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# DILATOMETRIC BEHAVIOUR OF CHABAZITE

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## Abstract

Powdered pressed compacts of different cationic forms of a natural chabazite were tested by dilatometry. The dilatometric curves of the various cationic forms displayed markedly different features, interpretable in terms of shrinkage by dehydration, thermal expansion, cation migration and thermal breakdown of the zeolitic structure.

**Keywords:** chabazite, dilatometry

## Introduction

The structure of zeolites involves an anionic framework characterized by the presence of cavities and interconnected channels in which water and weakly bound cations are found. Different cation sites characterize the framework of each type of zeolitic structure. The heating of zeolitic materials results in progressive dehydration, in possible cation migration from one particular cation site to another and, in general, in other structural changes which culminate in the final thermal collapse of the zeolitic structure [1].

The thermal behaviour of zeolites, together with their connected structural changes, are topics of active research all over the world. Investigations are performed by the simultaneous use of several experimental techniques, such as thermal analysis, X-ray and neutron diffraction, scanning and high-resolution electron microscopy, infrared spectoscopy, nuclear magnetic resonance, electron spin resonance and synchrotron X-ray diffraction [2, 3].

In the scientific literature, data on the thermodilatometric behaviour of zeolitic materials are lacking, probably because proper testing samples, such as single-crystals of appropriate size or polycrystalline materials free of porosity, are not available.

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The present paper is intended to make a useful contribution to a nearly unexplored research field, the dilatometry of zeolitic materials. Additionally, the interpretation of the dilatometric data on zeolitic materials based on thermal expansion, shrinkage by dehydration and structural changes occurring upon heating could allow an assessment of the validity of a simple experimental technique in characterizing the thermal behaviour of zeolitic materials. To fulfil this goal, pressed powder compacts of different cationic forms of a natural chabazite were tested by dilatometry. This choice was suggested by the extensive knowledge of the thermal behaviour of chabazite, which was thoroughly investigated by Passaglia [4]. This will allow a comparison of the results obtained by measuring lattice-constant variations in cation-exchanged chabazite [4] with those obtained by dilatometry.

## Experimental

The natural chabazite used in this investigation came from Mercogliano (Avellino, north-east of Naples).

More or less homoionic Li-, Na-, K-, Cs-, Mg-, Ca-, Sr- and Ba-chabazites were obtained by the following procedure: about 5 g of chabazite was contacted for 1 h, under continuous stirring, with 1 l of a 1 *M* solution of the relevant cation at 80°C. Cation solutions were prepared from Carlo Erba reagent grade chloride or nitrate salts. After chabazite was separated from the suspension by filtration, this same operation was repeated a total of three times. The resulting powders were washed with distilled water, dried overnight at 80°C and stored for at least 3 days in an environment of about 50% relative humidity to allow water saturation of the zeolites.

Such powders were pressed at 150 MPa to produce cylindrical pellets having a height of 10 mm and a diameter of 10 mm. Such pellets, characterized by a 35% apparent porosity measured by the RILEM procedure [5], were tested by dilatometry. A mod. 402 E/7 Netzsch dilatometer was utilized, with various heating rates: 2, 10 and 30°C $cm^{-1}$.

TG analyses were performed with a Stanton Redcroft apparatus, mod. 781, a 20 mg sample, $\alpha$-$Al_2O_3$ as reference and a 10°C $min^{-1}$ heating rate.

X-ray diffractometric analyses were performed with a Philips PV 1730 diffractometer.

## Results and discussion

Figures 1–4 depict dilatometric and thermogravimetric curves of Li-, Na-, K- and Ba-chabazites, respectively. Such curves illustrate the percentage variation in length and the percentage water loss with respect to the initial masses of the compacts as a function of temperature.

