

THERMAL BEHAVIOR OF GROUND TALC MINERAL

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Dedicated to Prof. Ing. Jaroslav Šesták, DrSc. at the occasion of his 70th birthday

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Abstract

Microstructure development and thermal behavior of ground talc mineral samples (from locality Puebla de Lillo, Spain) was characterized by X-ray diffraction, scanning electron microscopy (SEM), surface area measurements differential thermal analysis, thermogravimetry and emanation thermal analysis (ETA). A vibratory mill and grinding time 5 min. was used to prepare the ground talc sample. It was found that grinding caused an increase in the surface area of the natural talc from $3 \text{ m}^2 \text{ g}^{-1}$ to $110 \text{ m}^2 \text{ g}^{-1}$. A decrease of particle size after sample grinding was observed by SEM. The increase of structure disorder of the ground sample and the crystallite size reduction from 40 to 10 nm were determined from the XRD results. ETA results revealed a closing up of surface micro-cracks and healing of microstructure irregularities on heating in the range 200 - 500°C of both un-ground and ground talc samples. For the ground talc sample a crystallization of non-crystalline phase into orthorhombic enstatite was characterized as by a decrease of radon mobility in the range 785-825°C and by a DTA exothermal effect with the maximum at 830°C. ETA results were used for the assessment of transport properties of the talc samples on heating.

Keywords: talc, grinding, microstructure, thermal behavior, radon mobility

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1. Introduction

Talc is used as raw material in the production of ceramics, as a filler in paper production and in many other industrial applications [1]. Grinding has been used to make suitable size of particles in order to control the reactivity of raw materials. It is known that dry grinding leads to random delamination of the silicate layers, to a strong structural alteration with important particle size reduction, to an increase in surface area [1]. It was demonstrated by various authors [2-5] that at the beginning of grinding of talc the original stacking layers were delaminated resulting in a decrease of particle size, in an increase of surface area as well as in an increase of structure disorder; by increasing the grinding time of the talc mineral an amorphous material can be obtained. It was observed [1,6] that grinding of the talc mineral caused modifications of its thermal reactivity.

The aim of paper is to characterize the effect of grinding on the microstructure changes and thermal behaviour of talc mineral. Results of differential thermal analysis, thermogravimetry, emanation thermal analysis, surface area measurements, X-ray diffraction, and scanning electron microscopy were used for this purpose.

2. Experimental

2.1 Samples and methods

Talc from Puebla de Lillo (Leon, Spain) [3] was studied. The idealized structural formula $Mg_3Si_4O_{10}(OH)_2$ was supposed for the talc. A vibratory mill (HERZOG, Type HSM 100) was used to produce the

ground sample. Grinding time was 5 minutes.

The B.E.T. surface area was determined by using the results of N_2 adsorption obtained by equipment Micrometrics 2200 A Model, Norcross GA (USA).

Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed in air at a heating rate $10^\circ C \text{ min}^{-1}$ by using Seiko TG/DTA 6300 equipment. Emanation thermal analysis (ETA) measurements were carried out on heating in air at a heating rate of 10 K min^{-1} , using the updated NETZSCH ETA-DTA instrument, type 404. The ETA [7-10] involves measurements of radon release rate from samples previously labelled by ^{220}Rn atoms. The ^{220}Rn atoms were incorporated into the sample to a maximum depth 80 nm [11] due to recoil energy (85 keV atom^{-1}), which the atoms gained by the spontaneous α -decay.

ETA has been already used to characterize microstructure changes in surface and subsurface of the samples during heating [7-10]. An increase in the emanation rate, E, may characterize an increase of the surface area of the interfaces, whereas the decrease in E may reflect processes like closing up structure irregularities that serve as paths for radon migration, closing pores and/or a decrease in the surface area of the interfaces [10]. This method was already used in the characterization the thermal behaviour of various minerals, such as kaolinite [12], montmorillonite saturated with various cations [13], vermiculite [14,15], boehmite [16], brannerite [17], hematite [18].

