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USE OF EMANATION THERMAL ANALYSIS TO CHARACTERIZE THERMAL REACTIVITY OF BRANNERITE MINERAL

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Emanation thermal analysis (ETA) was used to characterize the thermal reactivity of amorphous brannerite mineral of general formula $U_{1-x}Ti_{2+x}O_6$ (locality El Cabril, near Cordoba, Spain). It was demonstrated that on sample heating up to 880°C microstructure changes taking place in the sample were accompanied by the formation of new radon diffusion paths, followed by their closing up during the final transformation of amorphous to crystalline brannerite in the range 900–1020 °C. Relative changes in structure irregularities that served as radon diffusion paths during heating and subsequent cooling of the sample to temperatures of 300, 550, 750, 880, 1020 and 1130°C, respectively, were determined from the ETA results. Mass losses in temperature ranges of 230–315, 570–760 and 840–1040°C were observed by thermogravimetry. Mass spectrometry indicated the release of CO_2 mainly due to the decomposition of minor carbon amount in the brannerite mineral sample.

Keywords: *brannerite, emanation thermal analysis, MS, SEM, thermal reactivity, thermogravimetry*

Introduction

Brannerite mineral with the general formula $U_{1-x}Ti_{2+x}O_6$ can be found in nature as amorphous due to α-decay damage caused by high content of U, Th. Natural brannerite generally contains impurity elements like Pb, Ca, Th, Y and REE on the U-site and Si, Al and Fe on the Ti-site [1]. Brannerite is a minor phase in titanate-based ceramics designed for the geological immobilization of surplus Pu [2–4]. Therefore, it was of interest to investigate the thermal behavior of brannerite mineral as a natural analog of the brannerite ceramics to be used for immobilization of hazardous radioactive elements. The re-crystallization of natural amorphous brannerite on annealing at temperatures of ~1000°C has been studied by X-ray diffraction (XRD), thermogravimetry (TG), differential thermal analysis (DTA) and scanning/transmission electron microscopy [5–7].

In this paper, emanation thermal analysis (ETA) has been used to characterize the thermal reactivity, formation and annealing of the structure irregularities in the sample on heating to various temperatures up to 1200°C. The ETA results are discussed in comparison with thermogravimetry, DTA and scanning electron microscopy.

Experimental

Sample

The natural brannerite mineral of general formula $U_{1-x}Ti_{2+x}O_6$ was from locality El Cabril mine, near Cordoba, Spain. The sample was X-ray amorphous and contained Ca, Pb and other impurity elements [6, 8].

Methods

ETA measurements were carried out by using modified NETZSCH DTA-ETA equipment Type 404. Details of ETA measurements and data treatment have been described elsewhere [9, 10]. ETA involves measurements of radon release rate from samples previously labelled. The sample amount of 0.122 g was heated at the rate of 6 K min^{-1} in argon carrier gas, which took the released ^{220}Rn into the detector chamber [9]. The specific activity of the labelled samples was 10^5 Bq g^{-1}. The ^{224}Ra and ^{220}Rn atoms were incorporated into the sample due to recoil energy (85 keV $atom^{-1}$). The maximum depth of ^{220}Rn penetration was 80 nm as calculated with Monte Carlo method using TRIM code [11].

TG and DTA measurements were carried out using NETZSCH STA 404 equipment. The sample amount of 0.043 g was placed in an alumina crucible and heated at the rate of 6 K min^{-1} in the argon flow.

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SEM micrographs were obtained with PHILIPS Equipment (Type XL 30CP).

Results and discussion

Figure 1 shows ETA results of the brannerite mineral sample measured during heating in an argon flow in the temperature range 20–1200°C and during heating runs and subsequent cooling runs in this temperature range, respectively. Curves 1a and 1b depict ETA results measured during the heating run and subsequent cooling run in the range from 20 to 1200°C. The increase of emanation rate, *E*, observed in the temperature range of 40–300°C characterized the diffusion mobility of radon atoms along surface cracks and other subsurface defects to the depth of 80 nm. The effect superimposed on the smooth ETA curve in the range of 200–250°C indicated that microstructure changes took place in this range.