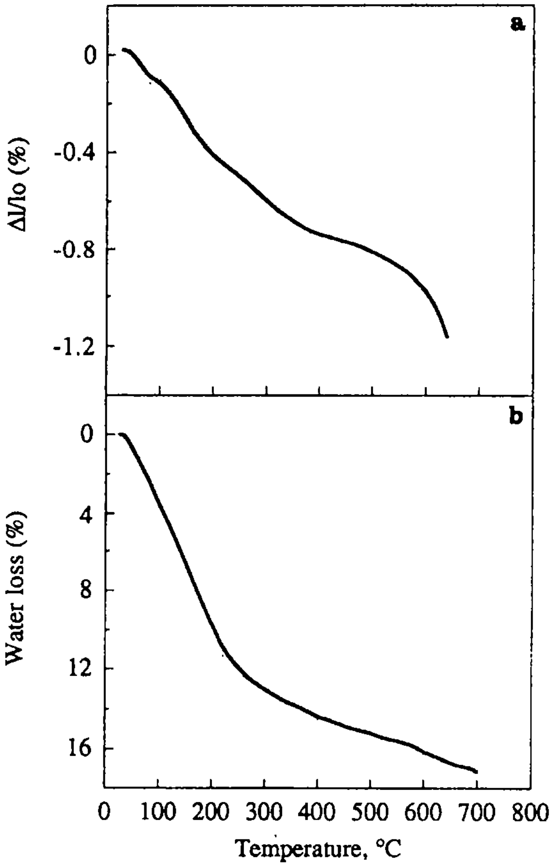

**Fig. 1** Dilatometric (a) and thermogravimetric (b) curve of Li-chabazite; heating rate = 10°C $\text{min}^{-1}$

The following phenomena affect the shapes of the dilatometric curves:

i) the continuous dehydration with increasing temperature, which results in shrinkage of the compacts;

ii) the thermal expansion upon heating;

iii) the thermal collapse of the lower-density zeolitic structure, which results in a noticeable shrinkage of the compacts;

iv) possible cation migrations from one particular cation site to others, which affects the dimensional stability of the compacts.

The variety of contrasting effects, sometimes occurring simultaneously, hampers the interpretation of the dilatometric data.

Moreover, the known existence of various forms of zeolitic water, bound to the zeolite framework with different strengths and thus released in different,

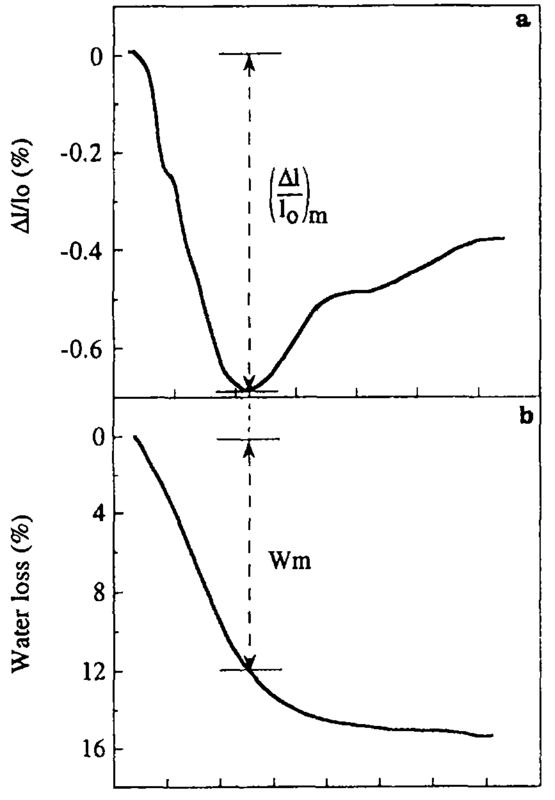

**Fig. 2** Dilatometric (a) and thermogravimetric (b) curve of Na-chabazite; heating rate = 10°C $\text{min}^{-1}$

partially overlapping, temperature ranges, with different kinetics, further complicates the problem. At least the following three types of waters, reported in order of increasing bond energies, are present in zeolites:

i) water filling channels and cavities, whose molecules are bound to each other mainly by hydrogen-bonds;

ii) water covering the walls of channels and cavities and interacting with extraframework cations;

iii) water bound to the framework by strong chemical bonds (OH groups).

