J MATER SCI **41** (2006) 4327–4333

Electrical behaviour of materials based on monoclinic celsian derived from cation-exchanged commercial zeolites

A. MOTORI, F. PATUELLI, A. SACCANI*
Dip. di Chimica Applicata e Scienza dei Materiali, Viale Risorgimento 2, 40136 Bologna I
E-mail: andrea.saccani@mail.ing.unibo.it

F. ANDREOLA, F. BONDIOLI, C. SILIGARDI
Dip. di Ingegneria dei Materiali e dell'Ambiente, Via Vignolese 905, 41100 Modena I

A. M. FERRARI
Dip. di Scienze e Metodi dell'Ingegneria, Via Fogliani 1, 42100 Reggio Emilia I

Monoclinic celsian has been obtained by a non-conventional way, i.e. the thermal treatment of 4A-type commercial zeolite: a stoichiometric amount of barium ions was included in the zeolite by means of a cation-exchange treatment. A small concentration of alkali ions (either sodium or lithium) was also present in the exchanged zeolite, since previous studies had underlined the positive effect of these ions on the formation of monoclinic celsian. This particular synthesis proves to be economic, due to the low-cost precursors, the low temperatures and the short times required. However, the presence of even a small content of alkali ions and a residual amorphous phase can negatively affect the insulating properties of the material, thus hindering its use in electrical insulating systems. The results so far obtained show that the material keeps good insulating properties at low temperature, but its conductivity and dielectric losses strongly increase above 200 °C. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Monoclinic celsian is currently used in radomes [1], inert substrates [2] and as a matrix for fiber-reinforced composites [3]. In many of these applications, the electrical insulating properties of the material, which also exhibits excellent dimensional stability and resistance to oxidation at high temperature, are crucial [4]. The synthesis of celsian is particularly delicate, due to the existence of an allotropic form (hexacelsian), which has no technological applications since it undergoes a structural transfomation inducing a volume expansion at about 300 °C. Previous studies showed the possibility of obtaining celsian from sodium-based commercial A- and X-zeolites, through a suitable cation-exchange process and a subsequent thermal treatment [5–8]. A small amount of alkali ions (sodium or lithium) should be present in the celsian precursor [9], in order to promote the formation of monoclinic celsian at the lowest temperatures and in the shortest times.

2. Materials and experimental tests

A 4A-type zeolite (formula: $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$) was subjected to a multiple cation (Ba^{2+}) exchange process, according to a procedure described in details elsewhere [6]. At the end of the process, two materials with the residual concentrations of sodium ions of 0.43 and 0.74 meq/g, respectively, were obtained. A third material, with a final lithium content of 0.13 meq/g, acting as mineralizer, was also derived from the same zeolite precursor. The amount of sodium and lithium was calculated according to the procedure described in details elsewhere [8]. The three types of powders thus obtained had an average size of 10–12 μm, with 90% in volume lower than 21.5 μm and 5% in volume lower than 1 μm. The powders were then humidified with 6 wt.% distilled water and compacted under a pressure of 21 MPa, in order to obtain samples in the form of disks with a diameter of about 40 mm and a thickness ranging from 3 to 4 mm. Subsequently, samples were dried for 5 h at 105 °C and

---

[*] Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-7021-x

TABLE I. Characteristics of the investigated samples

Sample	Maximum cycle temperature (°C)	Alkali content, (meq/g)	Celsian (wt%)	Hexacelsian (wt%)	Amorphous phase (wt%)	Rietveld agreement indices
Na1	1300	0.43	79.1(2)	–	20.8(2)	$\chi^2 = 2.83$ $R_{\mathrm{wp}} = 0.056$ $R_{\mathrm{p}} = 0.042$
Na2	1300	0.74	68.9(1)	1.0(1)	30.0(2)	$\chi^2 = 3.53$ $R_{\mathrm{wp}} = 0.061$ $R_{\mathrm{p}} = 0.042$
Na3	1100	0.43	57.3(1)	15.0(1)	27.6(2)	$\chi^2 = 4.20$ $R_{\mathrm{wp}} = 0.066$ $R_{\mathrm{p}} = 0.047$
Na4	1100	0.74	24.4(1)	43.7(1)	31.8(2)	$\chi^2 = 15.8$ $R_{\mathrm{wp}} = 0.125$ $R_{\mathrm{p}} = 0.077$
Li1	1300	0.13	90.7(2)	–	9.2(2)	$\chi^2 = 2.40$ $R_{\mathrm{wp}} = 0.048$ $R_{\mathrm{p}} = 0.036$
Li2	1100	0.13	88.9(1)	–	11.0(2)	$\chi^2 = 2.50$ $R_{\mathrm{wp}} = 0.050$ $R_{\mathrm{p}} = 0.037$

