New Insight into the Thermal Transformation of Barium-Exchanged Zeolite A to Celsian

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The thermal transformation of a sample of Ba-exchanged zeolite A, containing a residual Na content of 0.20 meq/g, into monoclinic celsian is thoroughly investigated. The samples were thermally treated at temperatures ranging from 200 to 1500 °C for times up to 40 h and subsequently were characterized by room-temperature X-ray diffraction. The following are the main results of this investigation:(1) Above 500 °C, the presence of small crystalline aggregates of monoclinic celsian dispersed in the amorphous phase arising from the thermal collapse of Ba-exchanged zeolite A is recorded.(2) Above 900 °C, crystallization of hexacelsian occurs.(3) Above 1100 °C, hexacelsian converts into monoclinic celsian. The conversion is complete with thermal treatments at 1300, 1400, and 1500 °C within 22, 15, and 22 h, respectively.The presence of monoclinic celsian nuclei above 500 °C appears to favor the conversion of hexacelsian into monoclinic celsian at temperatures higher than 1100 °C. The residual Na content of Ba-exchanged zeolite A was found to strongly affect the temperatures and times at which the transformations of amorphous phase → hexacelsian and hexacelsian → monoclinic celsian occur. Actually a higher Na residual content results in lower temperatures and times, ceteris paribus.

Introduction

The monoclinic polymorph of the barium feldspar celsian, $BaAl_2Si_2O_8$, is a material of great technological interest on account of its thermal and electrical properties.[1] It exhibits high electrical resistance, low dielectric constant, low dielectric loss, high melting point, low thermal expansion coefficient up to about 1000 °C, and does not undergo a phase transition up to 1590 °C.[1] Thus, uses of this material as a refractory, high-temperature electrical insulator, or as substrates for integrated circuits have been known for a long time. In the past few years, the interest of the scientific and technological community for celsian has increased dramatically on account of its possible use for aeronautic and aerospace applications. Actually celsian is being investigated as a matrix material for reinforcement with continuous ceramic fibers for high-temperature structural composites to be used in hot sections of turbine engines.[2−9]

The essential literature concerning the synthesis of celsian was reviewed in a previous paper.[10] It is reported that the high temperatures and/or the long reaction times required, as well as the use of expensive alkoxides, may give rise to high process costs or unsatisfactory yields. This review also points to another serious drawback of these synthesis procedures. They actually lead to the crystallization of the hexagonal polymorph of celsian (hexacelsian) which is stable at temperatures higher than 1590 °C.[11] Below this temperature, even though the stable phase is monoclinic celsian,[11] hexacelsian is the first polymorph to nucleate. This behavior was attributed to the simpler crystal structure of the high-symmetry modification presenting a lower kinetic barrier to nucleation.[12]

The early crystallization of hexacelsian gives rise to two different kinds of problems. On one hand, hexacelsian cannot be used as a refractory material, because at 300 °C, it undergoes a reversible transformation into an orthorhombic form accompanied by a detrimental volume change (≥3%).[11] On the other hand, the transformation of hexacelsian to monoclinic celsian occurs after prolonged heating (more than 20 h) at temperatures higher than 1500 °C in the presence of mineralizers and monoclinic seed particles.[13]

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(1) Talmy, I. G.; Haught, D. A.; Wuchina, E. J. *Proceedings of the 6th International SAMPE Electronic Conference*; Goldberg, A. B., Harper, C. A., Eds.; Society for the Advancement of Materials and Process Engineering: Covina, CA, 1992; pp 687−698.

(2) Bansal, N. P.; Drummond, C. H., III. *J. Am. Ceram. Soc.* **1993**, *76* (5), 1321.

(3) Bansal, N. P. *J. Mater. Sci.* **1998**, *33*, 4711.

(4) Bansal, N. P. *J. Am. Ceram. Soc.* **1997**, *80* (9), 2407.

(5) Bansal, N. P. U.S. Patent 5,214,004, May 25, 1993.

(6) Bansal, N. P. U.S. Patent 5,389,321, Feb 14, 1995.

(7) Bansal, N. P. NASA TM 106993, Aug 1995.

(8) Bansal, N. P. NASA TM 210216, Jun 2000.

(9) Gyekenyesi, J. Z.; Bansal, N. P. NASA TM 210214, Jul 2000.

(10) Dell'Agli, G.; Ferone, C.; Mascolo, M. C.; Pansini, M. *Solid State Ionics* **2000**, *127*, 309.

(11) Lin, H: C.; Foster W. R. *Am. Mineral.* **1962**, *53*, 134.

(12) Chen, M.; Lee, W. E.; James, P. F. *J. Non-Cryst. Solids* **1991**, *130*, 322.