From TG results (Fig. 2) it followed that in the temperature ranges from 200–300, 570–760 and 840–1040°C mass losses of 0.93, 2.04 and 1.69%, respectively took place. The release of CO_2 was detected by mass spectrometry in these temperature ranges. Consequently, a thermal degradation of minor carbonate containing components of the sample took place. Moreover, we assumed that the mass decrease in the range 840–1040°C was associated with the reduction of Pb and Ca impurities. As it has been published in [8] the amount of CaO, PbO and other impurities of the brannerite mineral decreased on sample heating from 900 to 1100°C. From Fig. 2 it followed that the re-crystallization of the sample was accompanied by a DTA exothermal effect with maximum at 740°C.

It should be mentioned that the release of CO_2 observed in the temperature range before the sample re-crystallization gave rise to porosity of the sample. The microstructure changes associated with the changes of the sample porosity were indicated by the ETA results during heating and subsequent cooling in the selected temperature intervals (Fig. 1). The slight decrease of *E* observed in Fig. 1, curve 1a in the temperature range of 400–500°C indicated an annealing of surface cracks and voids. On further heating in the range of 550–750°C the values of the emanation rate, *E*, did not change. The effect observed on the ETA curve in the range 800–880°C was ascribed to a closing up porosity of the sample considered as the first step of the formation of crystalline brannerite. The increased emanation rate observed in range 900–965°C indicated the next step of the phase transition resulting in the formation of crystalline brannerite [6, 7]. The sample was heated up to 1200°C and subsequently cooled at the same rate to room temperature. As it followed from the SEM micrographs in Fig. 3 the microstructure of the brannerite samples before and after heating to 1200°C differed.

In order to characterize in details the annealing of brannerite microstructure on heating in argon, the ETA measurements during subsequent heat-treatments of the sample to selected temperatures were carried out.

The temperatures for the heat treatments were selected as 300, 550, 750, 880, 1020 and 1130°C. The heating at the rate of 6 K min^{-1} to the selected temperature was followed by cooling runs to room temperature at the same rate. The ETA results measured during the heat treatments are presented in Fig. 1 as curves 2a/2b to 7a/7b, respectively, and compared with the ETA results measured in the temperature range 20–1200°C (curve 1a, Fig. 1).

Before and after each heat treatment the emanation rate values *E*(r.t.), were measured at room temperature, with the aim to obtain a parameter proportional to the surface area [9]. The results are presented in Fig. 4.

It should be mentioned that the emanation rate *E*, measured at a constant temperature depends on surface area as follows [9]

$$E=E(\text{recoil})+E(\text{pores})+E(\text{solid}) \quad (1)$$

The emanation rate due to recoil, *E*(recoil), can be expressed as

$$E(\text{recoil})=K_1S_1 \quad (2)$$

where K_1 is a temperature independent constant, proportional to the penetration depth of recoiled radon atoms in solids investigated and S_1 is external geometrical surface area of sample particles. The emanation rate due to surface diffusion in pores, *E* (pores), is

$$E(\text{pores})=K_2S_2 \quad (3)$$

where K_2 is a constant that depends on temperature and S_2 is internal surface area of the sample depending on the surface of open pores, cracks and intergranular space. The emanation rate due to volume diffusion in a solid sample, *E*(solid), can be expressed as

$$E(\text{solid})=K_3\exp(-Q/2RT)S_3 \quad (4)$$

where K_3 is a constant related to the atomic properties of the lattice, Q is the activation energy of Rn diffusion in solid matrix, S_3 is surface area, R is molar gas constant, and T is temperature.

The increase in the emanation rate (*E*) may characterize an increase of the surface area of interfaces, whereas a 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 [9, 10, 12, 13].