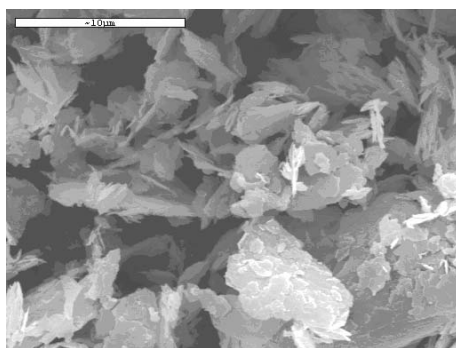
X-Ray diffraction was measured by using the Siemens Kristalloflex D-501 equipment.

The diffractometer with Cu K_{α} radiation 40 kV and 40 mA was used. The values of coherent scattering thickness (crystallite size) were determined from the Scherrer's equation [19] and by using the MudMaster software. SEM micrographs were obtained by using JEOL equipment, model JSM 5400.

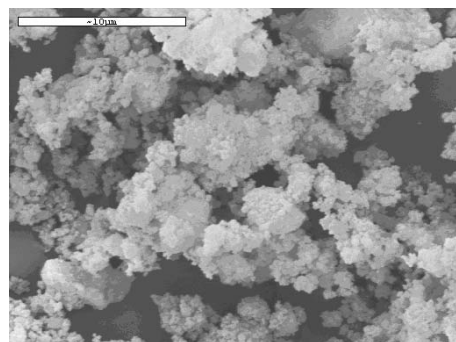
3. Results

3.1 Microstructure properties of the un-ground and ground talc samples

From SEM micrographs (Fig.1) it is obvious that 5 min. grinding caused a reduction in particle size and changes in their shape. From XRD patterns (Fig.2) it followed that grinding produced the structural alteration with smearing of the [001] basal reflections.



a)



b)

Fig.1. SEM micrographs of talc samples
a) un-ground sample, b) ground sample

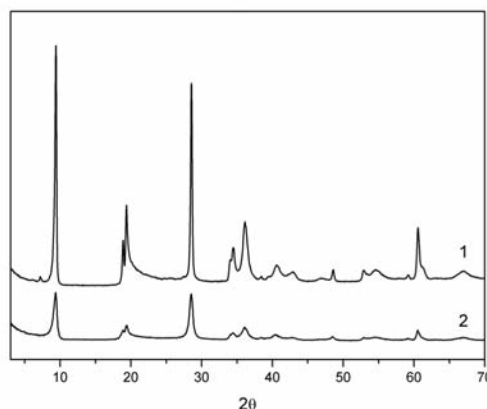


Fig.2. XRD patterns of talc samples
curve 1 - un-ground sample,
curve 2 - ground sample

The values of the crystallite size determined from the Scherrer's equation [19] indicated the reduction of thickness due to crystalline degradation along [001] basal reflection. It was determined that the crystallite size decreased due to sample grinding from 40 to 10 nm.

From B.E.T. surface area measurements it followed that the surface area of natural talc before grinding was $3 \text{ m}^2\text{g}^{-1}$ and that it increased after grinding to $110 \text{ m}^2\text{g}^{-1}$.

Results of TG and DTA presented in Fig.3a,b characterized the thermal behavior of natural un-ground and ground talc samples, respectively. From the TG results of the ground talc sample (Fig.3b) it followed that a mass loss took place decrease in the range from 30°C up to 150°C . Only a small mass loss was observed in this temperature range with the un-ground sample (Fig.3a). These results are in agreement with the observed particle size diminution and surface area evolution of the ground sample and are associated with the weakly bound OH groups on the broken edges of the ground talc particles.

From Fig. 3a it followed that on further heating of the natural un-ground talc sample an DTA endothermal effect was observed in the range of 960°C, due to the loss of structural water and accompanied by the formation of enstatite (MgSiO_3) and silica[20]. This was confirmed by the mass loss that took place with the natural un-ground talc sample in range 900 - 1050°C.

