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MODIFICATION OF THE THERMAL DEHYDROXYLATION OF ANTIGORITE BY ULTRASOUND TREATMENT

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The differences on the thermal behaviour (DTG-DTA) of antigorite sample measured before and after sonication have been studied. Sonication treatment produces negligible changes in the structure of the material but substantial textural modifications. These modifications produce changes in the thermal behaviour of antigorite sample. Thus, it has been observed a decrease in the dehydroxylation temperature as measured by DTG and DTA effects. For sonication treatments longer than 20 h, two new effects of dehydroxylation are observed, the intensity of these two new effects increases with the sonication time showing a modification in the release of structural OH. It has been also observed that the formation of forsterite takes place simultaneously with the dehydroxylation of the antigorite. The high temperature exothermic effect is due to the recrystallization of forsterite and not to the formation of forsterite as traditionally assumed. Modifications in the thermal dehydroxylation of antigorite observed in this study are related to the pronounced decrease in particle size obtained by sonication.

Keywords: *antigorite, dehydroxylation, differential thermal analysis, serpentine, sonication, thermogravimetry*

Introduction

Thermal behaviour of clay minerals is an issue of significant importance. Thus, thermal analysis methods such as TG, DTA, DSC, high temperature XRD, or even ETA are extensively used for the characterization of clay minerals in their natural estate or after chemical or mechanochemical modifications [1–8].

Grinding is a conventional procedure in the processing of clay minerals for reducing their particle size [9]. The effect of grinding on different serpentine samples, including antigorite, has been recently studied [10–12]. Thus, the mechanical treatment by dry grinding of serpentine produces a decrease in the particle size of the original material followed by agglomeration of the ultrafine particles as grinding proceeds. Grinding also produces partial release of Mg by the preferential destruction of the octahedral sheet, increasing the ratio Si/Mg in the remaining semicrystalline particles and enhances the extraction of metals from the structure of serpentine by acid solutions. Progressive grinding eventually produces complete destruction of the structure. All these transformations produced by grinding modify the thermal behaviour of clay minerals [9, 13, 14]. In particular for antigorite [10], it has been reported that grinding modifies mineral dehydration accelerating the dehydroxylation process and transforming the structural OH to absorbed water in the resulting matrix.

An alternative method recently proposed for particle size reduction is sonication. Thus, nanometric and submicron-sized particles that retain the crystalline structure of the precursors have been prepared from natural kaolinite, pyrophyllite, talc, micas and vermiculites [15–21]. However, until now, little consideration has been given to the effect of sonication on the thermal behaviour of clay minerals, except pyrophyllite and mica [22, 23]. The purpose of this work is to study the effect of sonication on the thermal behaviour of antigorite.

Experimental

Materials

The material used is a serpentine rock from the Mulhacen group of the Sierra Nevada Complex in the Betic Cordillera (SE-Spain). Antigorite was the major serpentine mineral with small amounts of chrysotile and berthierine (both 5%, [10]). The sample was obtained from Prof. F. Nieto of Granada University.

Sonication

Ultrasonic treatment was performed with a Misonix ultrasonic liquid processor of 600 watts output with a 20 kHz converter and a tapped titanium disruptor horn

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of 12.7 mm of diameter that produces a double (peak to peak) amplitude of the radiating face of the tip of 120 mm. The horn tip was dipped into a cylindrical jacketed cooling cell of 5 cm internal diameter, where 3 g of samples were mixed with 50 mL of freshly deionized water. The dispersions were sonicated for periods ranging between 10 and 40 h at 20ºC.

Characterization

Differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) were carried out simultaneously in static air with an automatic thermal analyser system (Seiko, TG/DTG 6300). Samples of about 40 mg were gently packed into a platinum holder and thermally treated at a heating rate of 10ºC min^{-1}. To check reproducibility, experiments were repeated three times.

The specific surface areas were determined with an automatic system (Micromeritics 2200 A Model Norcross GA) using the BET method, at liquid-nitrogen temperature. Nitrogen gas was used as adsorbent. The equivalent spherical diameters were calculated from the specific surface area using a procedure previously proposed in [24].

High temperature X-ray powder diffraction experiments were performed on a Philips (X'Pert) diffractometer with a high temperature chamber (HTK 1200, Anton Paar) using Ni-filtered CuK_α radiation.

