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Densification and crystallization of Ba-exchanged zeolite A powders

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Abstract

The effect of thermal treatment, Na content and mineralizer ion on the sintering process of Ba-exchanged zeolite A on the zeolite → celsian thermal transformation are investigated. The powder samples containing different amounts of Na^+ and Li^+ were pressed at 30 MPa and thermally treated at temperatures from 1000 to 1400 °C for times up to 5 h and subsequently were characterized by room temperature X-ray diffraction and by scanning electron microscopy. Increasing the Na residual content in the Ba-zeolite A samples improves the sintering process, even if the highest Na content appears to inhibit the zeolite → celsian transformation, since a new crystalline phase appears at the highest temperature. Moreover, the porosity of all samples thermally treated is quite high. Finally the manufacture of pressed samples allowed lower temperatures and times to be used to obtain the transformation zeolite Ba-A → monoclinic celsian, which suggests it is a potential method to prepare celsian low temperature refractory materials. At last an ANOVA analysis was carried out to identify the independent parameters from a statistical point of view.

Keywords: A. Powders: solid state reaction; A. Sintering; D. Glass–ceramics; Zeolite

1. Introduction

Since the discovery of the preparation of monoclinic celsian by Ba-exchanged zeolite A thermal transformation, intensive of studies have been conducted [1–3].

Monoclinic celsian has excellent physical properties: high melting point, low thermal expansion coefficient up to 1000 °C, and the absence of phase transitions up to 1590 °C, so that many technical application have been exploited.

Interesting works concerning the study of the thermal transformation of alkaline-earth or alkaline cation exchanged zeolites into celsian are present in the literature [4,5]. However, systematic investigations aiming at determining the optimal conditions for sintering system of technological interest starting from cation exchanged zeolites are limited [5]. In a previous paper [6] the authors reported the thermal transformation of a barium-exchanged zeolite A, containing a residual Na^+ content of 0.20 meq/g into celsian, considering different thermal treatments; the effect of the use of pressed sample on the zeolite → monoclinic celsian transformation was not considered.

In the present work powders of Ba-exchanged Na^+ and Li^+ zeolites A containing different residual amount of Na^+ and Li^+ were pressed at 30 MPa and sintered with different thermal treatments. The effect of zeolite composition, temperature, time and mineralizer on the sintering and zeolite → monoclinic celsian transformation are the main objects of this paper.

2. Materials and experimental tests

Carlo Erba reagent grade synthetic zeolite 4A ($Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$) was subjected to various cation exchange operations in order to obtain four samples of Ba-exchanged zeolite A bearing different residual amounts of Na. The samples which will be identified from this point onwards as Na1 (0.27 meq/g of Na residual), Na2 (0.43 meq/g of Na residual), Na3 (0.58 meq/g of Na residual), Na4 (0.74 meq/g of Na residual) and were obtained according to the same procedure used for the authors in previous work [6]. Homoionic Li zeolite A was obtained by the procedure reported in previous papers and was subjected to cation exchange operation in order to obtain one sample (Li1) of Ba-exchanged zeolite A bearing

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residual amount of Li (0.13 meq/g of Li residual) [7]. In order to verify the efficiency of the cation exchange operations, chemical analysis on the samples was performed according to the following procedure. The zeolites were 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. Since the sintering process is dependent on the form and dimensions of particles, the powder particle size distribution of zeolites was determined by using a laser particle size analyser (Malvern Instruments, Master Sizer Hydro 2000S, Malvern, UK).

The zeolites transformation temperatures were determined by a Netzsch, STA 409 differential thermal analyzer (DTA) on samples ground to an average particle size of less than 25 μm. The DTA measurements were carried out using a 10 °C/min heating rate up to 1200 °C.

In order to prepare the samples for sintering, 6 wt% of water was added to the zeolite powders which were then pressed with an axial cold-press at 30 MPa to obtain disks of 40 mm diameter and 5 mm thickness. The disks were dried in an oven at 105 °C for 24 h to remove the water.

The sintering and crystallization behavior of the pellets was studied by performing thermal treatments in an electrical kiln (Lenton, mod. EHF 17/17) with the following heating cycles: from 20 to 500 at 5 °C/min, from 500 °C to the maximum temperature (1000, 1100, 1200, 1300, 1400 and 1500 °C) at 10 °C/min, with 1, 2, 3, 4 and 5 h soaking times; finally, a cooling stage from the maximum temperature to 800 °C at 20 °C/min in an oven, was conducted followed by cooling in air. The linear shrinkage (LS%) was evaluated using the formula:

$$\mathrm{LS}\% = \frac{L_g - L_f}{L_g} \times 100 \quad (1)$$

where L_g and L_f are measured length of green and fired samples, respectively, while the measurements of open porosity were conducted by an Intrusion Mercury Porosimeter, Micromeritics, mod. AutoPore 1215-II.