(13) Hoghooghi, B.; McKittrick, J.; Helsel, E.; Lopez, O. *J. Am. Ceram. Soc.* **1998**, *81* (4), 845.

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The synthesis of monoclinic celsian at low temperature was obtained by Talmy and co-workers.[14] The process consisted in preparing monoclinic celsian from AlF_3, Al_2O_3, $BaCO_3$, and fused SiO_2 powders by heating an intimate mixture of the powders from about 700 to 900 °C, to form topaz, and then by heating at a temperature as low as 900 °C to produce monoclinic celsian. A crucial point of this process was that the reaction had to take place in an atmosphere of the gases generated by the reactions.

A possible alternative to the process adopted by Talmy and co-workers[14] may be the technique which Subramanian and co-workers[15−18] proposed for the synthesis of alkaline-earth and alkaline framework aluminosilicates, which belong to the class of feldspars. These authors crystallized such materials by thermal treatment of cation exchanged zeolites at temperatures slightly higher than 1000 °C for some hours. This thermal treatment gave rise to the thermal collapse of the microporous zeolitic structure with the formation of an amorphous phase and, subsequently, to the crystallization of the corresponding alkaline-earth or alkaline feldspar. The following are the main advantages of this technique: (1) the desired starting composition of the system may be easily reproduced by selecting zeolites displaying the needed Si/Al ratio[19] and by properly adjusting the cation exchange operations; (2) the thermal collapse of the microporous zeolitic structure gives rise to an amorphous phase with a composition that is perfectly homogeneous at the atomic scale; (3) the low cost of many zeolitic terms which may act as starting materials.

Very interesting work concerning the study of the thermal transformation of alkaline-earth or alkaline cation exchanged zeolites into ceramics is described in the literature.[13,20−27] However, systematic investigations with the aim of determining the optimal conditions of synthesis of various ceramics of technological interest starting from cation exchanged zeolites are very scarce.

Starting from these considerations a long term study has been undertaken with the aim of carefully investigating the potentiality of the technique proposed by Subramanian and co-workers.[15−18] Very interesting preliminary results were obtained and reported in a previous paper.[10] Actually, it was found that upon a thermal treatment at 1100 °C, Ba-exchanged zeolite A, which after dehydration exactly reproduces the stoichiometric composition of celsian, gave rise to the following sequence of transformations: zeolite → amorphous phase → hexacelsian → monoclinic celsian. Moreover, it was found that 6 h of this treatment were sufficient to obtain a fully monoclinic celsian. The same result was obtained by starting from Ba-exchanged zeolite X only through a 24 h thermal treatment at 1550 °C.

The very positive results obtained by starting from Ba-exchanged zeolite A need to be further confirmed and interpreted on the basis of a mechanism which could likely explain its high reactivity. A more complete comprehension of the mechanism involved in the thermal transformation is very interesting from the point of view of fundamental research, but it could also give indications for the optimization of the operational conditions of the thermal transformation of Ba-exchanged zeolite A into monoclinic celsian. Such indications may result in being very useful in the setup of a process leading to the low-temperature synthesis of monoclinic celsian.

Experimental Section

Cation exchange operations were performed according to the following procedures. Carlo Erba reagent-grade synthetic zeolite 4A ($Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$) was contacted overnight with a warm (60−70 °C) $[Ba^{2+}] = 0.2$ N solution with a weight solid/liquid ratio (S/L) = 1/25. The solution was prepared using bidistilled water and Carlo Erba reagent-grade $Ba(NO_3)_2$ (purity 99.5%). The solid was separated from the liquid through filtration and again contacted with the exchange solution for a total of four times. Then a fifth exchange was performed at a weight S/L = 1/50, all other conditions being equal to previous ones. The remaining exchange operations were performed by contacting the zeolite with barium solutions prepared using extremely pure $BaCl_2$ (purity > 99.999%), provided by Aldrich. In particular, a sixth exchange was performed at a weight S/L = 1/20 and $[Ba^{2+}] = 0.5$ g/dm^3, a seventh one at a weight S/L = 1/30 and $[Ba^{2+}] = 7.5$ g/dm^3, and an eighth one at a weight S/L = 1/40 and $[Ba^{2+}] = 7.5$ g/dm^3, all other conditions being equal to the previous ones. The initial pH of the salt solutions used for the exchanges is about 5.8.

The original Na content of zeolite A and the residual Na content of the zeolite at the various stages of Ba exchange was determined according to the following procedure. The zeolite was chemically dissolved in a hydrofluoric and perchloric acid solution, and its Na^+ concentration was determined by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer Analyst 100 apparatus. The consistency of concentration measurements related to cation exchange operations was checked by determining Ba^{2+} concentration by titration with EDTA using erio T as the indicator and a NH_3 and NH_4^+ solution at pH 10 as buffer.[28]

The resulting powders were washed with bidistilled water, dried overnight at 80 °C, and stored for at least 3 days in an environment having about 50% relative humidity to allow water saturation of zeolite.