It must be added even the apparent porosity of the tested samples affects the extent to which shrinkages or expansions occur.

In spite of all these difficulties, several findings may be pointed out. In the temperature range 20–200°C, the shrinkage associated with dehydration usually

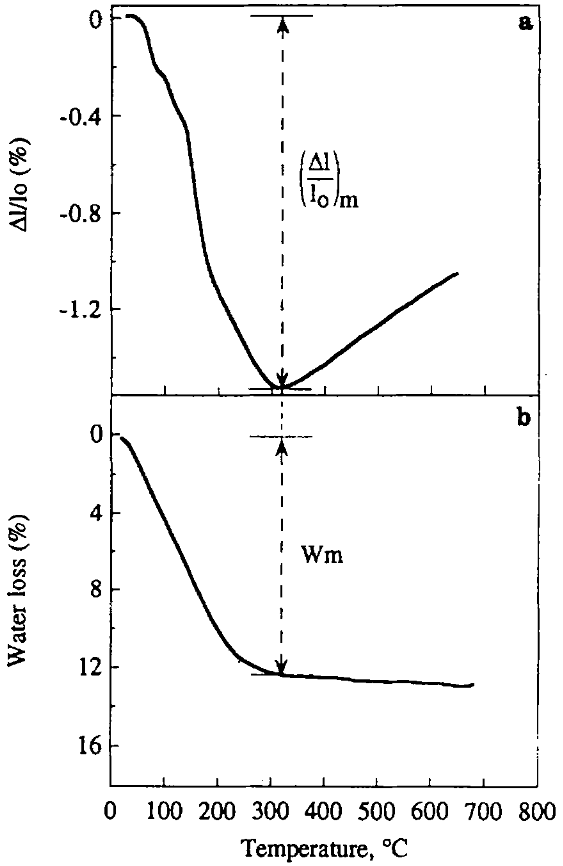

**Fig. 3** Dilatometric (a) and thermogravimetric (b) curve of K-chabazite; heating rate = 10°C $min^{-1}$

prevails on the thermal expansion. The presence of inflection points in this temperature range of the dilatometric curves for the various chabazite cation forms (Figs 1–4) confirms the presence of various zeolitic waters bound with different strengths and thus released with different kinetics.

In the dilatometric curves of Na-, K-, Cs-, Mg-, Ca- and Sr-chabazites, there is an evident minimum in the temperature range 220–320°C. Table 1 reports the value of the minimum, $(\Delta l/l_o \cdot 100)_{min}$ ($l$ is the actual length of the compact and $l_o$ the initial length), the temperature at which it occurs, $T_m$, the water loss at this temperature, $W_m$, and the water loss at 700°C, $W_{700}$. $W_m$ and $W_{700}$ are expressed as percentage water loss with respect to the initial mass of the hydrated sample. K- and Cs-chabazites have in common that, after the occurrence of the minimum, the changes in thermal expansion of the compact with temperature are almost linear and parallel. Such a linear dependence suggests that shrinkage connected with dehydration is practically absent after the minimum,

**Table 1** Value of the minimum in the dilatometric curve $(\Delta l/l_0 \cdot 100)_{min}$, temperature at which occurs $T_m$, water loss at this temperature $W_m$ and the water loss at 700°C $W_{700}$

| | Na | K | Cs | Mg | Ca | Sr |
|---|---|---|---|---|---|---|
| $(\Delta l/l_0 \cdot 100)_{min}$ | −0.68 | −1.49 | −0.66 | −0.92 | −0.85 | −0.48 |
| $T_m$/°C | 220 | 320 | 280 | 320 | 300 | 300 |
| $W_m$/% | 11.0 | 12.4 | 7.3 | 13.8 | 13.0 | 12.6 |
| $W_{700}$/% | 15.5 | 12.8 | 7.8 | 16.8 | 16.0 | 15.8 |