subjected to the following thermal cycle: from room temperature to 500 °C at a heating rate of 5 °C/min and from 500 °C to (i) 1100 °C or (ii) 1300 °C at 10 °C/min. Samples were than kept at the maximum cycle temperature for 5 hs, cooled to 800 °C at a rate of 10 °C/min and afterwards quenched in air to room temperature. During the thermal treatment, the zeolite firstly collapses forming an homogeneous amorphous material (450–550 °C): the subsequent temperature increase leads to the nucleation and growth of the crystalline phases. Table I summarizes the alkali content and the maximum temperature of treatment of all the investigated samples. In order to determine the type and quantity of phases present after the different thermal treatments, samples were ground and submitted to X-ray diffraction (XRD, Philips PW3710). Samples were quantitatively analysed by the combined Rietveld-R.I.R. (Reference Intensity Ratio) method [10–11]. A 10 wt% of corundum (NIST SRM 674a) has been added to all samples as internal standard. The mixtures, ground in an agate mortar, were side loaded in an aluminum 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 [12], have been rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized. It must be noted that data accuracy is affected by the intrinsic limits of this method, which can lead to overvalue the amorphous phase content; however, this has no practical relevance on the subsequent explanation of the results concerning the electrical characterization.

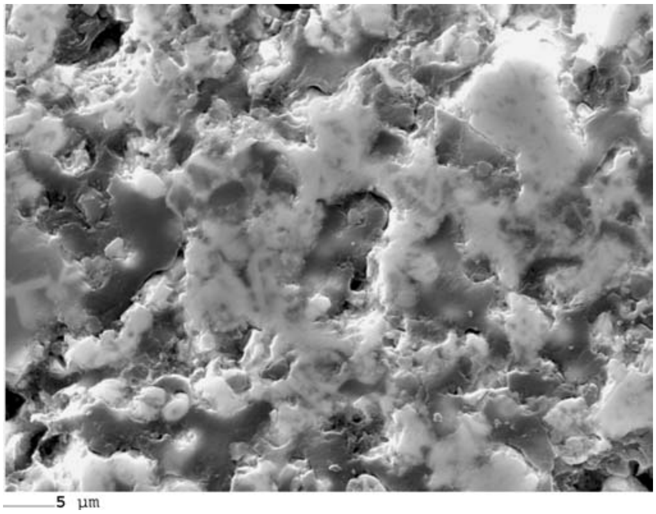

Figure 1 SEM micrograph of the Na2 sample.

Samples have been submitted to ac and dc electrical characterization in nitrogen atmosphere by means of a three-terminal cell; the electrode configuration was obtained by surface gold coating under vacuum. The ac dielectric constant and loss factor were determined over the frequency range 10^{-2}–10^{6} Hz (by means of the Novocontrol Instrument WinETA 3.9) and temperature range from 50 to 550 °C. The dc conductivity was measured over the same temperature range under an electrical field of 1 kV/cm, by the voltmeter-ammeter method (Keithley mod. 237 voltage supplier and mod. 6514 electrometer). Discharging currents were also recorded to investigate the ultra-low frequency ($<10^{-2}$ Hz) behavior of loss factor by means of Fourier transform. Eventually, scanning

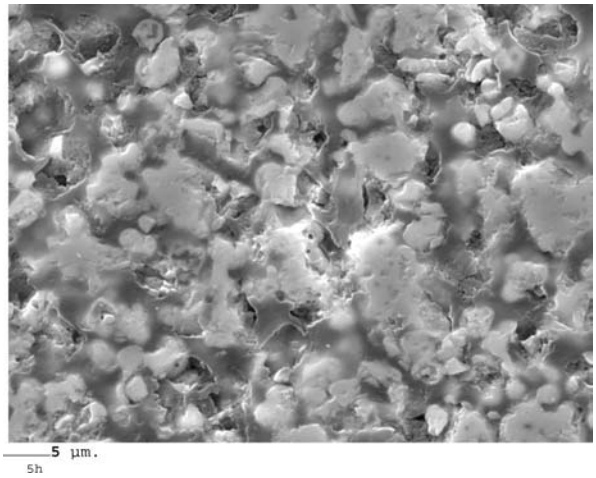

Figure 2 SEM micrograph of the Li1 sample.