Ba-exchanged zeolite A samples, obtained according to the procedure previously described, were subjected to various thermal treatments in a Lenton furnace, which ensures stable temperature to within ±2 °C, using Al_2O_3 crucibles. The thermal treatments, which are summarized in Table 1, were

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(14) Talmy, I. G.; Haught, D. A. U.S. Patent 5,041,400, Aug 20, 1991.

(15) Subramanian, M. A.; Corbin, D. R.; Farlan, R. D. *Mater. Res. Bull.* **1986**, *21*, 1525.

(16) Chowdry, U. V.; Corbin, D. R.; Subramanian, M. A. U.S. Patent 4,813,303, Mar 21, 1989.

(17) Subramanian, M. A.; Corbin, D. R.; Chowdry, U. V. *Adv. Ceram.* **1989**, *26*, 239.

(18) Corbin, D. R.; Parise, J. B.; Chowdry, U. V.; Subramanian, M. A. *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 213.

(19) Breck, D. W. *Zeolite Molecular Sieves*: *Structure, Chemistry and Use*; Wiley: New York, 1974.

(20) Bedard, R. L.; Flanigen, E. M. *Proceedings of the 9th International Zeolite Conference*, von Balmoos, R., Higgins, J. B., Tracy, M. M. J., Eds.; Butterworth-Heinemann: Montreal, 1993; 667.

(21) Prieto Valdes, J. J.; Victorero Rodriguez A. *J. Mater. Sci. Lett. II* **1992**, 678.

(22) Hoghooghi, B.; McKittrick, J.; Butler, C.; Helsel, E.; Lopez, O. *Mater. Res. Soc. Symp. Proc.* **1994**, *348*, 493.

(23) Hoghooghi, B.; McKittrick, J.; Butler, C. *J. Non-Cryst. Solids* **1994**, *170*, 303.

(24) Hoghooghi, B.; McKittrick, J.; Lopez, O *J. Non-Cryst. Solids* **1996**, *197*, 170.

(25) Ata, A.; Hoghooghi, B.; McKittrick, J.; Helsel, E. *J. Mater. Synth. Process.* **1997**, *5* (3), 217.

(26) Boskovic, S.; Kosanovic, D.; Dondur, V.; Dimitrijevic, R. *Ceram. Int.* **2000**, *26*, 33.

(27) Weidenthaler, C.; Schmidt, W. *Chem. Mater.* **2000**, *12*, 3811.

(28) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*; Methuen: London, 1969.

Table 1. Thermal Treatments to Which the Various Ba-Exchanged Zeolite A Samples Were Subjected and Figures Where the Corresponding XRD Patterns Are Reported

temp (°C)	thermal treatment[a]
200	Q (Fig 2a), 2 h (Fig 2b)
300	Q
400	Q
500	Q (Fig 2c)
600	Q
700	Q, 1 h, 4 h, 28 h
800	Q, 1 h, 4 h, 28 h (Fig 2d)
900	Q, 1 h, 4 h (Fig 3a), 28 h (Fig 3b)
1000	Q, 1 h, 4 h, 28 h
1100	Q (Fig 3c), 1 h, 4 h, 28 h (Fig 3d)
1200	Q, 1 h, 4 h, 28 h (Fig 3e)
1300	Q (Fig 4a), 4 h (Fig 4b), 10 h (Fig 4c), 22 h (Fig 4d), 28 h, 40 h
1400	Q (Fig 5a), 4 h (Fig 5b), 10 h (Fig 5c), 15 h (Fig 5d), 22 h, 28 h
1500	Q (Fig 6a), 1 h, 4 h (Fig 6b), 10 h (Fig 6c), 15 h (Fig 6d), 22 h (Fig 6e), 28 h

[a] Q means that the sample was heated at 10 °C/min up to the reported temperature and was subsequently quenched in air. In the other cases, the samples were heated at 10 °C/min up to the reported temperature, kept in these conditions for the reported time, and subsequently quenched in air.

performed as follows. In some cases, the samples were heated at rate of 10 °C/min up to the fixed temperature and subsequently quenched in air. In other cases, the samples were heated at 10 °C/min up to the fixed temperature, kept in this condition for the fixed time, and subsequently quenched in air.

These products were characterized by XRD at room temperature using a Philips X'PERT diffractometer, Cu Kα radiation, collection of data between 20 and 40° 2θ with a step width of 0.02° 2θ, and 1 s data collection per step.

Ba-exchanged zeolite A was also characterized by simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA), using a Netzsch thermoanalyzer model STA 409, α-Al_2O_3 as reference, and a 10 °C/min heating rate.