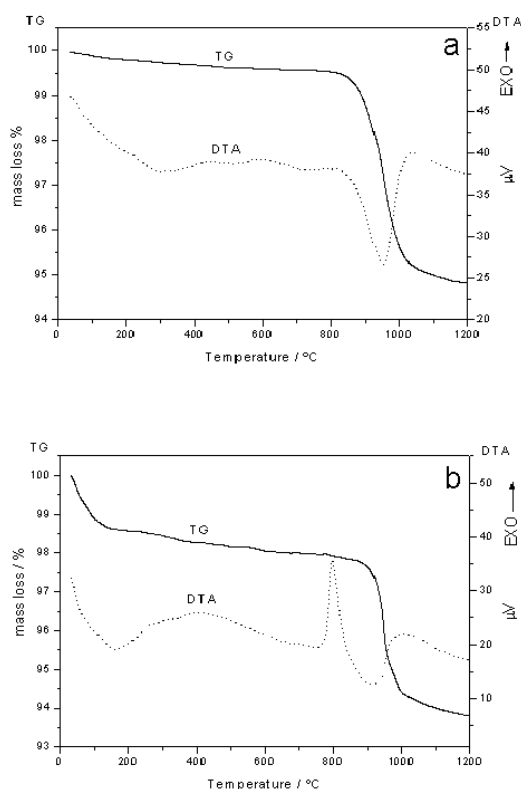


Fig.3. Results of DTA and TG of talc samples measured during heating and subsequent cooling in air: a - un-ground, b - ground sample

The DTA results in Fig.3b confirmed that grinding enhanced the formation of high temperature phases of the talc. An exothermal effect at 830°C characterized the crystallization of non-crystalline phases, formed by grinding of the talc sample, into

orthorhombic enstatite [20]. No exothermal DTA effect was observed with the natural un-ground talc sample (Fig.3a). A mass loss observed by TG (Fig.3b) in the range 900-1000°C characterized the loss of structural water due to dehydroxylation of the ground talc.

Fig.4 depicts the ETA results used to characterize the effect of grinding on the thermal behaviour of the natural talc mineral. The ETA results are presented in Fig.4 as temperature dependences of the emanation rate, $E(T)$ in the form of experimental data (points) and as curves (lines) obtained by fitting of the ETA experimental data with a mathematical model [21]. The ETA results brought about a new information about the thermal behavior of the talc samples. The increase in emanation rate, $E(T)$, observed in the range 30-250°C is in agreement with an assumption that grinding caused delamination of the silicate layers, a strong structural alteration with important particle size reduction and an increase in surface area of the talc mineral. It was assumed that the increase of the emanation rate, $E(T)$ in the range 30 - 250°C was due to radon diffusion along micro-cracks and micropores that served as radon diffusion paths. A "single jump" random diffusion mechanism was supposed to take place in this temperature range in the sample labeled by radon to the depth of 80 nm [11].

The decrease of the emanation rate, $E(T)$, in the range 250 - 450°C indicated a closing up the micro-cracks that served as paths for radon migration. No changes in the $E(T)$ were observed in the temperature range 600-800°C, consequently, no microstructure changes were supposed in this range.

However, on heating in the range of 785 - 870°C an abrupt decrease of $E(T)$ was

observed in Fig. 4b with the ground sample, ascribed to the crystallization of non-crystalline phase into orthorhombic enstatite [4,20]. On the contrary, no decrease of the emanation rate, $E(T)$, was observed for the un-ground talc sample at this temperature range (Fig.4a). This is in agreement with the DTA experimental data (Fig.3a).

The increase of the emanation rate $E(T)$ observed on heating above 870°C (Figs.4a,b) for both un-ground and ground talc samples, respectively, was ascribed to the enhanced mobility of radon in bulk of the samples. The loss of structural water from the talc samples took place in this temperature range as observed by TG (Fig.3a,b). However, the increase of emanation rate, $E(T)$ observed on heating of the sample in the temperature range above 1000°C differed for un-ground and ground talc sample(Fig.4), corresponding to the differences in the structure development of the respective samples. Hence, the ETA made it possible to characterize differences in the transport properties and microstructure development during thermal treatment of the ground and un-ground samples, respectively.

The ETA experimental data were used to assess the radon mobility on heating in both un-ground and ground talc samples.

