THERMAL STABILITY AND KINETIC STUDY OF $CaSO_4$-H_2O SYSTEM

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INTRODUCTION

Sulphate minerals are the main constituent of the evaporite deposits and are used as building material. Evaporite deposits preserve a wealth of information on Earth’s past surface conditions. Such deposits are sensitive indicators of depositional environment and climate, recorded in a wide variety of mechanically and chemically produced sedimentary structures and fabrics.

Gypsum is often exploited by plaster industry, for which it represents the raw material to be transformed into hemihydrate (plaster) by dehydration at 393-453 K and atmospheric pressure. The quality and properties of the final material is influenced by the starting material and by the working process. Consequently the study of the chemical-physical features of the phases of the system $CaSO_4$-H_2O is necessary.

Despite several studies having the $CaSO_4$-H_2O system as subject, considerable debate persists on many points, such as the stability and existence of sub-hydrate phases, the mechanism of the dehydration and rehydration processes (Abriel, 1983; Abriel *et al.*, 1990; Chang *et al.*, 1999; Prasad *et al.*, 2001; Follner *et al.*, 2002; Prasad *et al.*, 2005).

Consequently much attention have to be used to define the parameters controlling hydration-dehydration processes, thermal behaviour, reaction mechanisms and empirical activation energies.

The purpose of this work is to study the thermal stability and the kinetics of phase transition within the $CaSO_4$-H_2O system. In particular, the aim is to define the phases and the mechanism of hydration and dehydration of the system $CaSO_4$-H_2O. Moreover the thermal stability of γ-anhydrite (γ-$CaSO_4$), β-anhydrite (β-$CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and bassanite ($CaSO_4 \cdot 1/2H_2O$) have been evaluated. In addition, the kinetics of dehydration of gypsum and bassanite have been studied.

Some of the investigated minerals are hygroscopic and unstable in ambient conditions and are microcrystalline. For these reasons, angular dispersive X-ray powder diffraction (ADXD) in ambient and non ambient conditions was used. Experiments were carried out *in situ real time* by measuring diffraction patterns either in isothermal or in non isothermal conditions. Non ambient data were collected on a parallel-beam Bruker AXS D8 Advance automated diffractometer operating in θ-θ geometry with a PSD Våntec-1 detector set to a 6° 2θ aperture and a prototype of capillary heating chamber (Ballirano & Melis, 2007). Diffraction data were evaluated by the Rietveld method to obtain structural and quantitative information (Young, 1993). Two softwares were used to elaborate the experimental data, GSAS (Von Dreele & Larson, 2001) and TOPAS (Bruker AXS, 2005) that implements the Fundamental Parameters Approach, FPA (Cheary & Coelho, 1992). This study is divided into three main parts. The first one is dedicated to the structural characterization of the phases of the $CaSO_4$-H_2O system. The second part is devoted to the thermal stability of the phases of the $CaSO_4$-H_2O system. The last part reports the kinetics of the dehydration of gypsum and bassanite.

STRUCTURAL CHARACTERIZATION

A preliminary study was performed to define the structural features of the sub-hydrates phases. Reference data report the existence of different sub-hydrate phases $CaSO_4{\cdot}nH_2O$ with $0.5 < n < 1$.

Gypsum, bassanite and β-anhydrite structures are known in detail. These structures were characterized to check the quality of the structural refinements at room temperature from data collected with the available instrumental set-up. Results were found to be within 3σ of the corresponding single-crystal analysis from reference data confirming the reliability of data in non ambient also.

Soluble anhydrite (γ-$CaSO_4$) has been found to crystallise in space group $P6_222$ instead of in $C222$ as reported by Bezou *et al.* (1995). The structure is based on chain of alternating edge-sharing SO_4 tetrahedra and CaO_8 dodecahedra. This is the structural motif of all phases of the $CaSO_4$-H_2O system. Chains are related by a 6-fold axis to build hexagonal channels which house the water molecules in sub-hydrate phases.