To detect and identify the crystalline phases formed during the heat treatments, X-ray diffraction (XRD) was performed on finely ground specimens. Patterns were collected using a powder diffractometer (Philips PW3710) with Ni-filtered Cu Kα radiation in the 10–50° 2θ range, with a step size 0.02° 2θ and a 3 s data collection time step. The ratio of monocelsian to hexacelsian and the content of glassy phase in some heated specimens were determined on the basis of the XRD intensities and by using the Rietveld-Reference Intensity Ratio (R.I.R.) method [8,9].

Samples were quantitatively analysed by adding 10 wt% of corundum (NIST SRM 674a) to all samples as an internal standard. The mixtures, ground in an agate mortar, were side loaded in an aluminium flat holder in order to minimize the preferred orientation problems. Data were recorded in the 5–140° 2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-R.I.R. refinements, using GSAS software [10], were rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized.

Table 1
Chemical composition of Ba-exchanged zeolites (wt%)

Sample	SiO_2	Al_2O_3	BaO	Na_2O	K_2O	Li_2O	H_2O
Na1	26.21	22.98	30.80	1.04	0.04	0.00	13.40
Na2	27.52	24.32	28.01	1.55	0.00	0.00	12.00
Na3	25.26	24.94	26.30	1.82	0.00	0.00	16.70
Na4	27.55	27.40	25.81	2.62	0.00	0.00	10.25
Li1	32.48	27.60	39.13	0.62	0.00	0.17	[a]

[a] This analysis was performed on a dehydrated sample.

Information concerning the crystallisation process and the microstructure of the sintered materials were obtained by scanning electron microscopy, SEM (Philips, XL 40) on surface polished gold-coated specimens.

On experimental data of the samples containing sodium, an ANOVA analysis was carried out to identify the independent parameters from a statistical point of view. Subsequently, on the basis of previous step, mathematical models were developed using Design Expert v.7.0.1 by Stat-Ease Inc. [11].

3. Results and discussion

The particle size distribution of the studied zeolites show that, independently of the mineralizer content, all samples have a monomodal distribution with D_{50} 10–12 μm and D_{90} under 21.5 μm.

The chemical composition of the samples is reported in Table 1.

Fig. 1 shows the DTA curves of Li1, Na1 and Na4. An endothermic peak at around 150 °C corresponds to a dehydration reaction followed by the thermal breakdown of the microporous zeolitic structure with the formation of an amorphous phase. It is also evident in all samples a sharp exothermic peak at about 1000 °C which can be attributed to the formation of crystalline species. As reported by Dell'Agli et al. [1] it is possible to summarize the phenomena that occur upon heating Ba-exchanged zeolite A as follows: zeolite at 200 °C → amorphous phase at 800 °C → hexacelsian >900 °C → monoclinic celsian. The exothermic peak is slightly shifted towards lower temperatures

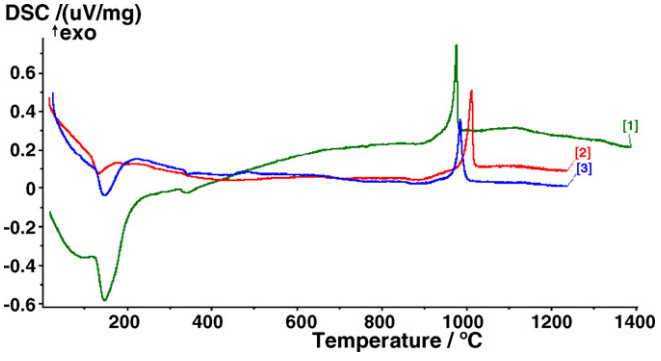

Fig. 1. DTA curves of the samples: [1] Li1; [2] Na1; [3] Na4.

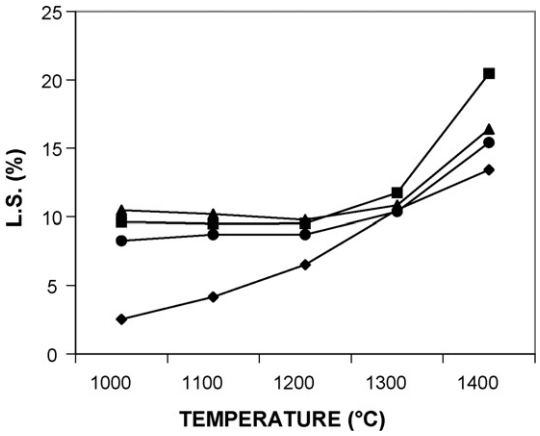

Fig. 2. Linear shrinkage (%) of the Na sintered samples: ◆ Na1; ● Na2; ■ Na3; ▲ Na4.