Results

Cation Exchange. Zeolite A in its original Na form was subjected to the chemical analysis procedures, reported in Experimental Section. The real initial Na content turned out to be 5.60 meq/g. The Na content calculated from the chemical formula of zeolite A is 5.48 meq/g. This discrepancy may likely be ascribed to the occlusion of some $NaAlO_2$ within the β-cages, similar to feldspathoid behavior.[19,29] Thus, it is extremely hard to remove from the zeolite framework the 0.12 meq/g of Na, arising from the presence of occluded $NaAlO_2$.

Subsequently, zeolite Na-A was subjected to Ba exchange. The residual Na content was determined after the first four exchanges and after the fifth, sixth, seventh, and eighth exchanges to be 0.65, 0.26, 0.25, 0.23, and 0.20 meq/g, respectively. As the final Na content (0.20 meq/g) includes the Na arising from the occlusion of $NaAlO_2$ within the β-cages,[19,29] which cannot be practically removed, it is evident that the residual exchangeable Na still present after the eighth exchange is between 1 and 2% of the total Na originally present in the zeolite framework.

X-ray Diffraction. XRD patterns of zeolite A in its Na (Na-A) and Ba (Ba-A) forms are reported in Figure 1. It is evident that Ba exchange gives rise to a dramatic loss of crystallinity of the zeolitic structure, as previously recorded.[10]

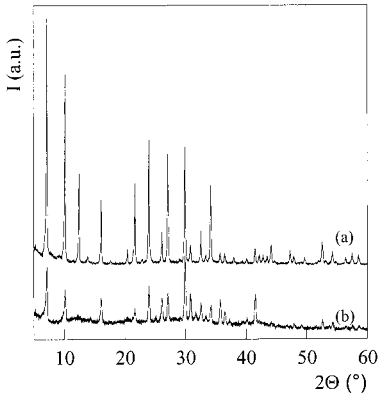

Figure 1. XRD patterns of zeolite Na-A (a) and Ba-A (b).

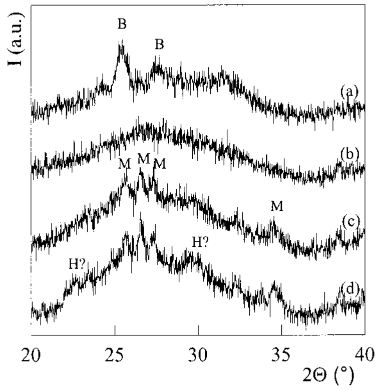

Figure 2. XRD patterns of zeolite Ba-A heated at 200 °C and then quenched in air (a), thermally treated at 200 °C for 2 h (b), heated at 500 °C and then quenched in air (c), and thermally treated at 800 °C for 28 h (d); B = banalsite, M = monoclinic celsian, and H = hexacelsian.

XRD patterns of zeolite Ba-A heated at 200 °C and then quenched in air, zeolite Ba-A thermally treated at 200 °C for 2 h, zeolite Ba-A heated at 500 °C and then quenched in air, and zeolite Ba-A thermally treated at 800 °C for 28 h are reported in Figure 2. Although zeolite Ba-A heated at 200 °C appears almost completely amorphous, the XRD apparatus is able to detect the presence of some extremely broad diffraction peaks (denoted with B in Figure 2a) which can be reasonably attributed to the presence of a small amount of the sodium−barium aluminosilicate banalsite, $Na_2BaAl_4Si_4O_{16}$, dispersed in an amorphous matrix. When zeolite Ba-A is kept for 2 h at 200 °C, banalsite diffraction peaks disappear, thus giving rise to a completely amorphous product (Figure 2b). The XRD patterns of zeolite Ba-A heated at 300 or 400 °C, which were not reported, closely resemble the XRD pattern of zeolite Ba-A thermally treated at 200 °C for 2 h. In the XRD patterns of zeolite Ba-A heated at 500, 600, 700, 800, or 900 °C and then quenched in air, the presence of extremely broad diffraction peaks, which can be ascribed to monoclinic celsian, may be recorded (Figure 2c). Protracting thermal treatments at 700 or 800 °C for times up to 28 h results in a hardly detectable increase of intensity of peaks ascribed to monoclinic celsian and in the appearance of some extremely broad diffraction peaks which could be reasonably ascribed to the presence of hexacelsian (Figure 2d). In Figure 2 and in the

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(29) Barrer, R. M.; Meier, W. M. *Trans. Faraday Soc.* **1958**, *54*, 1074.