Results

The evolution of the specific surface area (ssa) with the sonication time is shown in Fig. 1. The specific surface area increased from 7 $\text{m}^2\ \text{g}^{-1}$ for the untreated sample to about 90 $\text{m}^2\ \text{g}^{-1}$ after sonication during 250 h. The increase in ssa took place at two different speeds: at about 0.84 $\text{m}^2\ \text{g}^{-1}\ \text{h}^{-1}$, after 30 h of sonication the ssa increased to 32 $\text{m}^2\ \text{g}^{-1}$, and at 0.26 $\text{m}^2\ \text{g}^{-1}\ \text{h}^{-1}$, 250 h of sonication were required for the ssa to increase to 90 $\text{m}^2\ \text{g}^{-1}$. A similar behaviour has been reported for sonicated vermiculite where, as in the present case, sonication produces a fast increase of the ssa during the first stages of the treatment and a much slower increase as sonication continues [15, 16]. The values of the equivalent spherical diameters (esd) as calculated from the specific surface areas, as a function of treatment time are also shown in Fig 1. We must keep in mind that clay minerals are very anisotropic materials and, therefore, the values of the esd should not be considered as absolute values but as relative ones that indicate particle size trends. The esd decreased from about 300 nm for the untreated sample to 26 nm for the sample sonicated 250 h, showing two steps, one up to 30 h treatment where the decrease was very fast and another from 30 to 250 h at a much slower speed of decrease. The diffraction patterns of the antigorite sample before and after sonication are included in Figs 2a and 3a, respectively. The diffraction pattern after sonication of antigorite (Fig. 3a) shows broadening of the diffraction lines, as compared with that of the untreated material (Fig. 2a), produced by delamination and crystal size reduction, while the material remains crystalline. Moreover, sonication does not produce significant structural modification in the sample. These results obtained with sonicated samples contrast with those previously obtained for ground antigorite [10–12] where amorphization was observed even for much shorter treatment times than those reported here.

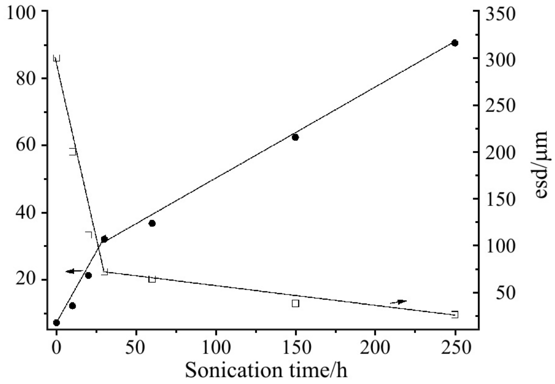

Fig. 1 Evolution of the specific surface area (ssa) and equivalent spherical diameter (esd) as a function of the sonication treatment time

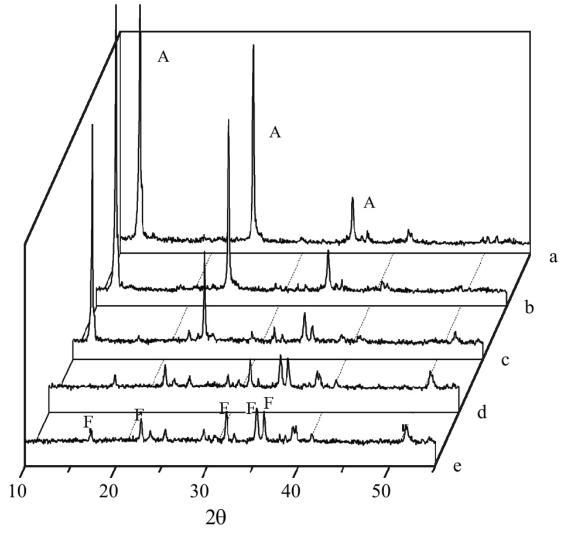

Fig. 2 High temperature X-ray diffraction patterns for the untreated antigorite at a – 25ºC, b – 600ºC, c – 660ºC, d – 780ºC and e – 900ºC. A: antigorite, F: forsterite

TG curves of untreated and sonicated antigorite are shown in Fig 4. The mass loss of the untreated sample (Fig. 4a) begins about 600ºC and reaction is over at 825ºC. The found mass loss percentage

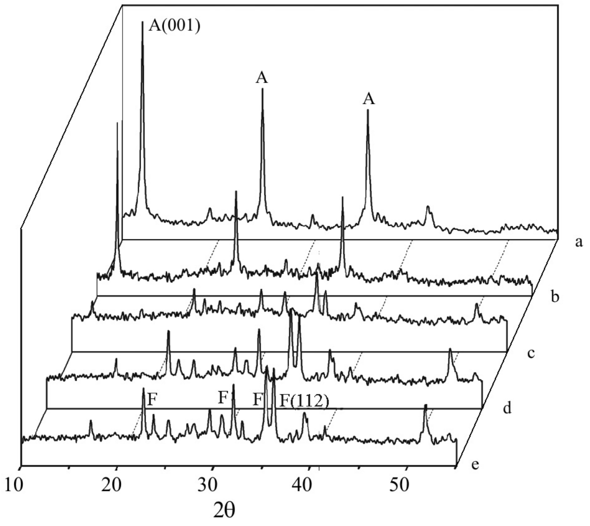

Fig. 3 High temperature X-ray diffraction patterns for the antigorite sonicated during 250 h at a – 25ºC, b – 600ºC, c – 660ºC, d – 780ºC and e – 900ºC. A: antigorite, F: forsterite