Only one sub-hydrate phase was found and described in the present work as a rehydration product of γ-anhydrite at high relative humidity (RH) conditions, $CaSO_4{\cdot}2/3H_2O$. The structure of $CaSO_4{\cdot}2/3\ H_2O$ is similar to that of bassanite ($CaSO_4{\cdot}1/2H_2O$). Both phases crystallise in space group $I2$ and are only slightly distorted from the trigonal substructure presented by Abriel & Nesper (1993). The only difference between sub-hydrate and hemihydrate structures is the H_2O position inside the channels. In hemihydrate structure one water molecule is in special position, on the contrary, in sub-hydrate structure both water molecules are in general position. Other sub-hydrate phases reported in reference data were not found. Sub-hydrate $CaSO_4{\cdot}nH_2O$ reported in reference data were identified as mechanical mixture between two phases of the system (γ-anhydrite/bassanite for $n < 0.50$ and bassanite/$CaSO_4{\cdot}2/3H_2O$ for $0.50 < n < 0.67$)

The rehydration mechanism of γ-anhydrite has been found to depend on the RH conditions: at high RH the sub-hydrate phase $CaSO_4{\cdot}2/3H_2O$ forms as intermediate product. At low RH bassanite, directly transforms to gypsum. Therefore, the rehydration mechanism could be described by reactions:

$$\gamma\text{-}CaSO_4 \rightarrow CaSO_4{\cdot}1/2H_2O \overset{\text{HR}}{\leftrightarrow} CaSO_4{\cdot}2/3H_2O \rightarrow CaSO_4{\cdot}2H_2O$$

THERMAL STABILITY

The second part of the study was devoted to the thermal expansion of the phases pertaining to the system $CaSO_4$-H_2O. Different thermal ranges were analyzed according to the stability of the different phases. In fact, determination of thermal behaviour of a phase is not reliable from mixtures because of correlations.

Thermal behaviour of all phases of system were been analyzed except sub-hydrate $CaSO_4{\cdot}2/3H_2O$ that is unstable at T exceeding 313 K.

Fig. 1 shows a magnified view of a complete data set represented under the form of a pseudo-Guinier plot. It is possible to follow the thermal expansion of the phase from the shift of the corresponding reflections.

Variation of lattice parameters and volume of each phase of the system shows that expansion is anisotropic, the exception being bassanite (Fig. 2). The expansion of γ- and β-anhydrite acts prevalently along [001] whereas gypsum expands prevalently along [010].

Thermal expansion is related to the expansion of polyhedra and to the expansion of the framework *via* tilting of polyhedra. The expansion of bond distances within a polyhedron is roughly proportional to the "softness" of the bond, therefore to its bond-valence (Brese & O'Keefe, 1991). The expansion of the

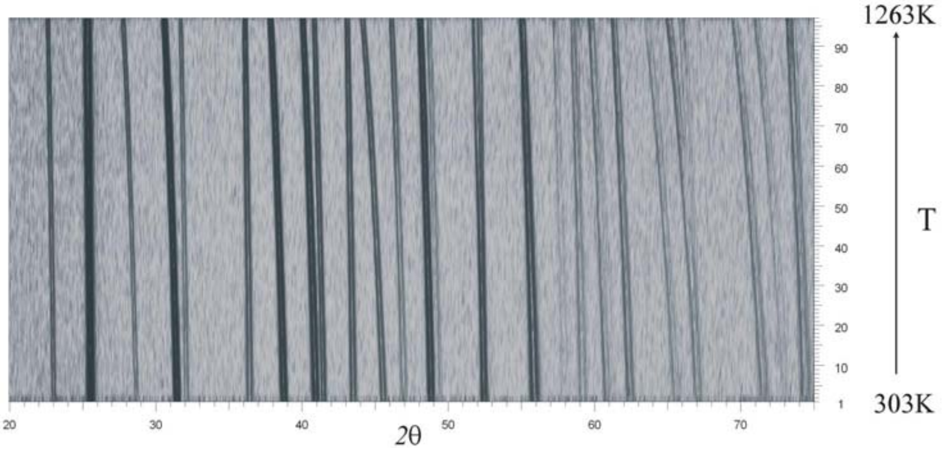

Fig. 1 – Magnified view (20-75° 2θ) of the complete data set of the thermal expansion of β-anhydrite shown as a pseudo Guinier plot.