From the temperature dependences of the emanation rate *E*, measured during the constant rate heat-

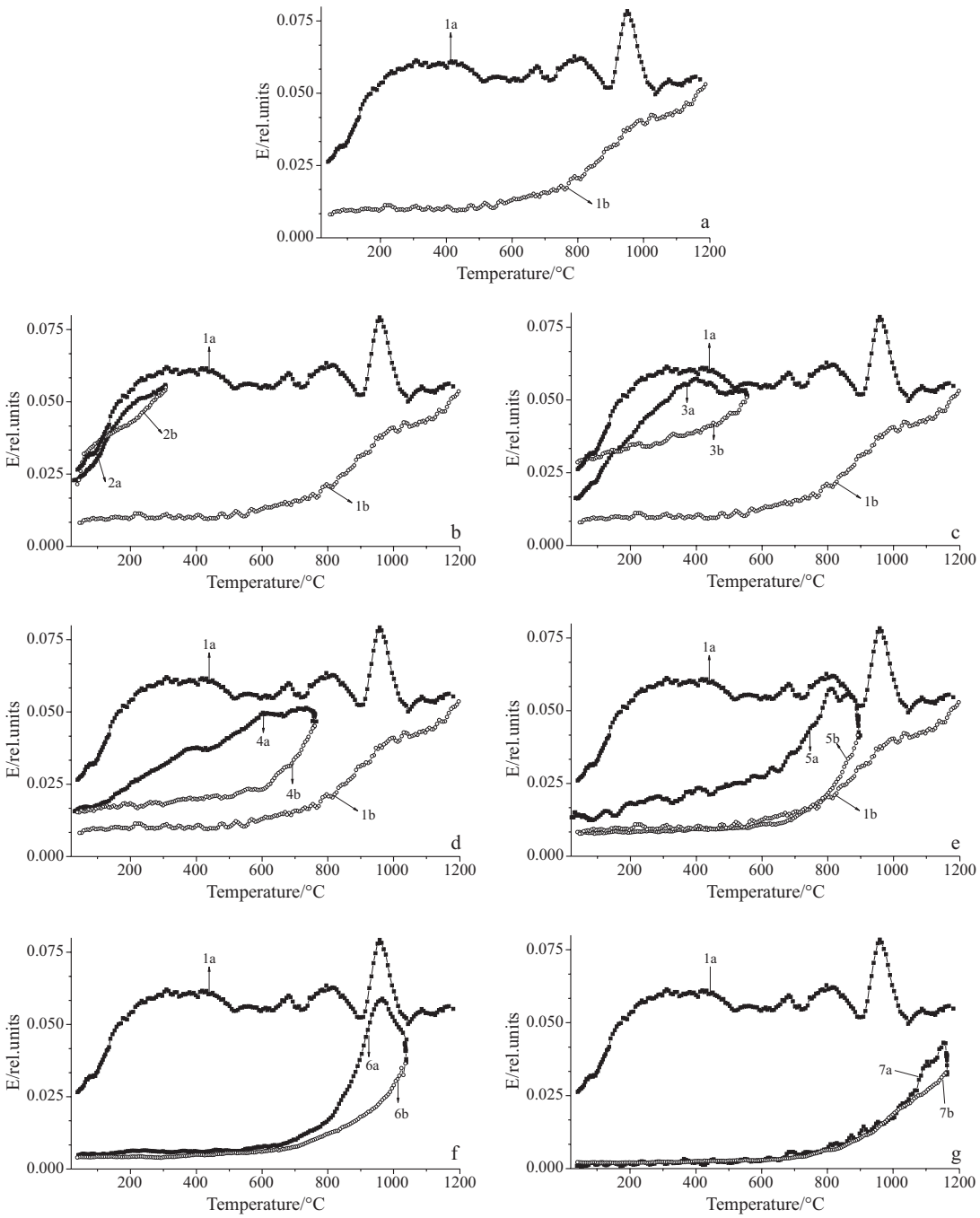


Fig. 1 Emanation thermal analysis results of natural brannerite mineral sample measured on heating and subsequent cooling in argon in the range 20–1200°C: curves 1a/1b were measured during heating and subsequent cooling in the range from 20 to 1200°C, curves 2a/2b, 3a/3b, 4a/4b, 5a/5b, 6a/6b and 7a/7b were measured with a parallel sample on the 'step by step' heating and subsequent cooling runs to the selected temperatures of 300, 550, 750, 880, 1020 and 1130°C, respectively

ing and subsequent cooling for each heat treatment step the values of defect amount characteristics ξ were determined as a parameter characterizing the amount of structure irregularities which served as diffusion paths for radon and determine the diffusivity (permeability) of radon atoms (atom size 0.4 nm) in the pre-heated sample.