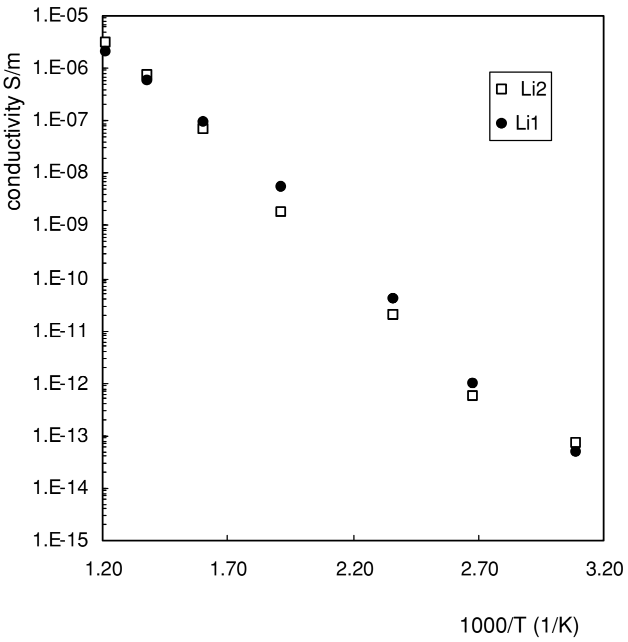

Figure 3 Dc electrical conductivity vs. the reciprocal of the absolute temperature for the specimens containing 0.13 meq/g of lithium ions.

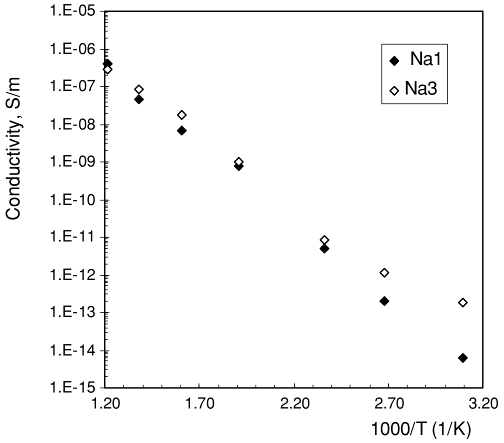

Figure 4 Dc electrical conductivity vs. the reciprocal of the absolute temperature for the specimens containing 0.43 meq/g of sodium ions.

electron microscopy observations (Philips, mod. XL 40) were performed on samples surfaces.

3. Results and discussion

Table I reports the phases content of the samples, provided by the quantitative XRD data elaborated according to the Rietveld-RIR method. As can be seen, lithium promotes more efficiently than sodium the transformation of the collapsed amorphous material (deriving from the thermal treatment of the exchanged zeolite) to monoclinic celsian. According to this observation, Li1 and Li2 samples, treated at 1300 and 1100 °C, respectively, exhibit negligible differences in composition; on the contrary, both Na3 and Na4 specimens contain a larger amount of amorphous phase than Na1 and Na2 samples, due to the lower temperature of thermal treatment; moreover, both the samples still contain a remarkable amount of hexacelsian. Rietveld-RIR results show that the glassy phase content in Li samples is less than that present in Na samples; this is due to the fact that the residual content of Li is less (0.13 meq/g) than Na content (0.43 meq/g). The increase in sodium amount (from 0.43 to 0.74 meq/g) does not lead to an increase in the reaction yield: indeed the amount of monoclinic celsian is lower both in the Na2 and Na4 samples compared to the Na1 and Na3. It must be underlined that Na4 x-ray spectrum disclosed the presence of further peaks in marginal amounts; although in the samples studied in the present work it was not possible to clearly identify the phase related to these peaks, the crystalline $NaAlSiO_4$ phase (JCPDS 33–1203) has been clearly identified in other works on exchanged zeolites of similar compositions [13]; moreover, in thermally treated zeolites containing higher amounts of Li ions (1.03 meq/g), the $LiAlSiO_4$ phase was also identified [14]. Therefore, it may be hypothesized that the peaks refer to $NaAlSiO_4$. The Rietveld-RIR analysis reported in Table I is thus less reliable than that of the others composition as indicated by the higher Rietveld agreement indexes. Although it was not possible to identify the same chemical form in Na2, it can be argued that the formation of sodium alumino-silicate subtracts sodium ions to the main reaction (i.e. monoclinic celsian formation), thus counter-balacing and even reducing the catalytic effect of the mineralizer. SEM observations on polished surfaces of Na2 and Li1 samples, representative of all the investigated samples, are reported in Figs 1 and 2, respectively. It is possible to note the crystalline phase (monoclinic celsian/hexacelsian) enveloped by the residual amorphous phase, as reported in [15].