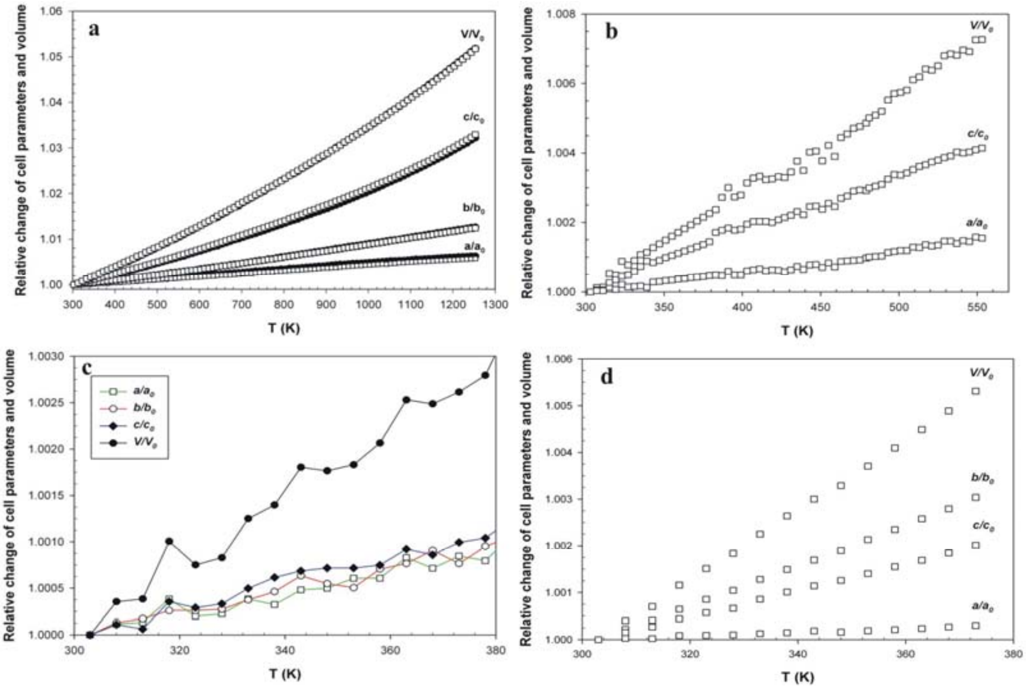

Fig. 2 – Relative expansion of lattice parameters and volume in phases of $CaSO_4$-H_2O system (***a*** β-anhydrite, ***b*** γ-anhydrite, ***c*** bassanite, and ***d*** gypsum).

framework is related to connectivity, especially to the presence of edge- or corner-sharing connections or weak-bonds between polyhedra.

Bassanite and γ-anhydrite structures are very similar with channels built by CaO_{8-9} polyhedra linked by edge-sharing to two SO_4 tetrahedra along [001]. Each CaO_{8-9} polyhedron is linked by edge-sharing to four further CaO_{8-9} polyhedra. Therefore, structure is very rigid and consequently thermal expansion of these phases is mainly due to the expansion of CaO_8 and CaO_9 polyhedra. Thermal behaviour of γ-anhydrite has been investigated up to 569 K. At 455 K the transformation γ-anhydrite → β-anhydrite starts and at 653 K is completed. Determination of the thermal behaviour of γ-anhydrite was possible up to 569 K keeping the lattice parameters of β-anhydrite fixed (see below). Thermal expansion of γ-anhydrite is related to the variation of bond distance $Ca-O^I$ (0.21 v.u.) of the CaO_8 dodecahedron, almost parallel to *c* axis.

Thermal behaviour of bassanite has been investigated up to 383 K because of the strong correlations due to the almost perfect overlap of the reflections of bassanite and γ-anhydrite. Only a qualitative analysis of the structural data has been carried out because the variation of bond distances of polyhedrons with temperature is strongly scattered. Therefore, only the Δ bond distance values between the minimum and the maximum temperature have been evaluated. These values have been correlated to bond-valence and orientation of all bond distances to discuss the thermal expansion of bassanite. Thermal expansion of $Ca2O_8$ and $Ca1O_9$ polyhedra is isotropic, whereas that of $Ca2O_8$ and $Ca4O_9$ is anisotropic being almost parallel to the *c* axis and preferentially acting on long bond-distances with low bond-valence values. Positive thermal expansion of $Ca2O_8$ polyhedron is counterbalanced by a negative thermal expansion of $Ca4O_9$ polyhedron. Therefore hemihydrate phase have a isotropic thermal expansion on the whole.

In gypsum and β-anhydrite structures, the chains of polyhedrons are connected by edge-sharing between adjacent CaO_8 dodecahedra and by corner-sharing between the tetrahedra and dodecahedra to form sheets. Structures are less rigid and thermal expansion can be connected to variation of tilt angles between polyhedra.

The thermal behaviour of β-anhydrite has been investigated to 1263 K. β-anhydrite expands anisotropically along [001] and despite its structural features it is due to the deformation of the CaO_8 polyhedron. In fact the two longest, independent, $Ca-O2^I$ and $Ca-O1^{IV}$ bond distances corresponding, respectively, to *ca.* 0.23 and 0.20 v.u., show principal components along the *c* axis justifying the largest thermal expansion along this direction.