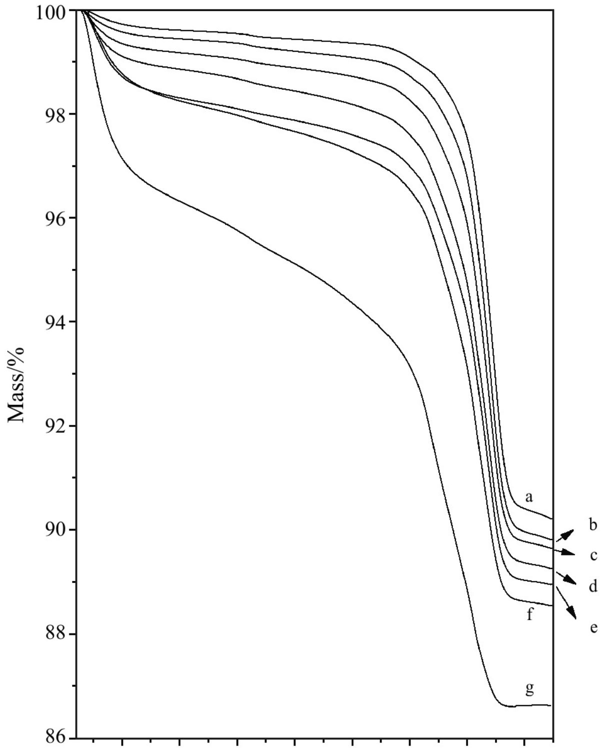

Fig. 4 TG curves for antigorite sample: a – untreated and sonicated for b – 10 h, c – 20 h, d – 30 h, e – 60 h, f – 100 h and g – 250 h

(~10%) is that expected from the release of structural OH for an ideal antigorite. For sonicated samples, the mass loss percentage for dehydroxylation of the dry sample (previously heated to 150ºC) is identical to that of the untreated sample, indicating that sonication apparently does not affect the mass loss of dehydroxylation. Nevertheless, in addition to this main mass loss, an increasing new mass loss at low temperatures (below 150ºC) is observed for the sonicated samples. This mass loss could be related to the sorbed water due to the increase of surface area, loosely bound hydroxyl group and, even to prototropic effect [25] similarly to what happen with sonication of pyrophyllite [22]. The broad DTG peak centred at 748 ºC for the untreated sample (Fig. 5a) is shifted to lower temperature with the sonication treatment (Fig. 5b–g). Thus, for the samples sonicated for 10 and 20 h, the DTG peaks have maxima at 743ºC (Fig. 5b) and 741ºC (Fig. 5c), respectively. Further sonication for 30 h produces a small shift to 739ºC, while longer sonication times do not produce any further modification of the maximum temperature. Nevertheless, as sonication proceeds, two new peaks with maxima at 716 and 643ºC are clearly detected. From 30 to 250 h of sonication no modification is observed in the temperature of the three dehydroxylation peaks while their relative intensities are very much affected. Thus, the intensity of the peak at 739ºC decreases while those of the peaks at 716 and 643ºC increase with the sonication treatment. The peak at 739ºC is eventually converted into a shoulder after 250 h of sonication time (Fig. 5g). Some correlations can be found between the modifications in temperature of the main dehydroxylation originally at 748ºC and the increase of specific surface area (and the consequent particle size reduction) shown in Fig. 1. Thus, for treatments of up to 30 h of sonication, that produce the most significant increase in the surface area and decrease in the particle size, the temperature of the main dehydroxylation peak is shifted towards lower temperatures, while for longer sonication times the temperature of this peak is not affected. Nevertheless, the thermal behaviour if very much affected for the entire sonication range by modifying the thermal profile and the contribution of the three different stages to the total dehydroxylation of the sample. In any case it is clear from Figs 4 and 5 that there is a general shift of the overall dehydroxylation process towards lower temperatures as sonication proceeds. We have observed that the decrease of the dehydroxylation temperature with the sonication treatment is a general behaviour in sonicated layer silicates, attributed to the decrease in particle size that facilitates the diffusion into the layer structure [22, 23]. ATD curves of untreated and sonicated antigorite are shown in Fig 6. The untreated sample (Fig. 6a) gives a dehydroxylation endothermic peak at 748ºC, which is followed by an exothermic peak at 816ºC traditionally attributed to the formation of forsterite [26–28]. The temperatures of the endothermic peak match that of the