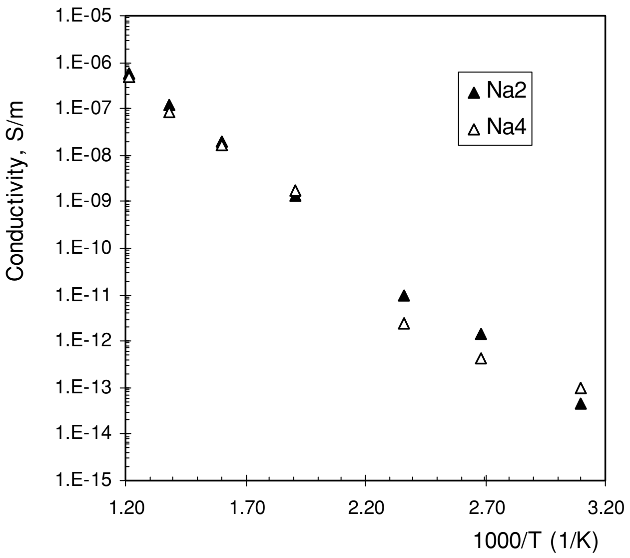

Figure 5 Dc electrical conductivity vs. the reciprocal of the absolute temperature for the specimens containing 0.74 meq/g of sodium ions.

The dc electrical properties of the specimens of Table I are shown in Figs 3–5, where conductivity (after

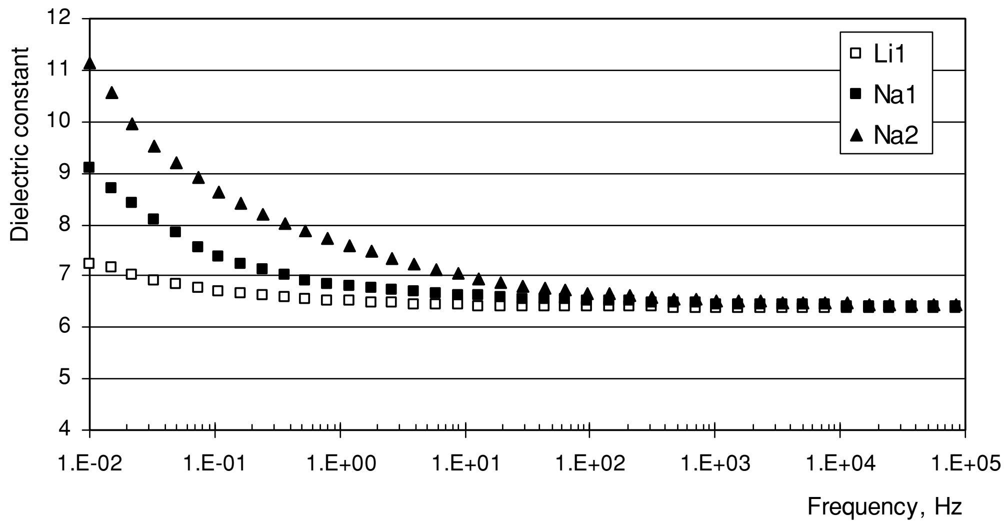

Figure 6 Dielectric constant vs frequency at 50 °C of samples treated at 1300 °C.