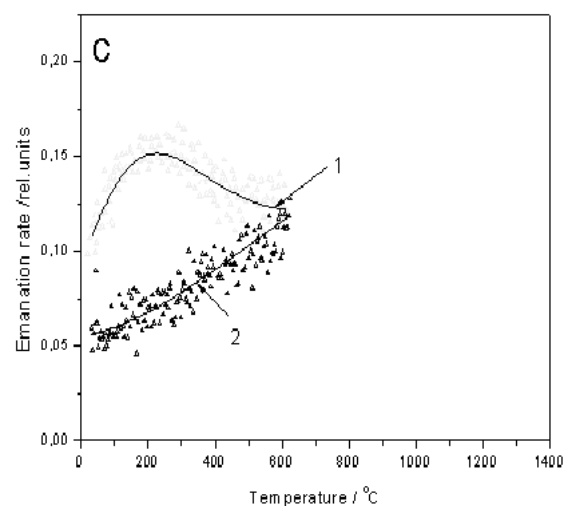
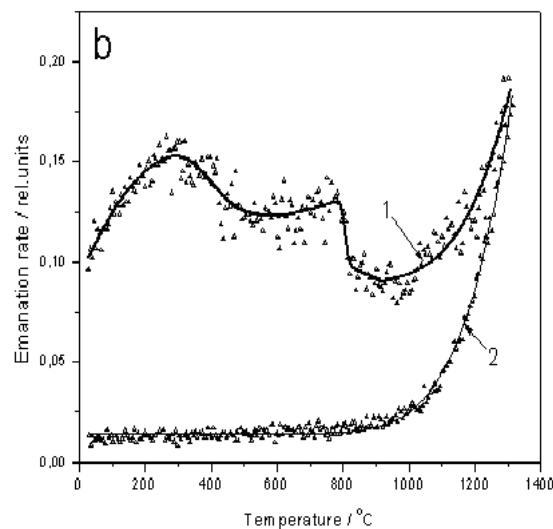
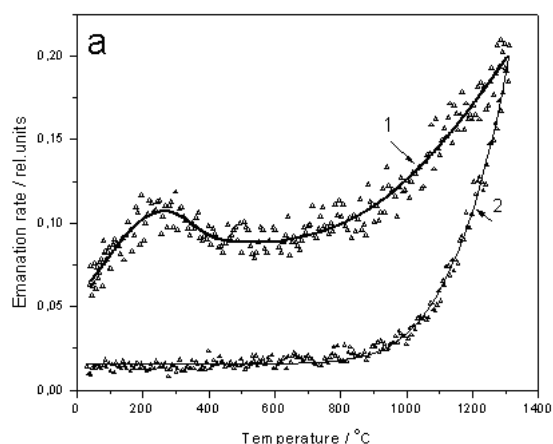


Fig.4. Emanation thermal analysis (ETA) results of talc samples. Temperature dependences of the emanation rate, $E(T)$ in the form of experimental data (points) and curves (lines) obtained by fitting the experimental data with a mathematical model:

a) un-ground sample heating to 1300°C

b) ground sample heating to 1300°C ,

c) ground sample heating to 600°C ,

Curves 1 and 2 were measured on sample heating and cooling, respectively.

3.2 Evaluation of the ETA results and transport properties of talc samples

The emanation rate E_D , due to radon diffusion can be expressed as [7,10]:

$$E_D = S (D/\lambda_{Rn})^{1/2} \cdot K \quad (1)$$

Where S is surface area, D is coefficient of radon diffusion in the sample,

$$D = D_0 \exp(-Q_D/RT), \quad (2)$$

Q_D is activation energy of radon diffusion, R is molar gas constant,

λ_{Rn} - is decay constant of the ^{220}Rn , K is a constant depending on temperature, T is temperature in [K].