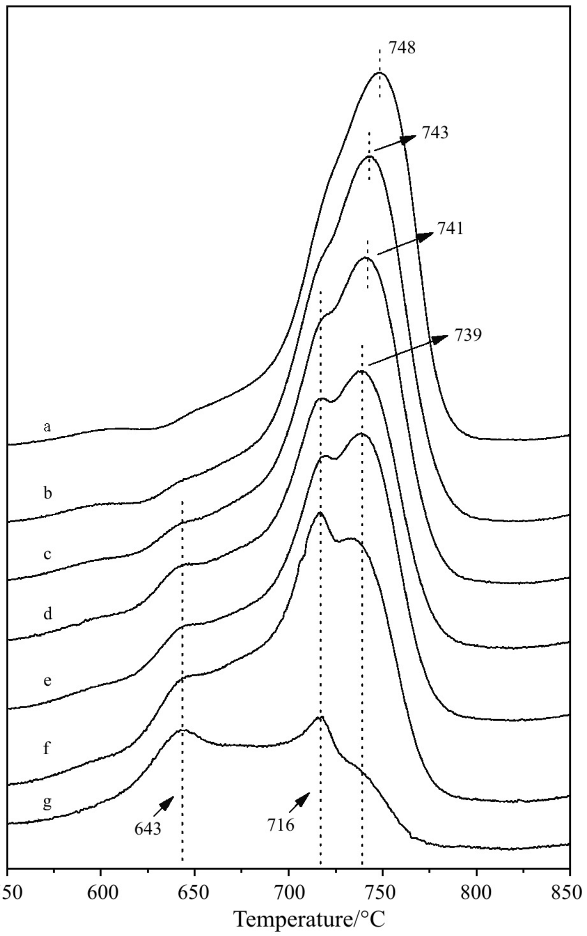

Fig. 5 DTG curves for antigorite sample: a – untreated and sonicated for b – 10 h, c – 20 h, d – 30 h, e – 60 h, f – 100 h and g – 250 h

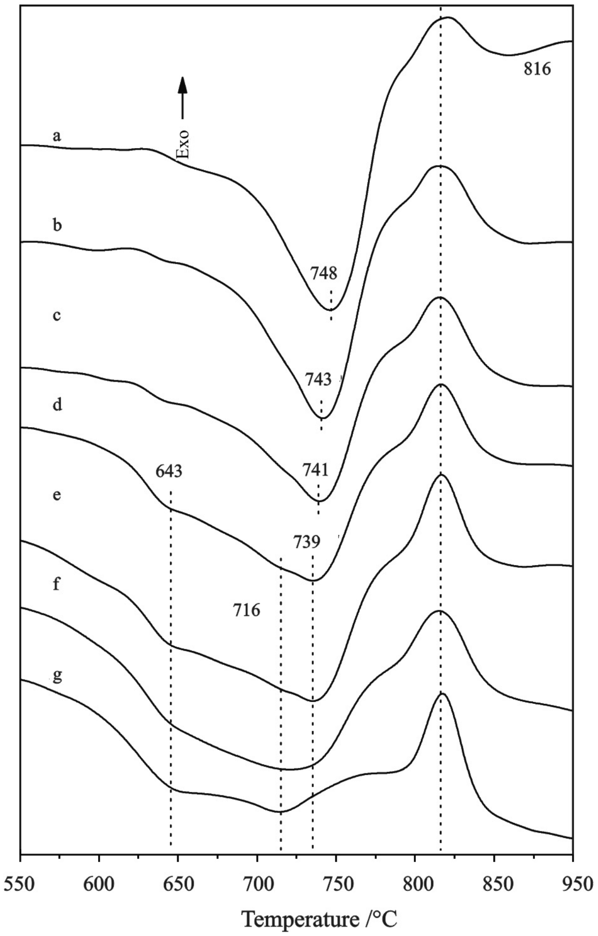

Fig. 6 DTA curves for antigorite sample: a – untreated and sonicated for b – 10 h, c – 20 h, d – 30 h, e – 60 h, f – 100 h and g – 250 h

mass loss in the DTG curve (Fig. 4). Sonication modifies the DTA profiles. Thus, the endothermic peak at 748ºC for the untreated material (Fig. 6a), is shifted to 743, 741 and 739ºC for the samples sonicated 10 h (Fig. 6b), 20 h (Fig. 6c), 30 h (Fig. 6d), respectively. Longer sonication times do not produce any further shift in the temperature of this endothermic effect, but two new endothermic effects with maxima at 716 and 643ºC are clearly observed (Fig. 6e–g). As sonication time proceeds, the intensities of these two new effects increases with the treatment times while that of the former peak decreases and eventually, it almost disappears after 250 h of treatment (Fig. 6g). This behaviour is identical to that reported above from TG-DTG data. Sonication does not modify the temperature of the exothermic peak at 816ºC.