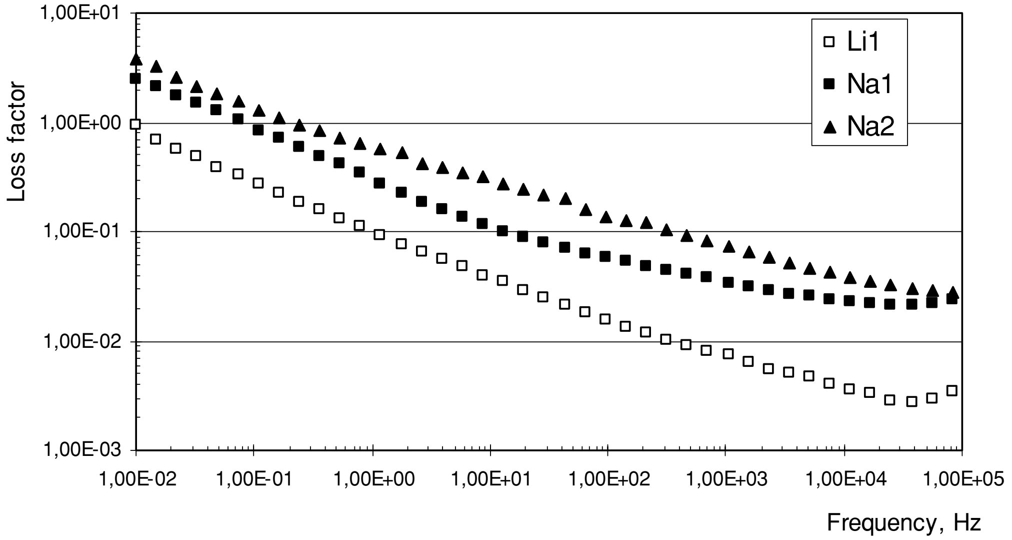

Figure 7 Loss factor vs frequency at 50 °C of samples treated at 1300 °C.

1 h of voltage application) is plotted vs. the reciprocal of the absolute temperature. A strong increase with temperature is observed; moreover, all the samples exhibit good insulating properties below 200 °C, while at higher temperatures conductivity increases rapidly and approaches the semiconducting range near 500 °C. The treatment temperature and the ion content do not significantly affect the conductivity of the samples containing lithium, as expected from their phase composition (Table I). For samples containing sodium, differences in the conductivity values are observed only below 200 °C: conductivity increases as ion content increases and treatment temperature decreases. This effect can be ascribed to the higher content of amorphous phase, which enhances the mobility of the ionic charge carriers: indeed the amorphous phase, even if present in small amounts, strongly affects the overall electrical behaviour. Comparing the effect of the lithium and sodium ions on conductivity, it can be underlined that the specimens containing lithium show higher conductivity values (about one order of magnitude) at all the investigated temperatures, despite their lower amorphous phase and ions content; this can be explained with the higher mobility of lithium ions, due to their smaller radius (0.076 nm for lithium and 0.102 nm for sodium). Samples with different sodium content have however comparable conductivity mainly at high temperatures: a possible explanation can again be ascribed to the formation of sodium alumino-silicates, as previously outlined. In this case, the excess of charge carriers (sodium ions) could be subtracted from the amorphous phase. The activation energy of the conduction process was calculated above 200 °C by linear regression of the experimental data of the Figures previously described; values of 80 kJ/mol and 70 kJ/mol were obtained for specimens containing lithium and sodium ions, respectively. It should thus be noted that there is no remarkable influence of ions content,

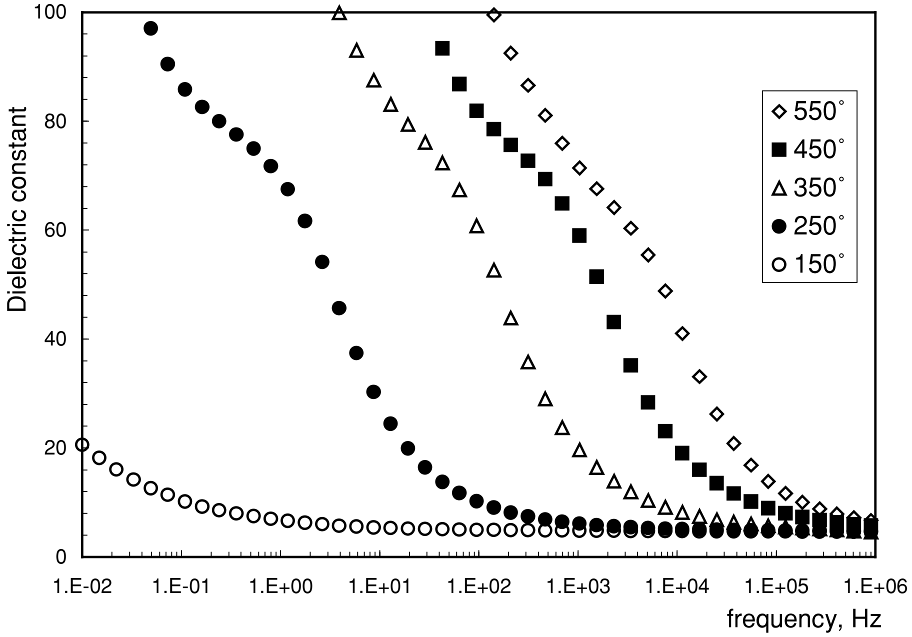

Figure 8 Dielectric constant of the specimen Na1 as a function of frequency, at different temperatures.

