordingly, the destruction of the crystalline structure of colemanite, caused by grinding, takes place just along this direction. It is simultaneously an excellent cleavage plane of this mineral caused by breaking of the hydrogen bonds and two of the seven Ca–O bonds.

To investigate the changes in the short-range ordering in the structure of colemanite subjected to grinding, IR spectroscopic examinations were carried out. Figure 3 shows the IR spectra of colemanite ground for various times. No distinct changes were observed in the IR spectra depending on the time of grinding. It was

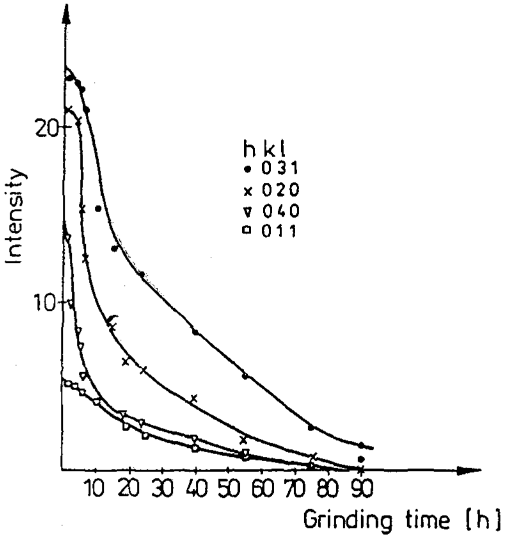

Fig. 2 Intensity of chosen (*hkl*) reflections of colemanite as a function of grinding time

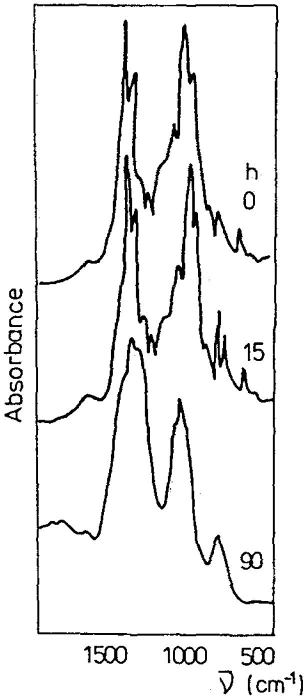

Fig. 3 IR spectra of colemanite after different times of grinding

only after 90 h of grinding that the diffuse band characteristic of the crystalline form of colemanite could be observed. IR spectra became similar to those of glasses of the composition $2CaO{\cdot}3B_2O_3$ obtained by the method of traditional melting [12].

The change in the morphology of powder particles with increasing milling time was followed by SEM for colemanite samples ground for various times.Unground colemanite forms prismatic crystals elongated along (010) (Photo 1). After short grinding times the colemanite particles reduced their size and became more irregular (Photo 2). After longer grinding times the colemanite particles became agglomerated (Photo 3). At the end of the mechanical treatment the colemanite particles changed their shape and became almost spherical, as shown in Photo 4.

Thermal dehydration and dehydroxylation of mechanically amorphized colemanite

From investigations performed under quasi-isothermal and quasi-isobaric conditions [13] it follows that the thermal decomposition of colemanite begins with the breaking-off of the OH groups and formation of water molecules (340°C). Next, the strong hydrogen bonds which bind the water molecules (360°C) with the borate structure are broken. Both types of water molecules remain enclosed in the empty voids of the colemanite structure as internal water. Part of them (0.5 mol) is released in an explosive way at 378°C, and the remaining molecules escape up to 600°C; in the maximum rate of their release is reached at 386°C.

Some TG and DSC data of the thermal dehydration and dehydroxylation of ground colemanite samples are presented in Figs 4 and 5 and in Table 1.

Under dynamic conditions, water is released from unground colemanite in the temperature range 300–600°C (Fig. 4).