The temperature dependences of the emanation rate, E_D , were used in the evaluation of ETA results and for the assessment of transport properties of the samples. Several diffusion mechanisms for radon release from the labelled samples were considered, depending on the temperature range [21]. On heating of the talc sample in a temperature range up to about 250°C the diffusion in open pores was supposed. It was assumed that radon migration along intergranular space or interface boundaries and the bulk diffusion in the matrix took place at more elevated temperatures. Changes in the temperature dependences of the emanation rate, $E(T)$, can be expressed as

$$E(T) = E_D(T) \cdot \Psi(T) \quad (3)$$

The Eq. 3 is a product of two functions: $E_D(T)$ characterizing the radon permeability along structure irregularities that served as radon diffusion paths, and $\Psi(T)$

characterizing the changes in the number of the radon diffusion paths. The radon diffusion along several independent paths were considered.

Temperature dependences of the radon release obtained by ETA were used for the determination of radon diffusion parameters, i.e. the radon permeability assessment and the characterization of transport properties that accompanied the microstructure development on heating the samples.

Following equations were used to fit the experimental ETA data. The equation describing the radon release rate, E_D , due to diffusion is given in Eq.(4)

$$E_s(T) = A [F(T_0) - F(T)] \quad (4)$$

$$\text{where } F(T) = \frac{1}{k_{D0} \exp\left(-\frac{Q_D}{RT}\right) + \lambda_{Rn}},$$

$A = \lambda_{Ra} C_{Ra}$ is a coefficient of parent nuclides concentration, $\lambda_{Ra} = 2.2035 \cdot 10^{-6} [\text{s}^{-1}]$, C_{Ra} is the equilibrium concentration of ^{224}Ra , the decay constant of ^{220}Rn $\lambda_{Rn} = 1.2464 \cdot 10^{-2} [\text{s}^{-1}]$, T_0 is the initial heating temperature;

k_D is the rate constant of radon diffusion, depending on temperature according to Arrhenius relationship,

$$k_D = k_{D0} \exp(-Q_D/RT) \quad (5)$$

where Q_D is activation energy of radon diffusion, the molar gas constant

$$R = 8.314 [\text{Jmol}^{-1}\text{K}^{-1}]$$

Eq.6 was used for the description of changes due to closing up microstructure changes that served as radon diffusion paths

$$\Psi(T) = 1 - \frac{\kappa}{2} \cdot \left[1 + \operatorname{erf} \frac{1 - \frac{T_m}{T}}{\frac{\Delta T \sqrt{2}}{T}} \right] \quad (6)$$

where erf is the sign for the integral Gauss function,

T_m is the temperature of the maximum rate of the healing of radon diffusion paths and ΔT is the width of at half height of the effect corresponding to the first derivative of $\Psi(T)$.

Transport properties of the talc samples were calculated from the ETA results (Figs.4a,b) by using the radon mobility measured in the temperature intervals 20-400°C and 900-1250°C, respectively. The parameters characterizing the radon mobility (values of activation energy of radon diffusion Q_D and constant k_0) for the un-ground and ground talc samples were determined by using Eq.5 and are summarized in Table 1.

5 ± 0.4 [kJ mol⁻¹ and values of $k = 6.8$ [s⁻¹] and 0.1 [s⁻¹], respectively (Table 1).

Hence, the grinding enhanced the radon mobility in surface and subsurface of the talc samples in this temperature range due to radon diffusion along micro- cracks and micro- pores.

In the temperature range of 900-1250°C following values of activation energy of radon diffusion were determined for the un-ground and ground talc samples: $Q_D = 68 \pm 4$ [kJmol⁻¹] and 232 ± 9 [kJmol⁻¹] and values of $k_0 = 0.7$ [s⁻¹] and $5.8 \cdot 10^5$ [s⁻¹], respectively.