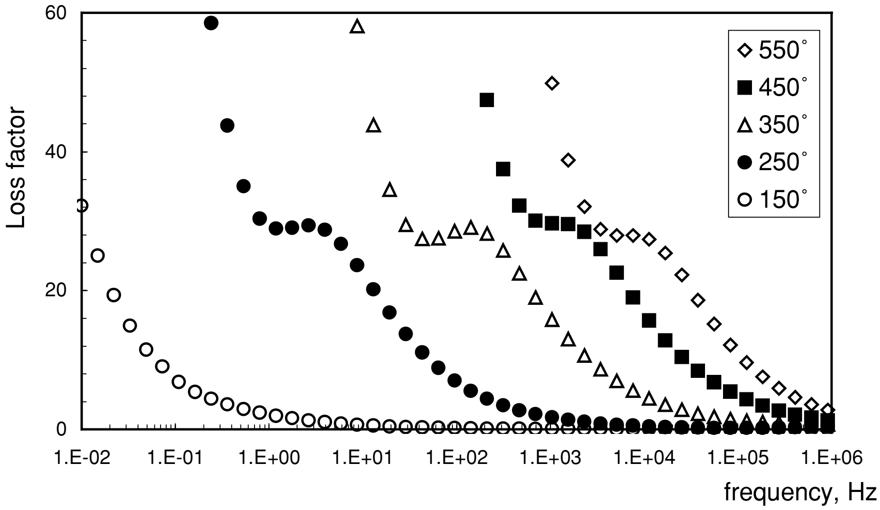

Figure 9 Loss factor of the specimen Na1 as a function of frequency, at different temperatures.

as well as of the treatment temperature on the activation energy. The small difference between lithium and sodium containing samples may be related to the different amount of amorphous phase.

As to the ac properties, Figs 6 and 7 show the values the dielectric constant and loss factor, respectively, as a function of frequency at low temperature for all the samples treated at 1300 °C (samples treated at 1100 °C have a similar behaviour and are not reported for the sake of brevity). Dielectric constant values are almost independent of frequency above 10^2 Hz and are close to those exhibited by pure celsian [4] (values lay between 6.5 and 6.9). Only at low frequency a sharp increase as frequency decreases is observed (Fig. 6). The loss factor shows a continuous and remarkable increase with decreasing frequency (Fig. 7). For both properties, the effect is higher in the specimens containing sodium ions.

At high temperature, however, the dielectric behaviour of all samples becomes more complex: Figs 8 and 9 report the dielectric constant and loss factor of the specimen Na1, at different temperatures, as a function of frequency; a similar behavior is exhibited by all the specimens of Table I and is not reported for the sake of brevity. A flex and a broad peak are present in the dielectric constant and loss factor curves, respectively, which shift to higher frequency with increasing temperature, thus diclosing a thermally activated relaxation process which is however present only at temperatures higher than 150 °C. The strong increase of dielectric constant and losses, observed at all temperatures as frequency lowers, can be ascribed to the mobility enhancement of the ionic charge