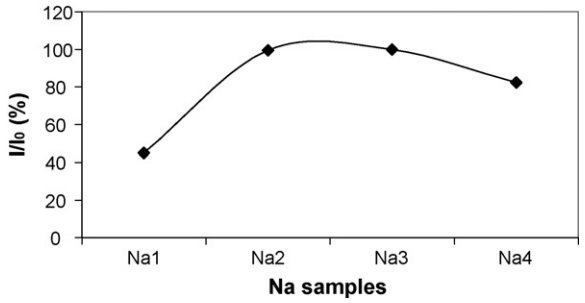

Fig. 3. Celsian relative peak intensity ratio, I/I_0 (%) vs. Na samples.

with increasing the Na content. The sequence of these transformations occurs at different temperatures depending on the composition considered. In fact the hexacelsian crystallization of Na4 sample occurs at lower temperature since the glassy phase, containing more network modifier ions, decreases the viscosity favoring the crystallization of hexacelsian.

As regarding Li1 curve, the exothermic peak falls at the lowest temperature. This behavior is explained considering the field strength (Z/a^2, Z valence, a ion radius) of lithium in glasses, since the zeolite powders during heat treatment are transformed to an amorphous phase [12]. The Z/a^2 of lithium in glasses is the greatest among the alkali metals, so Li^+ is strongly bound in the silicate network and shows an higher tendency for devitrification than does Na or K. Thus, it can act as a nucleant for a new crystalline phase [13,14].

3.1. Temperature and composition effect

In order to investigate the celsian crystallization during the zeolite sintering process, the Ba-exchanged zeolites were heated with different thermal treatments (temperatures and times).

The linear shrinkage is an important parameter in order to valuate the sintering behavior of the samples since it is related to their open porosity. The open porosity (accurancy: ± 2%) of the samples are: Na1: 54%, Na2: 52%, Na3: 51, Na4: 51%. Fig. 2 reports the linear shrinkage of the studied samples. It is possible to note that increasing the Na content, the linear shrinkage of the samples slightly increases while the porosity slightly decreases. This effect is due to the formation of a glassy phase, that improves the sintering conditions [14,15]. In order to understand the effect of the temperature on the transformation zeolite → monocelsian the Na1, 2, 3, 4 samples were treated at the 1000, 1100, 1200, 1300 and 1400 °C for 5 h following the above reported heating cycle.

Table 2 reports the qualitative trend in the sample crystalline phases calculated from the XRD experimental data. The relative peak intensity ratio percentage I/I_0 (%) has been taken into account, where (I_0) is the peak intensity corresponding to the maximum of counts in the XRD patterns. Thus, when the monoclinic celsian was the main phase the peak was taken at 3.35 Å, for hexacelsian at 3.95 Å and for nepheline at 4.17 Å (I) is the relative peak intensity corresponding to counts for each XRD pattern at the same reflection when the above mentioned phases are not the main ones. The conditions for the maximum celsian crystallization were recognized at 1300 °C for all analysed samples; for hexacelsian, it was found at 1000 °C except for the Na4 sample (1100 °C).

The results showed that monoclinic celsian is the main crystalline phase at higher temperatures while hexacelsian appears preferentially at low temperatures. Moreover, it is possible to observe that the transformation to monoclinic celsian occurs at lower temperature (1100 °C) in the Li sample with respect to the Na samples.

In agreement with powdered samples thermal treatment results [1,6,7], the monoclinic celsian percentage (Fig. 3) increases with raising the Na residual content of Ba-exchanged zeolite A samples. Nevertheless highest temperature samples Na3 and Na4 show a small decrease in intensity, since a new crystalline phase appears, $NaAlSiO_4$ (ICDD #33-1203). Moreover, the glassy phase increases with Na content as confirmed by RIR-Rietveld performed only on Na2 and Na4 samples treated at 1100 and 1300 °C as shown in Table 3.