As it follows from thermogravimetric data, with increasing grinding time of colemanite the amount of water released in the temperature range 25–300°C increases, while the amount of water released in the temperature range corresponding to the process of dehydration and dehydroxylation of coarse-crystalline colemanite,

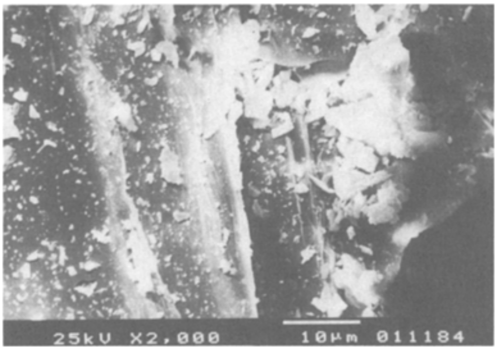

Photo 1 SEM of unground colemanite

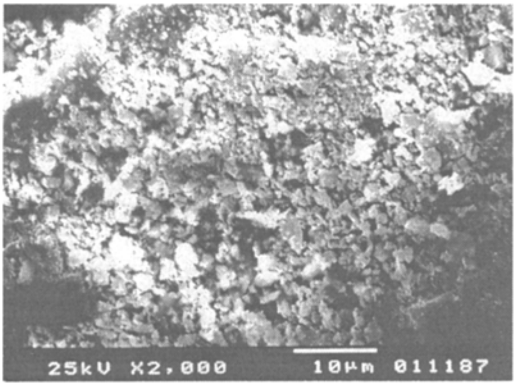

Photo 2 SEM of colemanite ground for 1 h

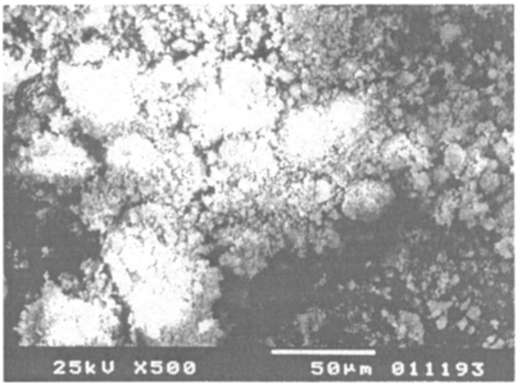

Photo 3 SEM of colemanite ground for 10 h

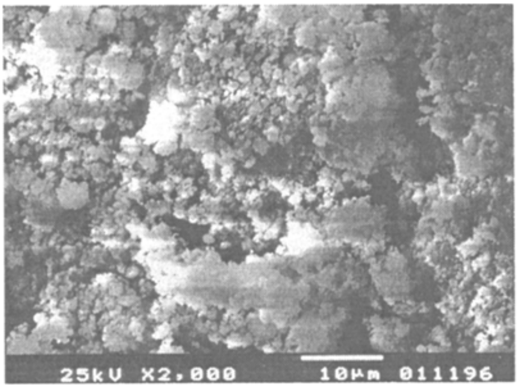

Photo 4 SEM of colemanite ground for 24 h

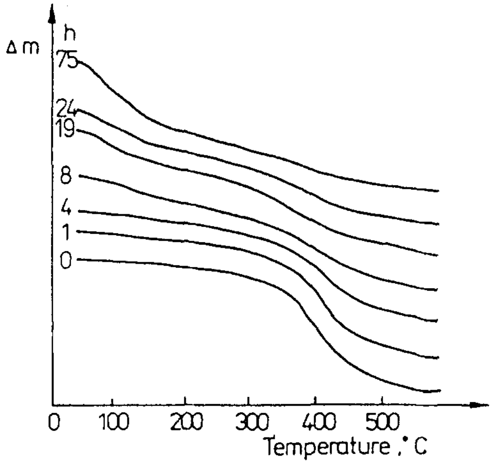

Fig. 4 TG curves of original and ground colemanite

decreases. The process of mechanical grinding causes the breaking of a part of bonds in the OH groups which may be removed from the structure of colemanite already at lower temperature. Elimination of this part of water is additionally facilitated by the diminishing size of colemanite grains with the progress of grinding. At the same time, the increase in the specific surface area of ground colemanite causes the increase in 'free moisture' which is released during heating in a lower temperature range.