Analysis of the thermal behaviour of gypsum was possible up to 373 K because at 368 K starts the conversion to bassanite that is completed at 393 K. Thermal expansion of gypsum is anisotropic and follow the $\alpha_b > \alpha_c >> \alpha_a$ trend.

Thermal expansion along [010] is caused by the weakening of the hydrogen bond H2···O1, linking adjacent polyhedra sheets. Using X-ray powder diffraction data is impossible to evaluate the weakening of the hydrogen bond. Therefore, it was evaluated the variations of the $O1^I$-Ow contact distance as a function of temperature. On the contrary the expansion of gypsum along *c* axis is due to the $Ca-O2^I$ bond distance that regularly increases as a function of temperature and acts mainly along [001].

Thermal dependence of lattice parameters and volume were fitted with a second-order polynomial $p = a_0 + a_1 T + a_2 T^2$ to calculate the thermal expansion coefficients (Fei, 1995). Lattice parameters and volume of gypsum and β-anhydrite were also fitted with the Einstein function $X = X_0 + [K / \exp^{\theta/T} - 1]$ correlate the results with reference data (Knight *et al.*, 1999).

Using the thermal coefficient the unit strain of phases was evaluated. Evaluation of the unit strain shows that in the $CaSO_4$-H_2O system gypsum expands more than the remaining phases (Fig. 3).

An anomalous behaviour was observed within the range 343-383 K for γ-anhydrite that re-hydrates to bassanite. Moreover, it was verified that thermal expansion of β-anhydrite is influenced by the release of strain as well as in case of transformation γ-anhydrite → β-anhydrite.

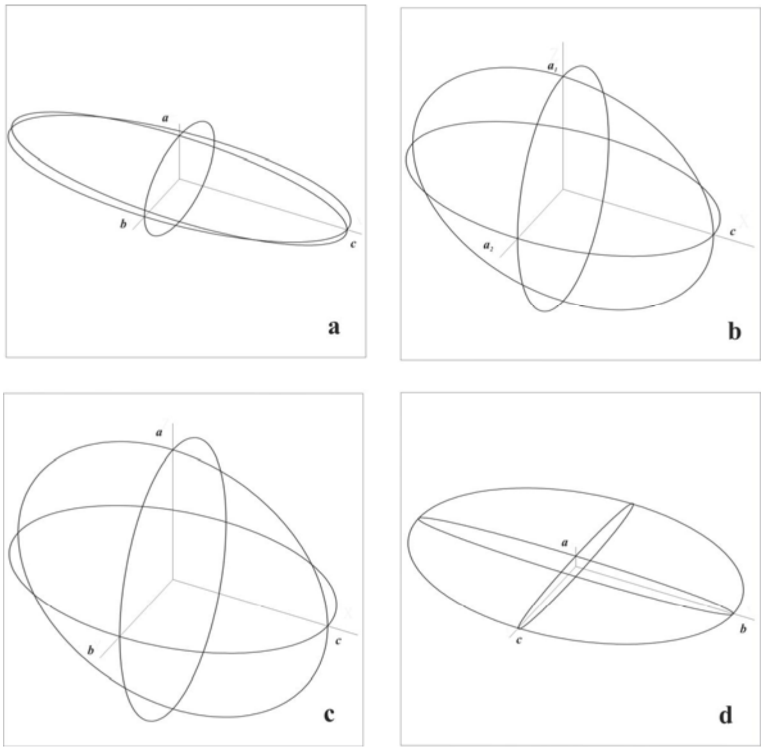

Fig. 3 – Unit strain ellipsoid (Ohashi, 1972) of the $CaSO_4$-H_2O system (***a*** β-anhydrite, ***b*** γ-anhydrite, ***c*** bassanite, and ***d*** gypsum).

KINETIC STUDY

In the last part of work the kinetics of gypsum (thermal range 348-403 K) and bassanite (thermal range 373-398 K) dehydration were studied in isothermal conditions with a temperature increase of 5 K. Quantitative analysis were carried out keeping the structural data fixed at the values determined during the thermal expansion analysis at the corresponding temperature.

The dehydration process of gypsum has been investigated because reference data are contrasting, suggesting the possible occurrence of subhydrates as intermediate phases. However, refined cell parameters of the products of dehydration were found to be fully consistent with those of bassanite (Bezou *et al.*, 1995; Ballirano *et al.*, 2001) instead of those of other sub-hydrate modifications of the type $CaSO_4 \cdot xH_2O$ with well-established structure ($x = 0.62$: Bezou *et al.*, 1995; $x = 0.80$: Abriel, 1983).