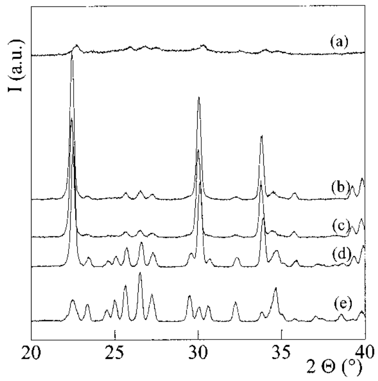

Figure 3. XRD patterns of zeolite Ba-A thermally treated at 900 °C for 4 h (a) and 28 h (b), heated at 1100 °C and then quenched in air (c), thermally treated at 1100 °C for 28 h (d), and thermally treated at 1200 °C for 28 h (e); M = monoclinic celsian and H = hexacelsian.

following ones, the main diffraction peaks of monoclinic celsian and hexacelsian are denoted with M and H, respectively.

Unlike thermal treatments at 700 or 800 °C, prolonged heating for 28 h at 900 °C results in the progressive crystallization of hexacelsian, as it is clearly detected from the XRD patterns of zeolite Ba-A thermally treated at 900 °C for 4 and 28 h, reported in Figure 3. It is noteworthy that in these XRD patterns the presence of diffraction peaks, ascribed to the presence of monoclinic celsian, is recorded. Moreover, the intensity of such peaks is comparable with the intensity of the peaks of monoclinic celsian recorded after thermally treating zeolite Ba-A at 800 °C for 28 h (Figure 2d). The XRD patterns of zeolite Ba-A thermally treated at 1000 °C, which are not reported, are similar to those recorded at 900 °C, ceteris paribus.

Figure 3 reports also the XRD patterns of zeolite Ba-A heated at 1100 °C and then quenched in air, thermally treated at 1100 °C for 28 h, and thermally treated at 1200 °C for 28 h. Thermal treatments of zeolite Ba-A at 1100 or 1200 °C give rise to an early crystallization of hexacelsian followed by the conversion of hexacelsian into monoclinic celsian after prolonged heating (28 h). At 1200 °C, the extent to which this conversion occurs is much greater than at 1100 °C, ceteris paribus. Even during the early stages of hexacelsian crystallization at 1100 or 1200 °C, the presence of diffraction peaks of monoclinic celsian, similar to those reported in Figure 2d and 3a, is recorded.

Even the thermal treatments of zeolite Ba-A at 1300, 1400, and 1500 °C result in an early crystallization of hexacelsian followed by the conversion of hexacelsian into monoclinic celsian. This can be observed in the figures showing the XRD patterns: Figure 4 reports the XRD patterns of zeolite Ba-A heated at 1300 °C and then quenched in air and of zeolite Ba-A thermally treated at 1300 °C for 4, 10, and 22 h; Figure 5 reports those of zeolite Ba-A heated at 1400 °C and then quenched in air and of zeolite Ba-A thermally treated at 1400 °C for 4, 10, and 15 h; finally Figure 6 reports the XRD patterns of zeolite Ba-A heated at 1500 °C and then quenched in air and of zeolite Ba-A thermally treated at 1500 °C for 4, 10, 15, and 22 h. It is noteworthy that conversion of hexacelsian into monoclinic celsian is completed upon thermal treatment at 1300, 1400, and 1500 °C. Actually, in the XRD patterns of zeolite Ba-A thermally treated at 1300 °C for 22, 28, and 40 h, zeolite Ba-A thermally treated at 1400 °C for 15, 22, and 28 h, and zeolite Ba-A thermally treated at 1500 °C for 22 and 28 h, the peaks denoting the presence of hexacelsian are not present.

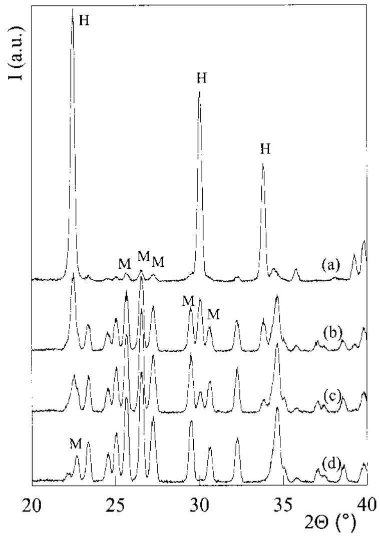

Figure 4. XRD patterns of zeolite Ba-A heated at 1300 °C and then quenched in air (a) and thermally treated at 1300 °C for 4 (b), 10 (c), and 22 h (d); M = monoclinic celsian and H = hexacelsian.