Figures 2 and 3 include the high temperature X-ray diffraction patterns for the antigorite sample untreated and sonicated for 250 h, respectively. At 600ºC (Figs 2b and 3b), the diffraction patterns of both samples show that antigorite is the only phase present. As temperature increases to 660ºC, for the untreated sample (Fig. 2c) most of the material is still antigorite, while for the sonicated sample (Fig. 3c) most of the antigorite phase has already disappeared. This observation agrees with the study performed by TG-DTA (Figs 4–6) that indicated a clear shift of the decomposition of the sonicated antigorite to a lower temperature as compared with the untreated sample. At 783ºC, antigorite has totally disappeared in both samples (Figs 2d and 3). It is also significant that in both samples, as antigorite disappears, a new phase, forsterite, appears. Figure 7 includes the evolution of the intensity of two diffraction peaks, one corresponding to antigorite (001) and another to forsterite (112), as obtained directly from the diffraction pattern, as a function of the temperature, for the antigorite sample sonicated for 250 h. This Fig. 7 clearly indicates that the decomposition of antigorite takes place in the same temperature range as the formation of forsterite takes place. Thus, it seems that the dehydroxylation of the antigorite directly produces a new crystalline forsterite phase. Thus, the exothermic peak at 816ºC in the DTA trace (Fig. 6) cannot be directly attributed to formation of forsterite,

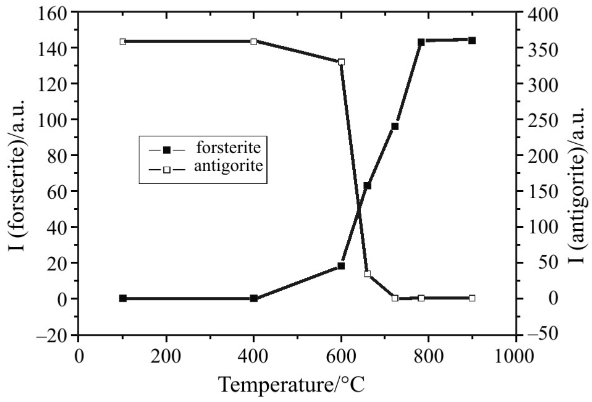

Fig. 7 Evolution of the intensity of the antigorite (001) and forsterite (112) diffraction peaks with the temperature

but to a recrystallization process where the forsterite phase formed during the decomposition of the antigorite recrystallizes into a lower defect phase. This interpretation is supported by the observation that the antigorite X-ray diffraction peaks at 783ºC (Figs 2d and 3d) that is after the dehydroxylation endothermic peak but before the exothermic peak are broader than those at 900ºC (Figs 2e and 3e) after the exothermic peak. This narrowing of the diffraction peaks can be understood as a decrease of the defects in the material produced by the recrystallization process. It is also noteworthy that the temperature of the recrystallization is totally independent of the particle size.

Conclusions

The thermal behaviour of antigorite sample is strongly influenced by the sonication treatment. Thus, the mass losses shown by DTG curves and the endothermic effects due to dehydroxylation are shifted to lower temperatures after sonication during 20 h. Longer sonication times do no modify the temperature of this effect, but two new effects appear whose intensity increases with the sonication time are observed. The modification in the temperature of these effects could not be attributed to structural changes, because X-ray diffraction has shown that the antigorite samples do not show significant alteration, but to the observed decrease in particle size with sonication in agreement with other sonicated laminar silicates. Sonication also produces increases in the mass loss in the range from room temperature to 150ºC that could be attributed to adsorbed water due to the increase of surface area, loosely bound OH, or prototropic effect. By high temperature X-ray diffraction it has been observed that the formation of forsterite takes place simultaneously with the dehydroxylation of the antigorite. Thus, the high temperature peak that is traditionally attributed to the formation of forsterite should be assigned to a recrystallization process as indicated by the narrowing of the diffraction peaks. This exothermic effect is not affected by the particle size reduction produced by the sonication treatment.

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