As a result, under the present experimental conditions, gypsum dehydration follows a two steps process:

$$CaSO_4 \cdot 2H_2O_{(s)} \rightarrow CaSO_4 \cdot 1/2H_2O_{(s)} + 1/2H_2O$$
$$CaSO_4 \cdot 1/2H_2O_{(s)} \rightarrow CaSO_{4(s)} + 1/2H_2O$$

Experimental data were plotted in a α *vs.* time plot and fitted with the Avrami function $y(t) = 1 - \exp(-kt)^n$ to define the rate coefficients and the *n* parameters related to the dimensionality of the reaction mechanism (Fig. 4). Reference data indicate that an *n* value greater than 4 is consistent with a phase boundary mechanism with a three-dimensional growth (Hulbert, 1969) or an autocatalytic

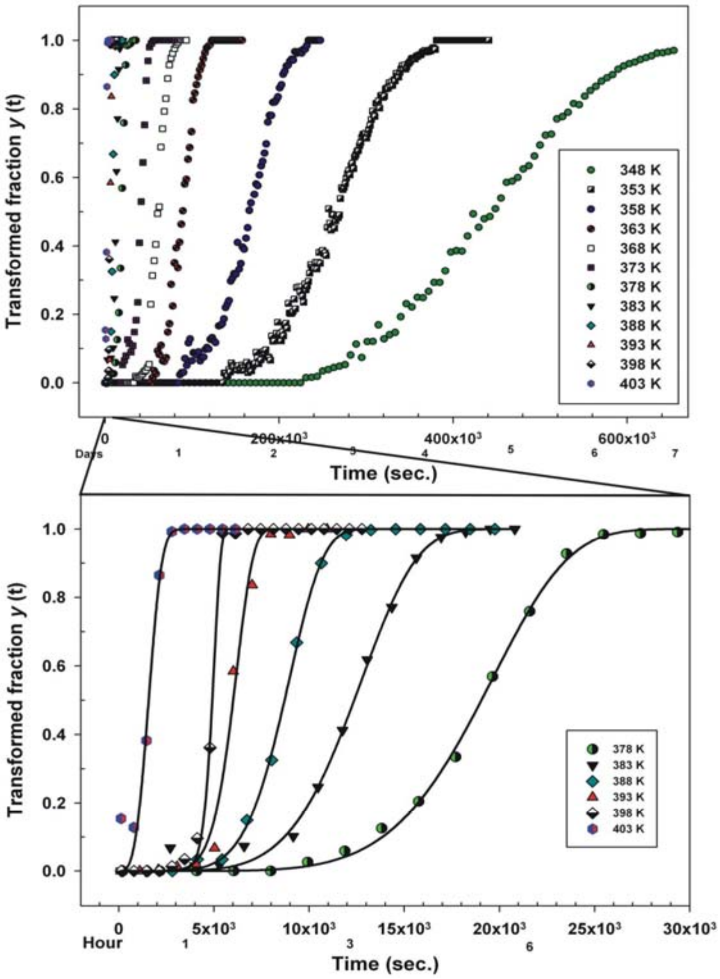

Fig. 4 – Curves α *vs*. time of dehydration of gypsum in the temperature range 348-403 K with a Δ of 5 K.

nucleation (Gualtieri, 2001). Therefore, using X-ray diffraction data only it is not possible to define completely the mechanism of transformation gypsum → bassanite.

The empirical activation energy (E_{att}) has been obtained using the logarithmic form of the Arrhenius equation $\ln k = A - [E_a/RT]$ (Fig. 5). An E_{att} of 26(3) Kcal/mol has been obtained for gypsum in agreement with reference data if the case of similar thermal ranges (Jordan & Astelliros, 2006).

Dehydration mechanism of bassanite has been analysed using the same capillary for five subsequent cycles in isothermal conditions. After every cycle the capillary was cooled to RT to permit the rehydration of γ-anhydrite into bassanite.

This approach was utilized to evaluate the influence of strain release in dehydration processes. As in the case of gypsum, diffraction data were fitted with the Avrami function (Fig. 6) and the Arrhenius equation was used to calculate E_{att} (Fig. 7).