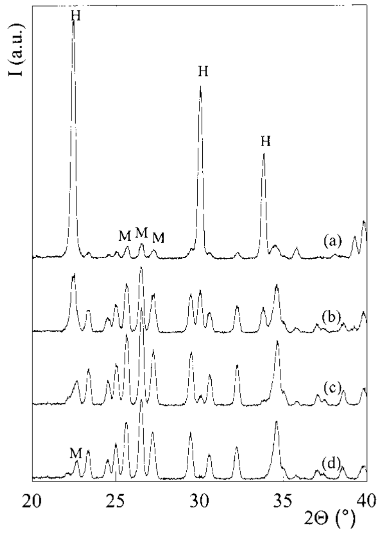

Figure 5. XRD patterns of zeolite Ba-A heated at 1400 °C and then quenched in air (a) and thermally treated at 1400 °C for 4 (b), 10 (c), and 15 h (d); M = monoclinic celsian and H = hexacelsian.

Thermal Analysis. In the DTA curve of zeolite Ba-A, which is reported in Figure 7, a large low-temperature endothermic effect and a sharp high-temperature exothermic effect are clearly recorded. The former, which attains its minimum at 179 °C, is related to the progressive dehydration of zeolite Ba-A upon heating (total water loss = 13.5%) followed by the thermal breakdown of the microporous zeolitic structure with the formation of an amorphous phase. The latter can be reasonably ascribed to the crystallization of hexacelsian from the amorphous phase.

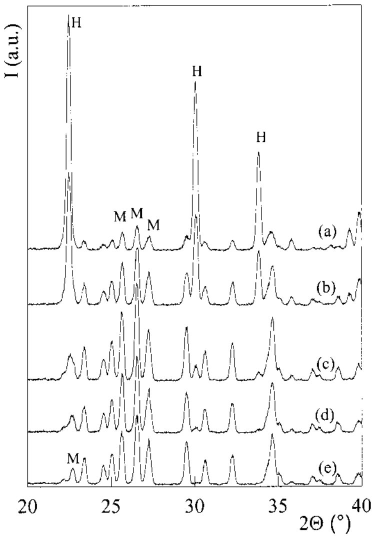

Figure 6. XRD patterns of zeolite Ba-A heated at 1500 °C and then quenched in air (a) and thermally treated at 1500 °C for 4 (b), 10 (c), 15 (d), and 22 h (e); M = monoclinic celsian and H = hexacelsian.

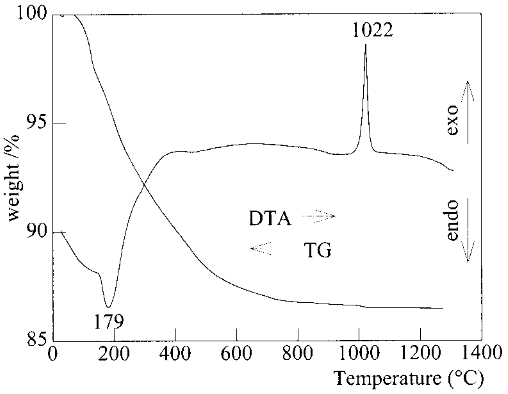

Figure 7. DTA and TGA curves of zeolite Ba-A.

The temperature at which the sharp exothermic effect is recorded (1022 °C) appears to be consistent with XRD data. Actually, the presence of hexacelsian begins to be hardly detected after 1 h of thermal treatment at 900 °C and becomes slightly more evident only after 4 h of thermal treatment at the same temperature. The difference between these temperatures is sufficiently accounted for by the fact that the former value (1022 °C) was recorded in dynamic conditions whereas the latter (about 900 °C) was obtained in static conditions.

No evidence of the sluggish hexacelsian → monoclinic celsian transition is noted in the DTA curve.

Discussion

Cation exchange operations were far more troublesome than expected. Actually, the first four exchanges resulted in a residual 0.65 meq/g Na content. The first attempt at decreasing it was performed by halving the S/L ratio to 1/50. Other attempts at further decreasing the residual Na content were performed by contacting the partially Ba-exchanged zeolite A with Ba^{2+} solutions prepared from $BaCl_2$ with a purity higher than 99.999%. It was thought that the Na^+ impurities present in the reagent grade reactant could hinder the exchange of Ba^{2+} for Na^+, but despite this, the procedure resulted in a residual Na content of 0.20 meq/g, including the Na present as $NaAlO_2$.

The difficulties encountered in performing cation exchange operations do not appear to be in agreement with Eisenmann's theory of cation selectivity of zeolites[30−32] according to which zeolite A is very selective for Ba^{2+}, which is a large, low hydration energy cation. Actually, zeolite A, owing to its low Si/Al ratio (1), displays a high framework charge density (1032 C/cm^3)[33] which results in a high strength of the electrical field of its anion framework. These zeolites are reported to be more selective for the cations displaying higher charge in the case of an exchange reaction involving heterovalent cations.