These values of activation energy Q_D of radon migration by bulk diffusion mechanism characterized differences in transport properties of the un-ground and ground talc samples. In the un-ground talc heated to 870°C the radon mobility was

Table 1. Radon mobility of talc mineral samples

Sample treatment (grinding and maximum heating temperature)	Measured on heating				Measured on cooling			
	Temperature range 20 - 400°C		Temperature range 900 - 1250°C		Temperature range 600 - 50°C		Temperature range 1250 - 50°C	
	Q_D [kJmol ⁻¹]	k_0 [s ⁻¹]	Q_D [kJmol ⁻¹]	k_0 [s ⁻¹]	Q_D [kJmol ⁻¹]	k_0 [s ⁻¹]	Q_D [kJmol ⁻¹]	k_0 [s ⁻¹]
1 Un-ground / 1300°C	21 ± 3	6.8	68 ± 4	0.7	–	–	127 ± 7	10
2 Ground / 600°C	5 ± 0.4	0.1	–	–	14 ± 3	6.5	–	–
3 Ground / 1300°C	5 ± 0.4	0.1	232 ± 9	$5.8 \cdot 10^5$	–	–	151 ± 8	96

Transport properties of the un-ground and ground talc samples were characterized in the temperature range 20-400°C by following activation energy values of the radon diffusion : $Q_D = 21 \pm 3$ [kJmol⁻¹] and

higher (the value of $Q_D = 68 \pm 4$ [kJ .mol⁻¹]) as compared to the ground talc sample ($Q_D = 232 \pm 9$ [kJ mol⁻¹]) heated to the same temperature of 870°C. This is in agreement with our observations obtained by thermal

analysis and other methods in this study.

The decrease of the emanation rate, $E(T)$, observed by ETA (curves 1, Figs. 4 a, b) on heating in temperature range up to 450°C was ascribed to the healing of structure irregularities that served as radon diffusion paths, whereas the decrease the emanation rate $E(T)$ in the temperature range 800-870°C corresponded to the crystallization of non-crystalline phase into orthorhombic enstatite.

Moreover, it was of interest to evaluate transport properties of the heat-treated talc samples to 1300°C. These samples can be considered as intermediate products of model talc based ceramics prepared from the un-ground and ground talc samples, respectively.

The ETA results presented in Figs. 4 a,b as curves 2 were used to characterize the transport properties of the samples pre-heated to 1300°C. Radon diffusion characteristics, namely the values of the activation energy Q_D and of the constant k_0 , for the respective natural un-ground and ground talc samples heat treated to 1300°C, were evaluated from the ETA results by using Eq.5 and are presented in Table 1. The corresponding values of activation energy Q_D and constant k_0 for the natural un-ground and ground talc samples are : $Q_D=127 \pm 7$ [kJmol⁻¹] and 151 ± 8 [kJmol⁻¹] and values $k_0=10$ [s⁻¹] and 96 [s⁻¹], respectively.

Consequently, it was assumed that the transport properties of the samples prepared by the heat treatment to 1300°C are slightly higher for the sample prepared from the natural un-ground talc in comparison to the sample prepared from the ground talc

sample. This confirmed the assumption that grinding facilitated the formation of high temperature phases [20] .

The ETA results measured during sample cooling made it possible to compare the transport properties of the intermediate products of talc based model ceramics samples prepared by heat treatment to 600°C and to 1300°C, respectively. The radon diffusion characteristics of the ground talc sample heated to 600°C were calculated by using ETA experimental data in Fig.4c, curve 2 and are summarized in Table 1.

From Table 1 it is obvious that the ground talc heat treated to 600°C has a considerably higher permeability for radon (radon diffusion activation energy $Q_D = 14 \pm 3$ [kJ mol⁻¹]) in comparison with the sample prepared by heat treatment to 1300°C (radon diffusion activation energy $Q_D = 151 \pm 8$ [kJ mol⁻¹]).

This is in agreement with the results of other methods demonstrating that the microstructure of the samples heated to temperatures 600°C and 1300°C differed.

Figure 5 depicts the results of the temperature dependences of the function $\Psi(T)$ calculated from the ETA experimental data presented in Figs 4 a,b. by using Eq.6. The function $\Psi(T)$ quantitatively described the microstructure changes by using the decrease of the radon mobility in the samples. The healing of surface cracks and structure irregularities that served as radon diffusion paths was characterized by ETA results on heating the un- ground and ground talc in the temperature range up to 400°C.

Moreover, microstructure changes corresponding to the crystallization of the non-crystalline phase into orthorhombic enstatite were revealed with the ground talc

sample by a decrease of emanation rate $E(T)$ in the range from 785°C to 870°C .