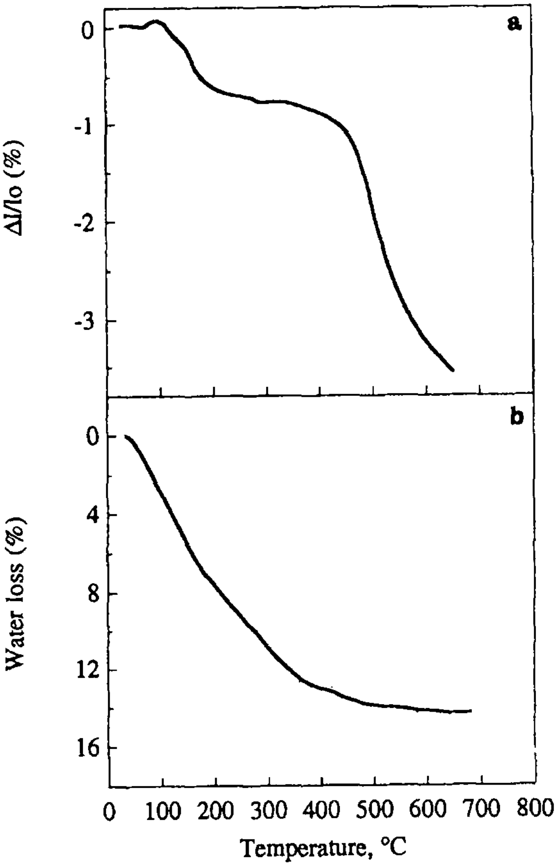

Fig. 4 Dilatometric (a) and thermogravimetric (b) curve of Ba-chabazite; heating rate = 10°C $min^{-1}$

and that only thermal expansion takes place. This is confirmed by the fact that water loss at the temperature of the minimum is about the same as the water loss at 700°C, which is not far from the total water loss as the thermogravimetric curves seem to tend to a horizontal line for temperatures higher than $T_m$. The entity of the minimum is far higher for K-chabazite (–1.49%) than for Cs-chabazite (–0.66%), which appears justified by the higher water loss $W_m$ (12.4% for K-chabazite, and 7.3% for Cs-chabazite).

The minimum in the dilatometric curve of Na-chabazite seems to displays different features from those for K- and Cs-chabazites:

i) it occurs at a lower temperature (220°C for Na-chabazite, 320°C for K-chabazite and 280°C for Cs-chabazite);

ii) after the minimum, an anomalous, sharp increase occurs in the thermal expansion coefficient.

This fact is even more noteworthy inasmuch as the $W_m$ value (11.0%) is quite far from $W_{700}$ (15.5%), which should result in an increase of the length lower than the thermal expansion or even in a further shrinkage. It appears that some phenomenon, not yet accounted for, other than shrinkage by dehydration or thermal expansion, is occurring. The structure described for chabazite [6–9] indicates that the possible exchangeable-cation positions are: a) site I in the small cage A, which can be entered through a six-membered ring whose free aperture has a radius of about 0.13 nm; b) site II in the large ellipsoidal cage B, which can be entered through six eight-membered rings 0.3–0.4 nm in diameter. Passaglia [5] concluded that site I, inside the pseudohexagonal prism, is already occupied in the hydrated phases by Sr and K. Li, Na and Ca enter site I only upon dehydration, while Cs is not allowed in it because of its high ionic radius (0.169 mm) and Ba causes framework destruction upon dehydration. These conclusions suggest that the sharp, anomalous increase in the thermal expansion coefficient could be connected with Na migration from site II to site I. Such a sudden thermal expansion increase is not observed for K- and Cs-chabazites as no cation migration occurs either in the former (because site I is already occupied in the hydrated phase) or in the latter (for steric reasons).

The dilatometric behavior of Mg- and Ca-chabazites is very similar to that of Na-chabazite, so that it appears as if the minima present in the Mg- and Ca-chabazite dilatometric curves may be justified in the same manner as the minimum in the Na-chabazite dilatometric curve.