Table 2
XRD results of Na and Li samples: relative peak intensity ratio, I/I_0 (%) vs. temperature (°C)

T (°C)	Na1	Na2	Na3	Na4	Li1
1000	M (6%); H (100%)	M (9%); H (100%)	M (16%); H (100%)	M (24%); H (92%)	M (36%); H (100 °C)
1100	M (71%); H (34%)	M (67%); H (70%)	M (85%); H (16%)	M (30%); H (100%)	M (100%)
1200	M (93%); H (13%)	M (99%); H (23%)	M (77%); H (25%)	M (80%); H (59%)	M (100%)
1300	M (100%)	M (100%)	M (100%)	M (100%)	M (96%)
1400	M (100%)	M (100%)	M (92%); N (5%)	M (94%); N (10%)	

M, monocelsian; H, hexacelsian; N, $NaAlSiO_4$.

Table 3
R.I.R.-Rietveld results of some studied samples at different temperatures

Sample	Monocelsian (wt%)	Hexacelsian (wt%)	Amorphous (wt%)	Rietveld agreement indices
Na2, 1100 °C	57.3 (1)	15.0 (1)	27.6 (2)	$\chi^2 = 4.20$; $R_{wp} = 0.066$; $R_p = 0.047$
Na2, 1300 °C	79.1 (2)	–	20.8 (2)	$\chi^2 = 2.83$; $R_{wp} = 0.056$; $R_p = 0.042$
Na4, 1100 °C	24.4 (1)	43.7 (1)	31.8 (2)	$\chi^2 = 15.8l$; $R_{wp} = 0.125$; $R_p = 0.077$
Na4, 1300 °C	68.9 (1)	1.0 (1)	30.0 (2)	$\chi^2 = 3.53$; $R_{wp} = 0.061$; $R_p = 0.042$
Li1, 1100 °C	88.9 (1)	–	11.0 (2)	$\chi^2 = 2.50$; $R_{wp} = 0.050$; $R_p = 0.037$
Li1, 1300 °C	90.7 (2)	–	9.2 (2)	$\chi^2 = 2.40$; $R_{wp} = 0.048$; $R_p = 0.036$

SEM observations on polished surfaces of sintered powder confirm the XRD results. Fig. 4 show the microstructures of samples Na1, Na2, Na3 and Na4 at 1300 °C. Moreover, it is possible to note a decrease in porosity with an increase in glassy phase from sample Na3 to sample Na4. The presence of a glassy phase in sample Na4 is also confirmed by the XRD pattern since an increasing base line intensity is found.

As far as the temperature effect is concerned, the results of the Na2 sample treated at different temperatures (Fig. 5) are reported. Increasing the temperature the crystalline phase morphology change since a hexacelsian → celsian transformation occurs. In fact at highest temperature it is clear that there is exaggerated grain growth in the form of white crystals in the glass matrix.

By statistical analysis, it is possible to conclude that both sodium percentage and temperature are influential parameters for monocelsian, according to a confidence level of 95%, the standard value of confidence level accepted in scientific and technical literature. It means that the probability to mistake in the above conclusion is only the 5%. In Fig. 6 the 3D plot monocelsian versus temperature and sodium percentage is presented. It substantially confirms the observations above made reducing only the effect of sodium. Low percentages of sodium and high temperatures permit to get the highest percentage of monocelsian. It is quite difficult to consider between temperature and time which is the most influential since the two parameters show different ranges and intervals. In fact temperature is