By this way the ETA results brought about an additional information about changes in the transport properties of talc samples on heating. By using this approach it was possible to determine the intensity of the radon mobility changes influenced by the processes in the mentioned temperature ranges.

Table 2 summarizes the temperature intervals (determined by temperatures T_{onset} and T_{final}) of closing up structure irregularities and the maximum rate (T_m) of this process for the talc samples investigated. It followed from Fig.5 and Table 2 that for the ground talc sample the onset of the closing up surface cracks and subsurface structure irregularities was shifted to higher temperatures and the intensity of the annealing was enhanced by 26% (see Fig.5, curves 1 and 2).

As to microstructure changes due to the crystallization of non-crystalline phase into orthorhombic enstatite, observed with the ground talc sample on heating in the range from 785°C up to 865°C, the ETA results made it possible to assess the decrease of the radon mobility in this temperature range and to compare it with the radon mobility changes in the range 250 -450°C (see Fig.5, curves 2 and 2').

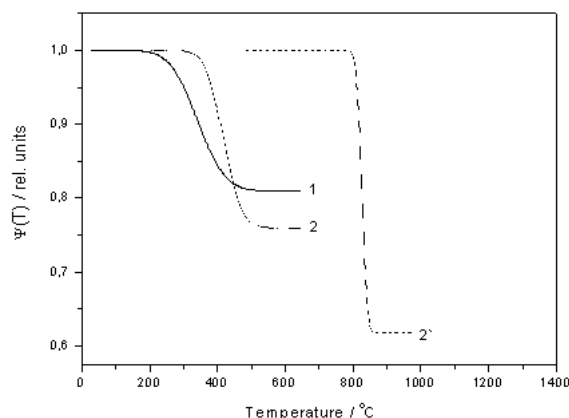


Fig.5. Temperature dependences of $\Psi(T)$ function obtained by evaluation of ETA results .

Curves 1 and 2 correspond to annealing of surface cracks and subsurface structure irregularities that served as radon diffusion paths on heating the un-ground and ground talc samples in the range 200-550°C ,

Curve 2' corresponds to a decrease of radon mobility due to crystallization of non-crystalline phase into orthorhombic enstatite on heating the ground talc sample in the range 785-865°C

From Fig. 5 and Table 2 it followed that the closing up surface cracks and structure irregularities in the range 250 - 450°C represented a less intense decrease of the radon mobility of the talc sample as compared to the crystallization of non-crystalline phase into orthorhombic enstatite, observed with the ground talc in the range 785 - 865°C. It should be mentioned that

Table 2 –Healing of microstructure irregularities of un-ground and ground talc mineral samples characterized by a decrease of radon mobility

Sample	Closing up of microcracks on heating up to 550°C				Crystallization of non- crystalline phase and formation of enstatite			
	T_{onset}	T_{final}	T_{max}	$\Delta\Psi_1$	T_{onset}	T_{final}	T_{max}	$\Delta\Psi_2$
	[°C]	[°C]	[°C]	[%]	[°C]	[°C]	[°C]	[%]
Un-ground	190	490	342.2	19	–	–	–	–
Ground	280	550	417.9	24	785	865	825	49

with the un-ground sample, no decrease of E was observed above 800°C.

The results presented in Fig.5 characterized the microstructure development of the talc samples and contributed to evaluate their transport properties on heating by using the radon mobility.

4. Conclusions

From results of TG and DTA it followed that grinding caused a decrease of the temperatures of the release of structure bound OH groups and of the crystallization of non-crystalline phase into orthorhombic enstatite. The results of emanation thermal analysis characterized closing up of microstructure irregularities on heating of both natural and ground talc samples as a decrease the radon release rate E in the range 200 - 500°C .

For the ground talc sample a crystallization of non-crystalline phase, formed by grinding, into orthorhombic enstatite was characterized as by a decrease of radon mobility in the range of 785 - 825°C and by the DTA exothermal effect in the range of 830°C. ETA results can be used for the assessment of transport properties of the talc samples on heating.

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