Special considerations should be given to the dilatometric behaviour of Li-chabazite, which does to seem to be in agreement with the results of Passaglia [4], who reported that Li enters site I only upon dehydration. Together with the absence of very evident minima, the high negative value of the slope of the dilatometric curve for temperatures higher than 600°C appears very striking. These two points could be explained by two concurrent phenomena:

i) the considerable shrinkage related to the very high water content of Li-chabazite; its water loss at 700°C is the highest (17.0%), and this value appears far from the total water loss, as the thermogravimetric curve still displays a considerable negative slope at 700°C;

ii) the partial thermal collapse of the low-density, zeolitic structure; this phenomenon was confirmed by recording the X-ray diffraction patterns of Li-chabazite before and after the thermal cycle; the comparison of the two patterns evidenced a partial loss of crystallinity.

An inflection point appears evident at 200°C in the Li-chabazite dilatometric curve: it could be the only trace of Li migration from site II to site I. This hypothesis is supported by the fact that the considerable shrinkage connected with the large water loss and partial thermal collapse could have transformed in an inflection point the sharp expansion of the compact, which should result in a minimum in the dilatometric curve, as for Na-, Mg- and Ca-chabazites.

A much more considerable structural change is evident in the Ag- and Ba-chabazite dilatometric curves, which are very similar to each other: Passaglia [4] reports that Ba-chabazite has already undergone thermal breakdown at 200°C, denoted in the dilatometric curve by the very large shrinkage (almost 4%). Such a value is not consistent with dehydration alone, and involves more dramatic structural changes, such as thermal breakdown of the low-density, zeolitic structure. Thermal breakdown appears to occur even for Ag-chabazite, as an almost 8% final shrinkage is recorded. Such a structural collapse is confirmed by the X-ray diffraction patterns of both Ag- and Ba-chabazites after the thermal cycle, which evidence an almost total loss of crystallinity.

Figure 5 presents dilatometric curves of Na-chabazite at different heating rates (2, 10 and 30°C min$^{-1}$). A minimum is observed in all three curves, but either the entity or the temperatures of the minima are different. This may be

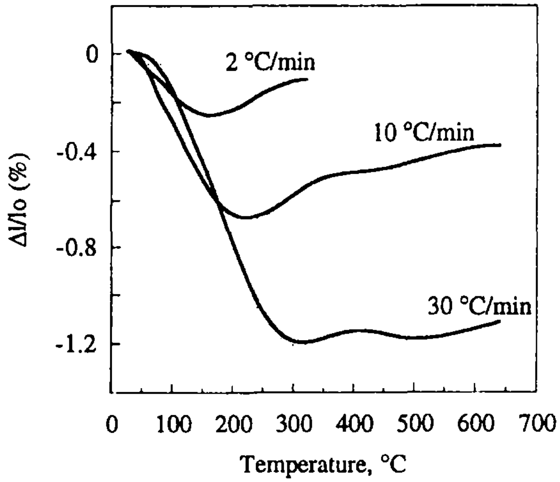

**Fig. 5** Dilatometric curves of Na-chabazite at various heating rates

explained by considering the complexity of the phenomena affecting the dilatometric behaviour of zeolitic materials. In this case, the dehydration, thermal expansion, cation migration and thermal breakdown display markedly different kinetics.

## Conclusions

The reported data relate to a still nearly unexplored research filed: the dilatometry of zeolitic materials. Various cationic forms of chabazite display dilatometric curves with markedly different features. An attempt was made to interpret the dilatometric curves on the basis of shrinkage by dehydration, thermal expansion, cation migration and thermal breakdown of the zeolitic structure. Although the simultaneous occurrence of contrasting phenomena hampers an understanding of the dilatometry of zeolitic materials, it may be useful in the characterization of their thermal behaviour. Moreover, the effect of the heating rate on the dilatometric curves might be of value in evidencing particular phenomena occurring upon heating.

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