The parameter ξ was defined as:

$$\xi(T) = \int_{T_{min}}^{T_{max}} E(T)_{heating}\,dT - \int_{T_{min}}^{T_{max}} E(T)_{cooling}\,dT \qquad (5)$$

The ETA results demonstrated in Fig. 1 as curves 2a–7a and 2b–7b were measured during step by step heating runs from 20 to selected temperatures of 300, 550, 750, 880, 1020 and 1130°C and subsequent cooling runs to room temperature, respectively.

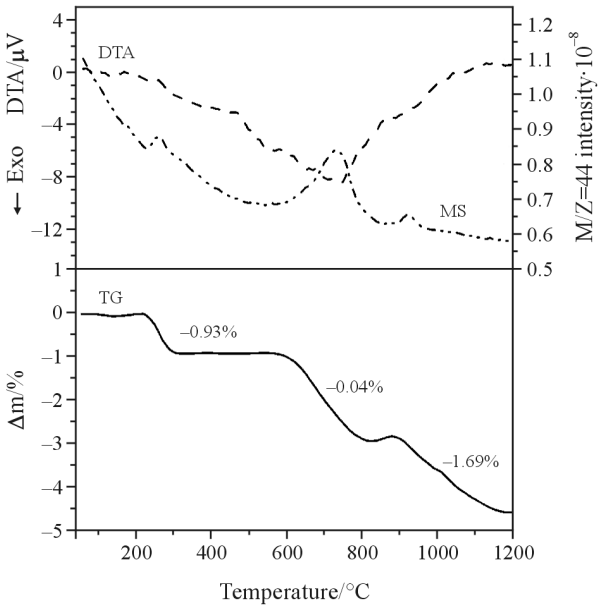
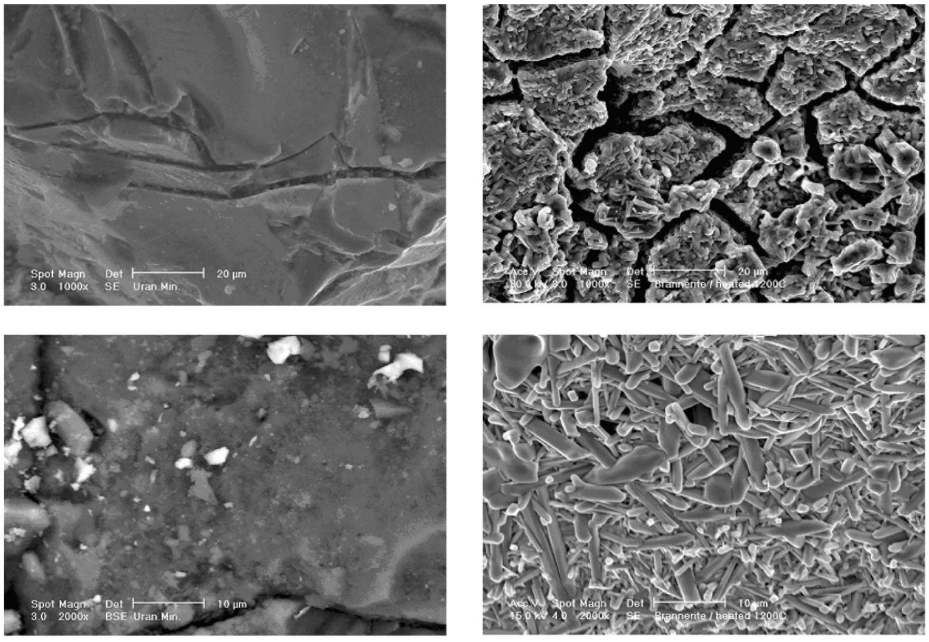


Fig. 2 Results of TG/DTA coupled with mass spectrometry (MS) detection of volatile products (CO_2) obtained during heating of as received brannerite mineral sample in argon

The curves 2a and 2b in Fig. 1 demonstrated a good reproducibility of the effects already observed with the parallel sample as curve 1a, that during the heating in the range 20–300°C, a microstructure change of the sample took place, as indicated by the effect at the temperatures 200–250°C, superimposed on the smooth increase of the radon release rate. From the ETA results measured on cooling from 300°C to room temperature (see curve 2b) it followed that the microstructure changes were irreversible.