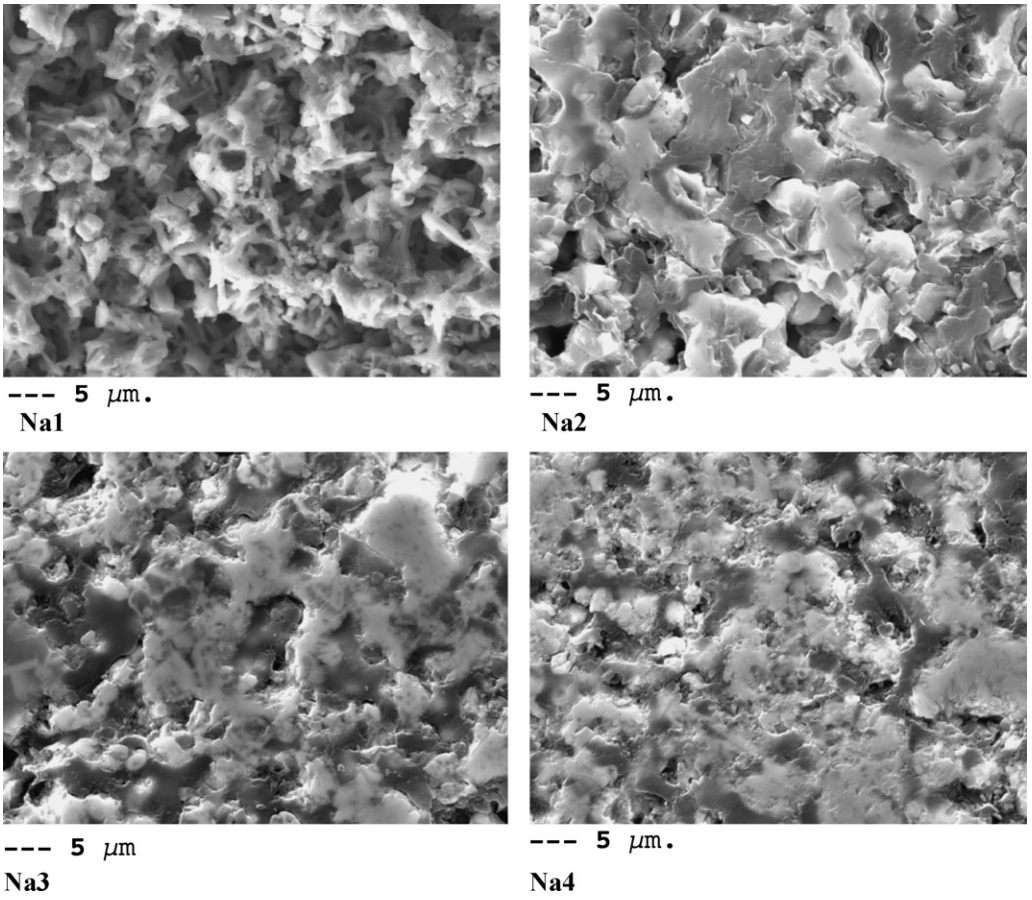

Fig. 4. SEM observation of Na samples treated at 1300 °C for 5 h.

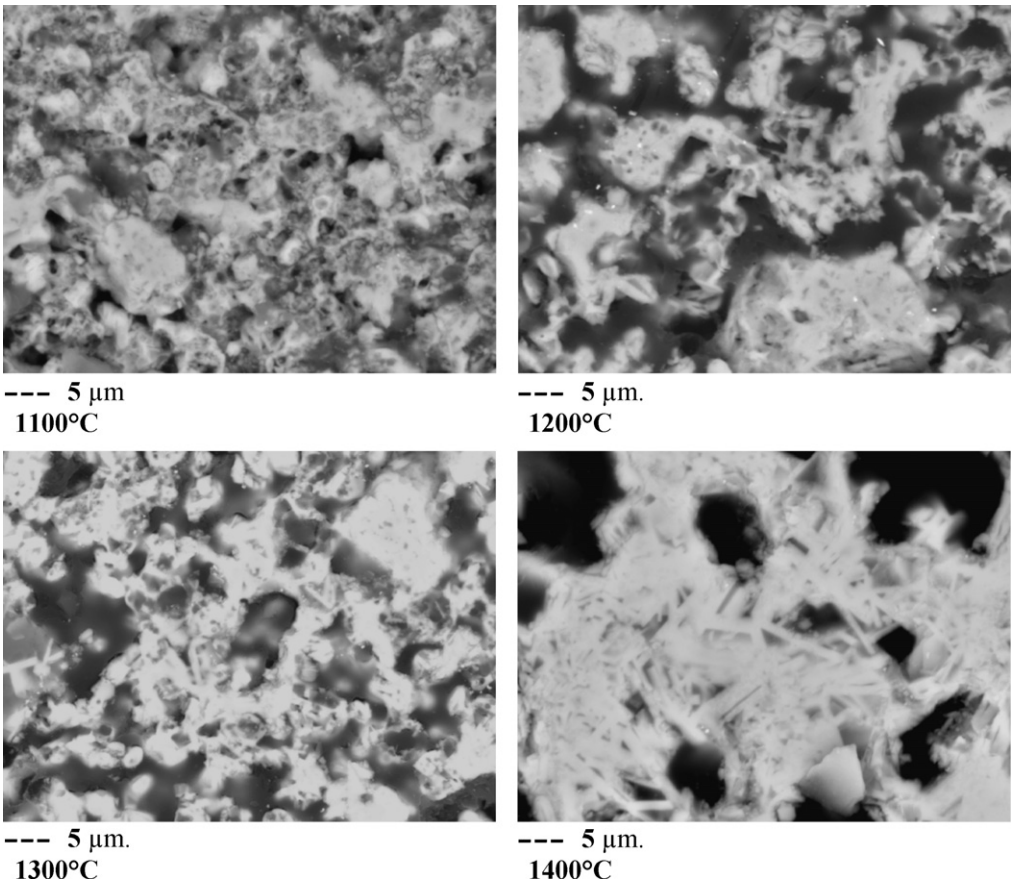

Fig. 5. SEM images of Na2 sample treated at different temperatures for 5 h.

varied of 100 unit per time and the time for 1 h. Moreover, there is not a equivalence between time and temperature so it is not possible to compare the influence of the two variables.