Longer times of grinding (10–24 h) slow down the process of water elimination from the structure of colemanite. This is probably due to an agglomeration of colemanite grains increasing with the progress of grinding and inhibiting the removal of water from the structure. It can be seen in Fig. 5 that a sample of unground colemanite, under conditions of dynamic heating, shows endothermal DSC effects at 359, 388 and 404°C, indicating the breaking of bonds which join OH groups and water molecules with the structure of borate. Already after 1 h of grinding an additional thermal effect appears on the DSC curve with a maximum at 315–317°C which suggests the decrease in bond energy of OH groups due to mechanical treatment and breaking of these bonds at lower temperature. With increasing grinding time the thermal effects connected with the breaking of the hydrogen bonds linking the water molecules with the borate structure, diminish. After 40 h of grinding the endothermal effect at 350°C disappears, which is evidence of complete breaking of the OH group bonds in the borate structure. The diffuse endothermal effect with a maximum at about 390°C suggests the existence of a small number of hydrogen bonds between the H_2O molecules in the boron-oxygen layer. With increasing time of grinding they become weaker, thus they are broken at lower temperature. The result is a decrease in the temperature at which the released water molecules are removed from the structure of colemanite, as it follows from thermogravimetric data. A complete disappearance of the thermal effects connected with the dehydration of colemanite occurs after 90 h of grinding. The influence of mechanical grinding of colemanite on the weakness of bonds in its structure is manifested by the decreasing values of the dehydration enthalpy (Table 1). Earlier examinations [13] have shown that the dehydration product of colemanite is an X-ray amorphous substance. Accordingly, the decreasing value of the dehydration enthalpy can be a quantitative measure of the degree of amorphization of colemanite.

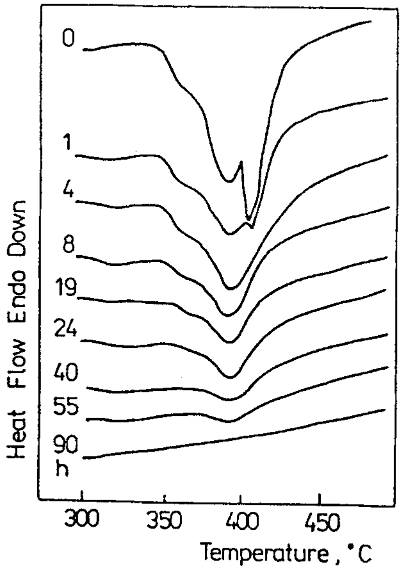

Fig. 5 DSC curves of the decomposition of original and ground colemanite

Table 1 TG and DSC data of thermal decomposition of original and ground colemanite samples

Grinding time/ h	Weight losses/%wt 25–300°C	300–600°C	$\Delta H_{dehydr.}$/ J g^{-1}
0	–	22.17	393.7
1	1.55	21.07	302.0
2	3.12	19.66	274.0
4	4.81	18.16	270.6
5	5.47	17.59	266.1
6	6.48	17.73	244.2
8	8.18	15.79	209.0
10	9.74	15.83	204.0
19	11.24	14.31	164.2
24	11.94	12.80	159.1
40	not determined	not determined	102.6
75	18.06	18.69	69.4
90	not determined	not determined	0.0

Marking: ΔH_0 is the dehydration enthalpy of coarse-crystalline colemanite; ΔH_t is the dehydration enthalpy after a grinding time of t; Degree of amorphization $\alpha = (\Delta H_0 - \Delta H_t)/\Delta H_0$.

The dependence of the degree of amorphization of colemanite on the grinding time shows an asymptotic course (Fig. 6). The greatest increase in the degree of amorphization of colemanite occurs in the early stage of its grinding. It follows from earlier results (Fig. 2) that at the same early stage of grinding the disappearance of X-ray diffraction patterns, responsible for the destruction of the crystalline structure of colemanite along the cleavage plane (010), was the fastest.

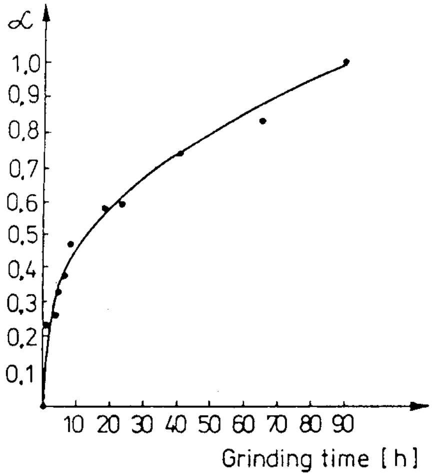

Fig. 6 Degree of colemanite amorphization as a function of its grinding time

The quickly progressing amorphization of colemanite at the early stage of its grinding is the result of breaking of the hydrogen bonds joining the boron-oxygen chains to forms sheets.