The ETA curves 3a/3b, 4a/4b and 5a/5b in Fig. 1 characterized the thermal behavior of brannerite sample pre-heated to 300, 750 and 880°C, respectively. The increase of the emanation rate, *E*, in the temperature range of 20–360°C, corresponding to the diffusion of radon along micropores in the sample, was followed by the decrease of *E*, characterizing the partial annealing of voids and structure irregularities serving as diffusion pathways for radon.

It should be mentioned here that the emanation thermal analysis revealed sensitively the differences in the amount of structure irregularities that served as radon diffusion paths in the amorphous brannerite mineral sample. These differences were most remarkably demonstrated by breaks observed on the ETA curves at maximum temperatures used for the 'step by step' heating and the following cooling of the samples, i.e. at temperatures of 550, 750 and 880°C, respectively (Fig. 1, curves 3a/3b, 4a/4b, 5a/5b). The curves 6a/6b in Fig. 1 characterized the thermal behavior of the sample pre-heated to 880°C. As already observed by curve 1a in Fig. 1 the structure irregularities serving as radon diffusion paths were further diminished in the sample pre-heated to 880°C. The increase of the emanation rate on sample heating above 600°C reflected an enhanced radon diffusion in the sample matrix, whereas the sharp decrease observed on heating above 970–1020°C indicated the next step of the formation of crystalline brannerite. A good reproducibility of the ETA measurements can be seen



a b

Fig. 3 SEM micrographs of brannerite mineral: a – as received, non-heated sample and b – sample heated to 1200°C

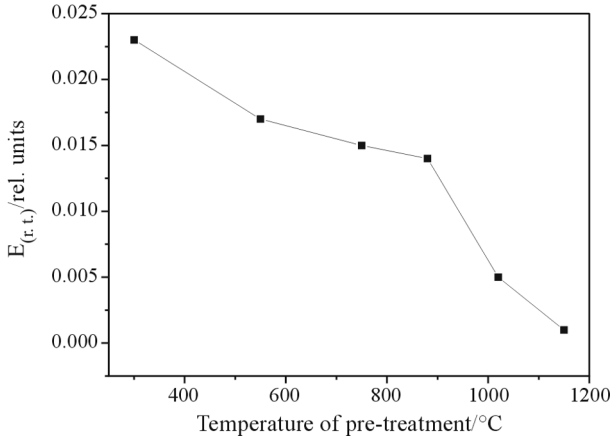


Fig. 4 The change of emanation rate values measured at room temperature, $E_{(r.\,t.)}$, before heat treatments of the brannerite sample to temperatures 300, 550, 750, 880, 1020 and 1130°C, respectively

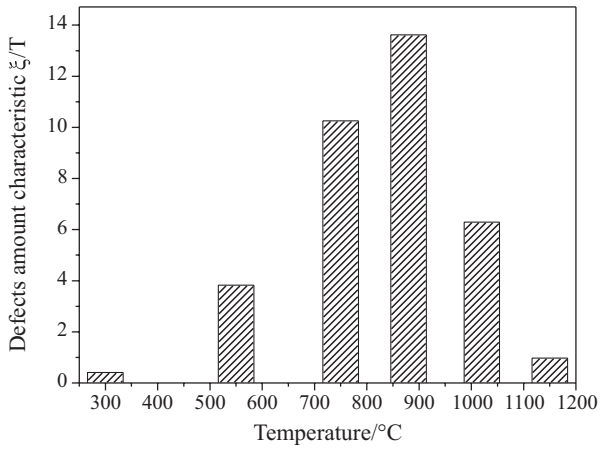


Fig. 5 Comparison of the relative amount of structure irregularities, expressed by parameter ξ, annealed in the heating runs to temperatures 300, 550, 750, 880, 1020 and 1130°C, respectively