On the contrary, temperature is the only important parameter in the case of hexacelsian, as shown in the 3D plot in Fig. 7. High temperatures decrease quickly its percentage. That does not mean that the percentage of sodium

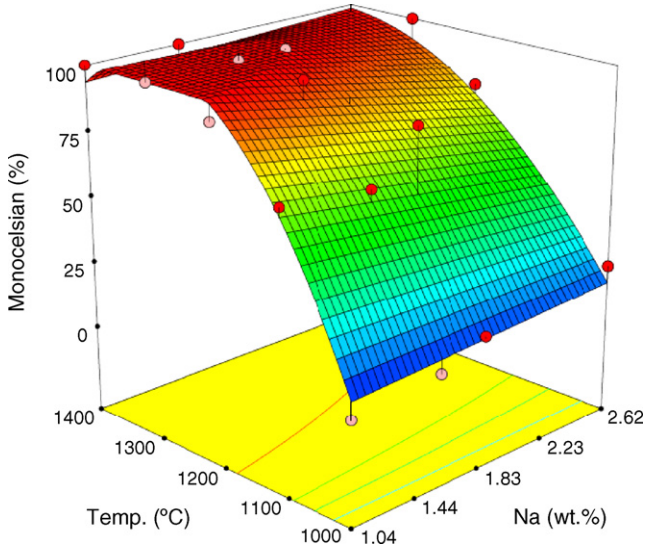

Fig. 6. 3D plot for Monocelsian (%) vs. Na concentration (wt%) and temperature (°C). The circles are the experimental data.

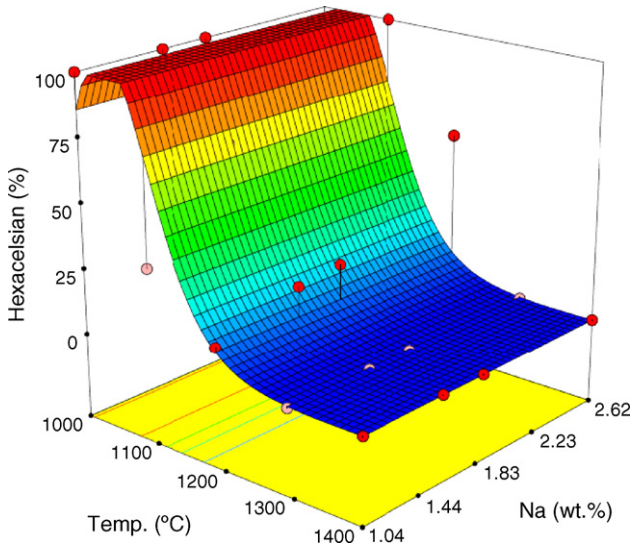

Fig. 7. 3D plot for Hexacelsian (%) vs. Na concentration (wt%) and temperature (°C). The circles are the experimental data.

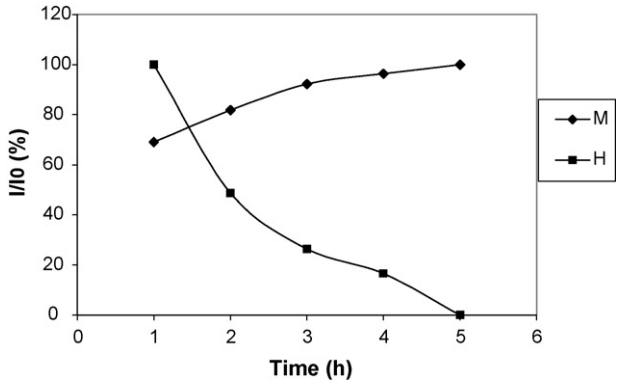

Fig. 8. Relative peak intensity ratio I/I_0 (%) vs. thermal treatment time of Na2 samples.

it is not important, but it is not in the range of concentration used in the present work.