An E_{att} of 4(1) Kcal/mol for bassanite has been obtained. This value is in poor agreement with reference data because of the release of the strain during the different heating cycle (McConnel, 1965; Winkler, 1996; Sarma *et al.*, 1998; Prasad *et al.*, 2001). In fact the release of the strain is very important

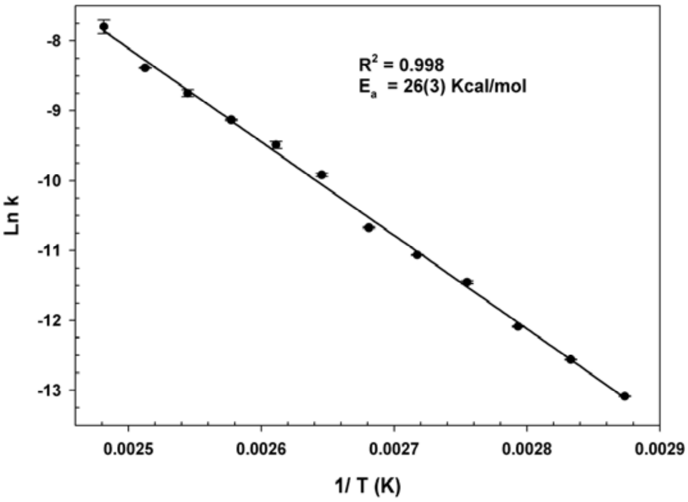

Fig. 5 – Arrhenius ln *k vs.* 1/T plot for the gypsum → bassanite conversion.

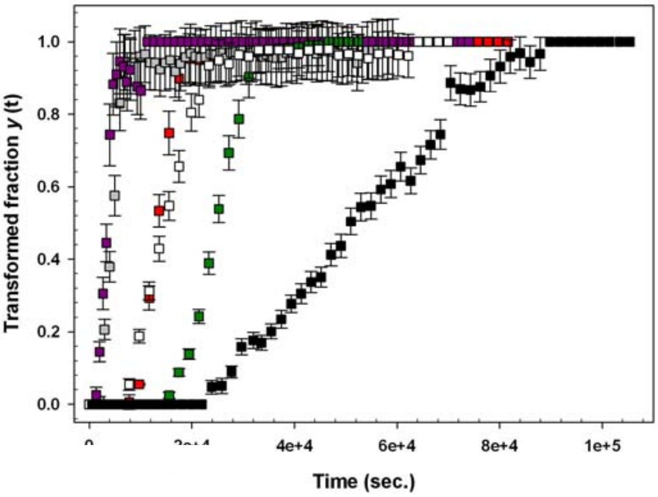

Fig. 6 – Curves α *vs.* time of dehydration of bassanite in the temperature range 373-398 K with a Δ of 5 K.

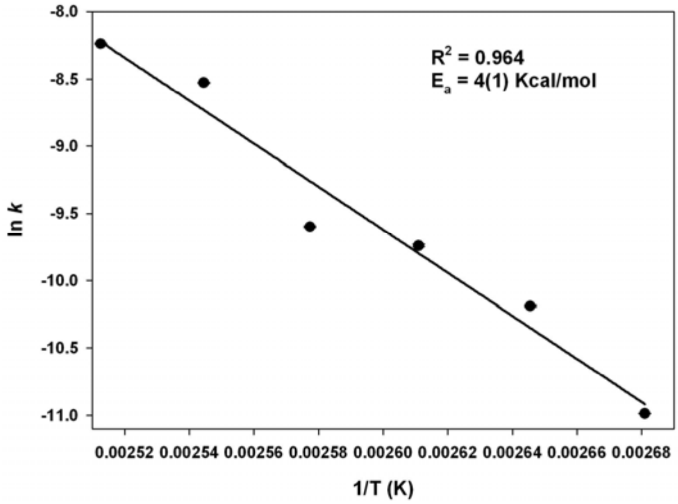

Fig. 7 – Arrhenius ln *k vs.* 1/T plot for the bassanite → γ-anhydrite conversion.

in dehydration of bassanite, it affects also the total dehydration of the phase. In fact at temperature lower or equal to 373 K, bassanite dehydration is incomplete during the first heating cycle. During the second cycle, after the release of strain, dehydration is complete also at 373 K.

The *n* value was found to be greater than 4 and therefore it is possible to assume that the transformation follows the same mechanism of gypsum dehydration.

In both cases it is impossible to define the mechanisms of transformations using only X-ray diffraction data. However the linear dependence of ln *k* on 1/T permit to assert that within the analysed thermal ranges both transformations follow a single mechanism (Fig. 5 and 7).

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