A possible explanation of the difficulties occurring in the $Ba^{2+} \rightarrow 2Na^+$ exchange on zeolite A might be supplied by the dramatic distortion of the framework and subsequent loss of crystallinity of zeolite A arising from Ba exchange (see Figure 1). Actually, such dramatic framework distortion and subsequent loss of crystallinity could very likely hinder the diffusion of Ba^{2+} and Na^+ in the zeolite channels, which are of molecular dimensions,[19] thus giving rise to slower exchange kinetics.

A careful inspection of the XRD patterns reported in Figures 2−6 infers a reconsideration of the sequence of transformations of zeolite → amorphous phase → hexacelsian → monoclinic celsian reported in ref 10. First of all, it must be said that the cations present in the zeolite framework are Ba and Na. When, at temperatures slightly lower than 200 °C, the thermal collapse of the microporous zeolite structure occurs, most of Ba is found in the resulting amorphous phase. Unlike Ba, residual Na (0.20 meq/g) is found in the small amount of the sodium−barium aluminosilicate banalsite, $Na_2BaAl_4Si_4O_{16}$, whose presence was recorded after heating at 200 °C. These findings are supported by the literature data. Actually, Ba exchange was found to give rise to a disrupting action even on other zeolite frameworks. For instance, Ba exchange in phillipsite was found irreversible on account of a marked framework distortion[34] and in chabazite Ba exchange resulted in thermal behaviors similar to zeolite Ba-A.[35,36] As far as Na is concerned, its presence in zeolite frameworks was often found to give rise to topotactic transformations into different crystalline structures on heating, as it occurs in the case of Na forms of chabazite and EAB-type zeolites.[37]

An other, more important, finding is that heating at 500, 600, 700, 800, or 900 °C results in the appearance of extremely broad diffraction peaks of monoclinic celsian in the XRD patterns prior to the crystallisation of hexacelsian. A similar finding was only hypothesized by Bansal and Drummond III[2] who reported that nuclei of the strontium feldspar homologous of monoclinic

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(30) Eisenmann, G. *Biophys. J.* **1962**, *2*, 259.

(31) Sherry, H. S. In *Ion Exchange. A Series of Advance*; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1969; p 89.

(32) Colella, C. *Miner. Deposita* **1996**, *31* (6), 554.

(33) O'Connor, J. F.; Townsend R. P. *Zeolites* **1985**, *5*, 158.

(34) Barrer, R. M.; Munday, B. M. *J. Chem. Soc. A* **1971**, 2904.

(35) Colantuono, A.; Dal Vecchio, S.; Mascolo, G.; Pansini, M. *J. Therm. Anal.* **1996**, *47*, 281.

(36) Passaglia, E. *Natural Zeolites. Occurrence, Properties, Uses*; Sand, L. B., Mumpton, F. A., Eds.; Pergamon Press: Elmsford, 1976; p 45.

(37) Cartlidge, S.; Meier, W. M. *Zeolites* **1984**, *4*, 218.

celsian might have formed in the starting hexacelsian material used in their study (a glass of stoichiometric composition $SrAl_2Si_2O_8$ melted at ∼2000 °C in a continuous electric melter starting from laboratory grade $SrCO_3$, Al_2O_3, and SiO_2).

The formation of nuclei of monoclinic celsian starting from 500 °C might likely be explained in the following way. The amorphous phase arising from the thermal collapse of Ba-A zeolite structure is made up of basic TO_4 (T = Si, Al) tetrahedra, which are the primary building units in every aluminosilicate. The framework of various zeolites may be thought to consist of slightly more complex units, called secondary building units (SBU).[38] The association of the basic TO_4 tetrahedra in SBUs is reported either in glasses[39] or melts,[40,41] and thus it appears likely to occur even in the amorphous phase arising from the thermal collapse of the Ba-A zeolite structure. In such glasses, the various SBUs are preferred, depending on the kind of extraframework cation as well as the Si/Al ratio.[42] For instance, in the case of a glass of anorthite composition ($CaAl_2Si_2O_8$), the existence of a three-dimensional framework structure was proven by Raman spectroscopy[41] and X-ray radial distribution analysis,[43] in which simple-four-ring (S4R) tetrahedral units are recognizable, or in $NaAlSiO_4$ glasses, where simple-six-rings (S6R) units were confirmed.[44] Each individual S4R or S6R tetrahedral unit is itself of a diameter of 1.0−1.5 nm. During nucleation, an association of several SBUs was reported to occur in blocks whose dimensions range between 5 and 25 nm.[39−45] Thus, the amorphous intermediates which are the precursors of the phases which crystallize at higher temperatures may be considered as nanostructured materials.[46] The different SBUs, which may occur in such glasses, and the different ways in which such SBUs may organize prior to recrystallization[42] may strongly affect the process of recrystallization itself and even their final products.[42] Thus, it appears likely that in a manner analogous to what occurs in the heating of other zeolites,[42] the SBUs present in the amorphous phase arising from the thermal collapse of the Ba-A zeolite structure associate, starting from 500 °C, in nuclei of monoclinic celsian. Such nuclei, at a first stage, remain unaltered even when, at higher temperatures (starting from 900 °C), crystallization of hexacelsian occurs. At a second stage, starting from 1100 °C, the monoclinic celsian nuclei previously formed favor the conversion of hexacelsian into monoclinic celsian at temperatures far lower than those reported in the literature.[10] To support this interpretation, a thorough structural investigation as well as a careful characterization of the amorphous phase arising from the thermal collapse of the microporous structure of zeolite Ba-A and the early stage of crystallization process would be needed, but it goes beyond the scope of this work and could be the subject of a forthcoming paper.