3.2. Time effect

In order to asses the effect of time on Ba-zeolite A to monoclinic celsian transformation some thermal treatments were performed only on the Na2 sample; in particular the samples were treated at 1300 °C for 1, 2, 3, 4, 5 h. In Fig. 8 we report the relative intensity ratio (%) of monocelsian (M) and hexacelsian (H) as a function of time treatment. It is possible to note that increasing the time, monocelsian increases while hexacelsian decreases. The metastable form, hexacelsian, usually nucleated more readily than the stable form, monocelsian [16].

3.3. Li effect

X-ray diffraction results of Li1 sample after different thermal treatments are reported in Table 2. It is possible to note that also in this case the temperature is the most important variable on Ba-zeolite A to monoclinic celsian transformation. In particular the complete transformation occurs at lower temperature (1100 °C for 5 h) with respect to Na samples.

Fig. 9 shows the scanning electron microphotographs of the specimens heated at different temperatures. In contrast to the Na samples the microstructure of the Li sample does not change with the temperature. In fact at 1100 °C it is possible to note that the sample shows monocelsian crystals (as confirmed by XRD results), immersed in a glassy matrix, even if the crystals size appear qualitatively smaller than those in the Na samples. Increasing the temperature the morphology of the samples does not change since the hexacelsian → celsian transformation does not occur. Rietveld results (Table 3) show that the glassy phase content in the Li samples is less than the one present in the Na samples; this is due to the fact that the residual content of

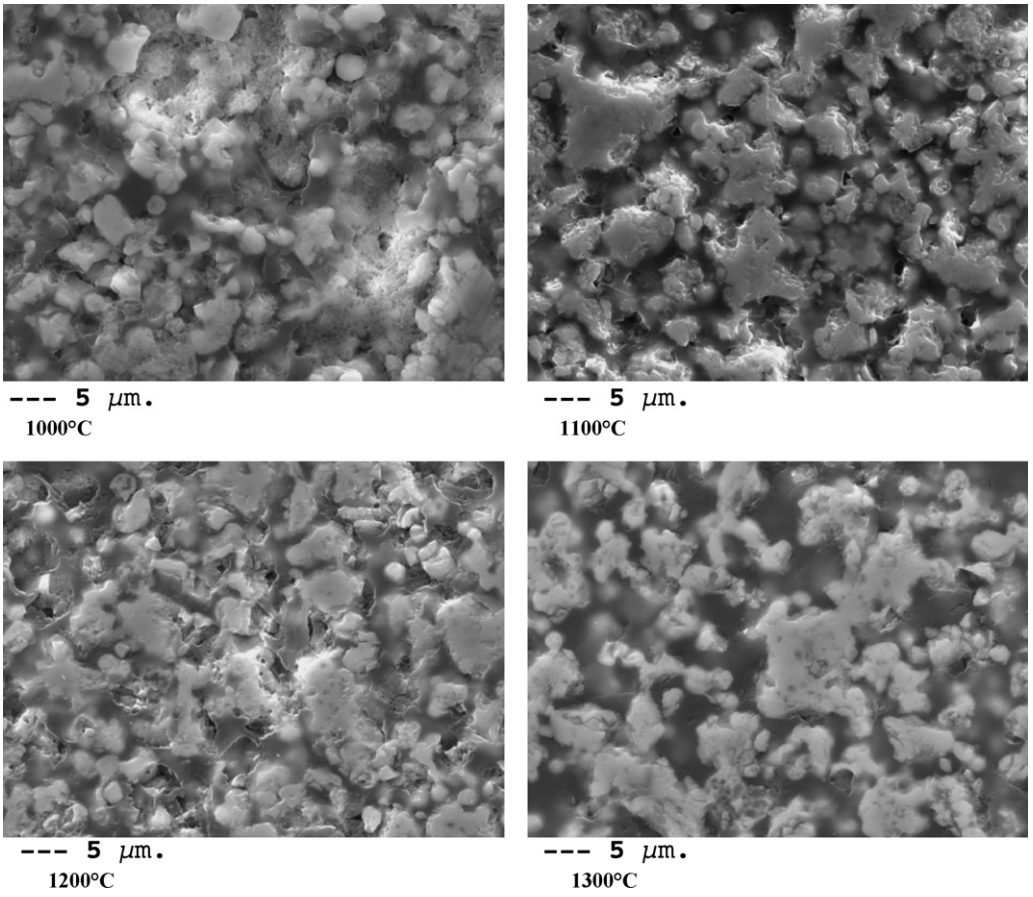

Fig. 9. Li samples treated at different temperatures for 5 h.

Li is less (0.13 meq/g) than Na content (0.43 meq/g) of Na-Zeolite A. As already reported for Na samples, the glassy phase promotes the sintering process of the powders even if the effect is not so marked. Moreover, the amount of crystalline celsian in the Li1 sample is higher than in all the Na samples.