As it follows from the presented data, the mechanical amorphization of colemanite proceeds with difficulty. In order to obtain a degree of amorphization of about 60%, a grinding time of 24 h is required. Literature data [5–10] indicate that the crystalline structure of layer silicates becomes destroyed after much shorter time of grinding. Undoubtedly, the effectiveness of grinding depends on the type and power of grinding [13]. Nevertheless, the flexible chain structure of calcium borate – colemanite appears to be more resistant to mechanical treatment than e.g. the rigid structure of layer silicates.

Conclusions

The mechanical treatment by dry grinding of hydrated colemanite strongly influences the thermal and structural transformations occurring in the mineral.

Grinding of colemanite causes solid-state amorphization of this mineral manifested by the disappearance of long-range ordering, characteristic of a crystalline structure. The destruction of the crystalline structure of colemanite takes place most quickly along its cleavage planes and is caused by breaking of the hydrogen bonds joining the boron-oxygen chains into sheets parallel to (010).

The decrease in the particle size of ground colemanite and the increase in the degree of its internal structural disorder affect the thermal dehydration and dehydroxylation of this mineral.

Dry grinding of colemanite causes the lowering of the dehydration and dehydroxylation temperatures of the borate, and as a final effect – the disappearance of the thermal effects connected with these processes.

The breaking of hydrogen bonds, progressing with the grinding time, is manifested by the diminishing values of the dehydration and dehydroxylation enthalpies and they can be a quantitative measure of the degree amorphization of colemanite.

Solid-state amorphization of colemanite by mechanical treatment is a structure disordering process. Crystalline borate stores energy supplied by milling in the form of lattice disorder and point defects. The crystalline-to-amorphous transformation occurs when the stored energy reaches a critical value at which the structure is unstable. Crystalline colemanite lowers its free energy by transformation into the amorphous state.

* * *

The author is grateful to Professor L. Stoch for helpful discussions.

Support for this work was provided by the Polish Committee for Scientific Research (KBN) – Grant No. 3 P407 034 06.

References

1 'Solid State Amorphizing Transformations', eds. R. B. Schwartz and W. L. Johnson, J. Less-Common Met., 1988, p. 140.
2 D. M. Follstaedt, Nucl. Instrum. Methods, B 7–8 (1985) 11.
3 L. Stoch and I. Waclawska, J. Thermal Anal., 42 (1994) 99.
4 L. Stoch and I. Waclawska, High Temperature Materials and Processes, 13 (1994) 181.
5 Z. A. Juhasz, Acta Miner. Petrogr., 24 (1980) 121.
6 B. Cicel and G. Kranz, Clay Minerals, 16 (1981) 151.
7 V. S. Fajnor and L. Kuchta, J. Thermal Anal., 45 (1995) 481.
8 Z. A. Juhasz and I. Sanogyi, Keram. Zeit., 36 (1984) 659.
9 J. L. Perez Rodriquez and P. J. Sanchez Soto, J. Thermal Anal., 37 (1991) 1401.
10 A. Wiewiora, P. J. Sanchez Soto, M. A. Aviles, A. Justo and J. L. Perez-Rodriquez, Appl. Clay Sci., 8 (1993) 261.
11 C. L. Christ, J. R. Clark and R. C. Evans, Acta Crystallogr., 11 (1958) 76.
12 I. Waclawska, Thermochim. Acta (1995) 269/270 (1995)457.
13 I. Waclawska, L. Stoch, J. Paulik and F. Paulik, Thermochim. Acta, 126 (1988) 307.
14 A. W. Weeber, W. J. Haag, A. J. H. Wester and H. Bakker, J. Less-Common Mat., 140 (1988) 119.
15 L. Stoch and I. Waclawska, Proc. XVII International Congress on Glass, Beijing, China, Vol. 2, 1995, p. 81.