Table 1 Emanation rate *E* and defect amount characteristics of brannerite pre-heated to various temperatures

Sample notation	Temperature range of pre-heating	Defect amount characteristics/ξ^{*}	$E_{(r.\,t.)}$/rel. units	$\Delta\xi^{**}$/%
1 as received	20–1150°C	38.10	0.026	1.00
2a as received	20–300°C	0.41	0.023	1.08
2b	20–550°C	3.82	0.017	10.02
2c	20–750°C	10.26	0.015	26.93
2d	20–880°C	13.62	0.014	35.75
2e	20–1020°C	6.30	0.005	16.54
2f	20–1150°C	0.98	0.001	2.57

$^{*}\xi(T)=\int_{T_{min}}^{T_{max}}E(T)_{heating}\,dT-\int_{T_{min}}^{T_{max}}E(T)_{cooling}\,dT$, $^{**}\Delta\xi=\frac{\xi_m}{\xi_1}\cdot 100\ [\%]$

from the temperature coincidence of the effects on the curve 1a and curve 6a in Fig. 1.

From curves 6a/6b in Fig. 1, characterizing the thermal behavior of the sample pre-heated to 1020°C, it is obvious that after the pre-heating the sample to this temperature an irreversible crystallization of amorphous brannerite took place. As it is obvious from Table 1, the number of structure irregularities serving as radon diffusion paths further diminished, the permeability of radon in the brannerite sample being considerably decreased.

Values of the emanation rate *E*(r. t.) measured at room temperature before and after each heating run were used for the assessment of the relative changes of the surface area effected by the respective heat treatments and are summarized in Table 1. The results of *E*(r.t.) are also presented in Fig. 4 for comparison. It follows from Table 1 and Fig. 4 that the *E*(r.t.) values are in agreement with the above statement regarding the annealing of surface area and surface irregularities.

The ETA results made it possible to estimate the relative contribution of the heat treatments used to the annealing of structure irregularities that served as pathways for radon diffusion characterizing the permeability of radon atoms in the samples. This contribution was calculated from the difference between the integrals of respective ETA heating and cooling curves measured during the heat treatments used. Figure 5 depicts a comparison of the relative amount of structure irregularities, expressed by parameter ξ, annealed in the respective heat treatments. The difference of integrals used for the assessment of the amount of the microstructure defects can be expressed as Δξ.

In Table 1 the values of ξ (Eq. (5)) are summarized along with the values of Δξ, defined as

$$\Delta\xi=\frac{\xi_m}{\xi_1}\cdot 100\ [\%] \qquad (6)$$

It followed from Table 1 that the most significant decrease of the structure irregularities was achieved

during the heat treatment in the temperature range of 20–880°C. This means that the major part of the structure irregularities serving as diffusion paths for radon diffusion was annealed prior to the crystallization of the sample in the range of 970–1020°C (see also Fig. 1, curves 1a and 5a).

It should be pointed out, as it followed from the increase of the emanation rate, *E*, on the sample heating that up to 880°C the microstructure changes were accompanied by the formation of new diffusion paths, followed by their annealing during the final re-crystallization stage, characterized by the decrease of *E* in the temperature range 970–1020°C.

Conclusions

Results of emanation thermal analysis measured during the heating treatments to selected temperatures up to 1200°C in argon brought about additional information on micro-structure changes in a natural amorphous brannerite sample. From the ETA results it followed that on sample heating in the range up to 880°C the microstructure changes were accompanied by the formation of new diffusion paths, followed by their annealing during the final re-crystallization stage in the temperature range 970–1020°C where the transformation of amorphous to crystalline brannerite was indicated in agreement with the X-ray diffraction results. The ETA can be recommended as a powerful tool for characterization of thermal reactivity of amorphous minerals.

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