4. Conclusions

Monoclinic celsian materials have been obtained by thermal treatment of Ba-exchanged zeolite precursor. The manufacture of pressed samples results in lower temperatures ($\Delta T = 200\ ^\circ C$) and times (5 h in contrast to the 8–20 h as reported in literature) necessary to obtain the zeolite → celsian transformation than un-pressed samples. It has been observed an optimum Na content (0.43 meq/g) which permits a complete celsian crystallization at 1300 °C for 5 h. Higher amounts of Na residual content promotes higher quantity of glassy phase and a new-formation crystalline phase ($NaAlSiO_4$).

As far as the Li sample is concerned, the transformation of hexacelsian to monoclinic celsian occurs at lower temperatures (1100 °C) than those exhibited by Na samples (1300 °C). Moreover, the monocelsian crystals size appears smaller than the ones showed by Na samples.

The materials obtained by sintering of Ba-exchanged zeolite precursor show high porosity (50%) so they can be used as low temperature refractory.

The ANOVA analysis results in agreement with the experimental data show that both sodium percentage and temperature are influential parameters in the formation of monocelsian, according to a confidence level of 95%. On the contrary, temperature is the only important parameter in the case of hexacelsian.

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References

[1] G. Dell'Agli, C. Ferone, M.C. Mascolo, M. Pansini, Thermal transformation of Ba-exchanged A and X zeolites into monoclinic celsian, Solid State Ionics 127 (2000) 309–317.
[2] B. Hoghooghi, J. McKittrik, C. Buttler, P. Desh, Synthesis of celsian ceramics from zeolite precursors, J. Non-Cryst. Solids 170 (1994) 303–307.
[3] T. Matsumoto, Y. Goto, Synthesis of monoclinic celsian from Ba-exchanged zeolite A, J. Ceram. Soc. Jpn. 110 (3) (2002) 163–166.
[4] S. Esposito, C. Ferone, M. Pansini, L. Bonaccorsi, E. Proverbio, Comparative study of the thermal transformation of Ba-exchanged zeolites A, X and LSX to celsian, J. Eur. Ceram. Soc. 24 (9) (2004) 2689–2697.
[5] B. Hoghooghi, J. McKittrik, E. Helsel, O.A. Lopez, Microstructural development, densification, and hot pressing of celsian ceramics from ion-exchanged zeolite precursor, J. Am. Ceram. Soc. 81 (4) (1998) 845–852.
[6] N.J. Clayden, S. Esposito, C. Ferone, M. Pansini, ^{29}Si and ^{27}Al NMR study of the thermal trasformation of barium exchangesd zeolite-A to celsian, J. Mater. Chem. 13 (2003) 1681–1685.
[7] A. Collantuono, S. Dal Vecchio, G. Mascolo, M. Pansini, Thermal shrinkage of various cations forms of zeolite A, Thermochem. Acta 296 (1997) 59–66.
[8] M. Bellotto, C. Cristiani, Quantitative X-ray diffraction rietveld analysis of low temperature coal ashes, Mater. Sci. Forum 79–82 (1991) 745–750.
[9] A.F. Gualtieri, G. Artioli, Quantitative determination of chrysotile asbestos in bulk material by combined Rieveld and RIR methods, Powder Diffr. 10 (1995) 269–277.
[10] A.C. Larson, R.B. von Dreele, GSAS: General Structure Analysis System LANSCE, MS H805, Los Alamos National Laboratory, Los Alamos, NM, 1998.
[11] Biblio Marcello.
[12] A. Ata, B. Hoghooghi, J. McKittrick, E. Helsel, J. Loam, The effect of lithium and barium concentrations on the zeolite → glass → celsian phase transformations, J. Mater. Synth. Process. 5 (3) (1997).
[13] M.B. Volf, Chemical Approach to Glass, Elsevier, Oxford, UK, 1984, pp. 219–228.
[14] K.-T. Lee, P.B. Aswath, Role of mineralizers on hexacelsian to celsian transformation in the barium aluminosilicate (BAS) system, Mater. Sci. Eng. 352 (2003) 1–7.
[15] M.G. Randall, Fundamental of sintering, Engineering Materials Handbook Ceramics and Glasses, vol. 4, Ed. ASM Int., USA, 1991, pp. 260–269.
[16] N.P. Bansal, M.J. Hyatt, Crystallization kinetics of $BaO–Al_2O_3–SiO_2$ glasses, J. Mater. Res. 4 (1989) 1257–1265.