Another point that is worth stressing is that the conversion of hexacelsian into monoclinic celsian reaches completion in times ranging from 10 to 22 h, 10 to 15 h, and 15 to 22 h at 1300, 1400, and 1500 °C, respectively. The fact that the time for completion goes through a minimum occurring at a temperature close to 1400 °C reflects a competition between the driving force for crystallization of monoclinic celsian and atomic mobility, as the former steadily decreases while the latter steadily increases with increasing temperature.[47]

The temperatures and times at which the conversion of hexacelsian into monoclinic celsian reaches completion are far higher than those (1100 °C, 6 h) recorded in ref 10. This finding may be related to different Na contents of the two different Ba-A zeolite samples. Actually, the sample used in ref 10 displayed a Na residual content of 0.58 meq/g, including Na present as $NaAlO_2$ (occluded), whereas the sample used in this study displayed a Na residual content of 0.20 meq/g. This hypothesis is supported by the fact that the presence of Li in zeolite A or zeolite X framework was found to result in lower temperatures and times of crystallization,[10,13,22,25] and thus it appears likely that an other alkaline cation, such as Na, behaves in the same way.

Another discrepancy between the results of this work and the results reported in ref 10 concerns the temperature at which the exothermic effect, recorded in the DTA curve and attributed to hexacelsian crystallization, occurs. Actually, the temperature (1022 °C) recorded in this work is higher than the temperature (982 °C) reported in ref 10. Even this discrepancy may be explained by the different residual Na contents of the two samples which very likely favors even the crystallization of hexacelsian.

Conclusions

This investigation supplies a valid explanation of the high reactivity of the amorphous phase arising from the thermal collapse of the microporous structure of zeolite Ba-A. The evidence reported indicates that the residual Na content of zeolite Ba-A strongly affects the various phase transformations which occur during the thermal treatments. In particular, a higher Na residual content was found to result in lower crystallization temperatures and/or shorter times, ceteris paribus. This last fundamental finding, if confirmed, would acquire great importance from a practical point of view. Actually, a wise control of the residual Na content of zeolite Ba-A could fulfill a double goal. On one hand, it could limit the trouble arising in the final part of the $Ba^{2+} \rightarrow 2Na^+$ exchange on account of the dramatic framework distortion and subsequent loss of crystallinity which give rise to slower kinetics of exchange. On the other hand, lower temperatures and/or shorter times could be needed to attain the full conversion of hexacelsian into monoclinic celsian.

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[38] Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of the Zeolite Framework Types*; Elsevier: Amsterdam, 2001; p 6.

[39] De Jong, B.; Schramm, C.; Parziale, V. *Geochim. Cosmochim. Acta* **1984**, *48*, 2619.

[40] Kirkpatrick, R. *Am. Mineral.* **1983**, *68*, 66.

[41] Seifert, F.; Mysen, B.; Virgo, D. *Am. Mineral.* **1982**, *67*, 696.

[42] Dimitrijevic, R.; Dondur, V.; Kremenovic, A. *Zeolites* **1996**, *16*, 294.

[43] Taylor, M.; Brown, G. *Geochim. Cosmochim. Acta* **1979**, *43*, 61.

[44] Taylor, M.; Brown, G. *Geochim. Cosmochim. Acta* **1979**, *43*, 1467.

[45] Kuo, L.; Kirkpatrick, R. *Am. Miner.* **1982**, *67*, 676.

[46] Gleiter, H. *J. Appl. Crystallogr.* **1991**, *24*, 79.

[47] Uhlmann, D. R. *J. Am. Ceram. Soc.* **1983**, *66* (2), 95.

It must be said that it is very likely that the residual Na content of zeolite Ba-A affects even the electrical and thermal properties of the monoclinic celsian which represents the final product of the whole process. Thus, an investigation aiming at fulfilling this last goal would be needed to evaluate the Na content that can be tolerated in monoclinic celsian based ceramics according to their various possible uses.

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