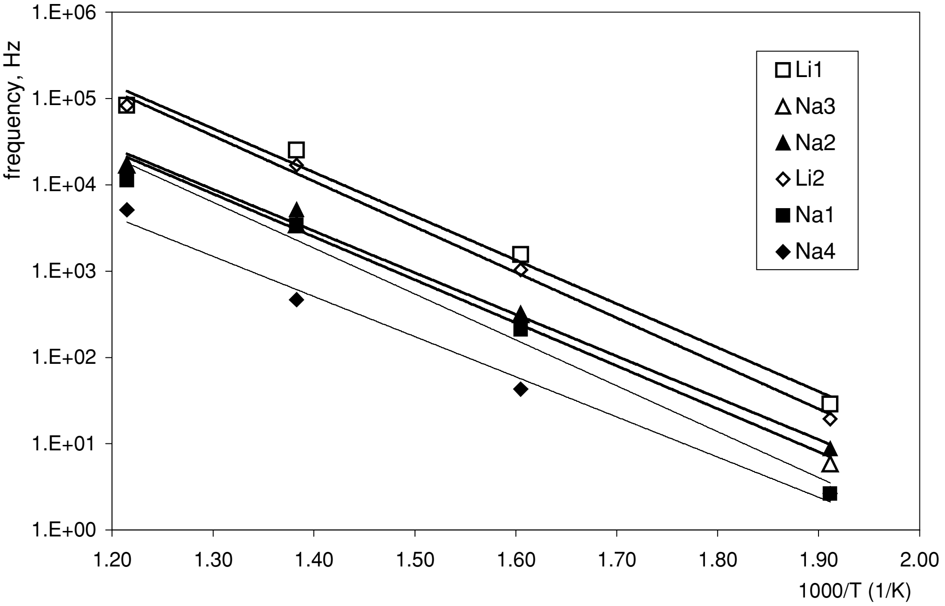

Figure 10 Arrhenius plot for the dielectric relaxation process, detected in the loss factor curves of all samples.

carriers. In Fig. 10, the frequency of the loss factor maximum is plotted as a function of the reciprocal of the absolute temperature for all the specimens investigated. The activation energy of the relaxation process, provided by the slope of the regression lines, is quite close for all the samples (average 96 ± 9 kJ/mol). On account of the rather high values of the frequency of the maxima (*f*max >10 Hz), the origin of the relaxation process can be ascribed to the motion of dipoles and particularly to the non-bridging atoms in the network of the residual amorphous phase [16–18], which is still present in the materials after the thermal treatment. It can also be observed that, at each temperature, in the specimens containing lithium the maximum of the relaxation peak lies at higher frequency, due to the higher mobility of lithium containing dipoles. Treatment of the discharging currents did not disclose relaxation processes of the Maxwell-Wagner-Sillar type deriving from the charge carriers accumulation at the boundaries between the different phases, even at the lowest frequency investigated. According to the reported results, obtaining high temperature insulating materials requires an optimization of zeolites composition, thermal treatment and sintering technology, which will be the task of the future work.

4. Conclusions

The results obtained confirm the possibility of deriving monoclinic celsian-based materials from low-cost zeolitic precursors, by means of short treatments carried out at comparatively low temperatures.

Lithium promotes the formation of monoclinic celsian more efficiently than sodium; moreover, high sodium content causes a decrease of the monoclinic celsian yield due to the presence of side-reactions leading to the formation of sodium silicates.

The presence of a residual amorphous phase and small content of alkali ions remarkably affects the electrical behaviour of the materials.

Below 200 °C good insulating properties are found, i.e. low values of dc conductivity and ac dielectric losses. Above 200 °C, all materials show a strong increase of dc conductivity, which approaches the semiconducting range close to 500 °C, as well as of ac dielectric constant and loss factor.

A thermally activated dielectric relaxation process is observed over a broad frequency and temperature range; it can be ascribed to the dipolar vibrations in of the residual amorphous network present in the materials.

Acknowledgements

This work was carried out with the finantial contribution of the Ministry of University and Scientific and Technological Research COFIN 2002.

References

1. R. A. MCCAULEY, *J. Mater. Sci.* **35** (2000) 3939.
2. Y. SUNG and S. KIM, *J. Mater. Sci. Letters* **18** (1999) 1657.
3. N. B. BANSAL, *Mater. Sci. Eng. A* **342** (2002) 23.
4. I. G. TALMY, D. A. HAUGHT and E. J. WUCHINA, in Proceedings of 6th International SAMPE Electrical Conference June 1992, p. 687.
5. B. HOGHOOGHI, J. MCKRITTRICK, E. HENSEL and O. A. LOPEZ, *J. Am. Ceramic Soc.* **81** (4) (1998) 845.
6. M. PANSINI, G. DELL'AGLI, M. C. MASCOLO and C. FERONE, *Solid State Ionics* **127** (2000) 309.
7. G. DELL'AGLI, C. FERONE, M. C. MASCOLO and M. PANSINI, *Chem. Mater.* **14** (2) (2002) 797.
8. A. ARONNE, S. ESPOSITO, C. FERONE, M. PANSINI and P. PERNICE, *J. Mater. Chem.* **12** (2002) 3039.

9. K. T. LEE and P. B. ASWATH, *Mater Sci. and Eng. A.* **352** (2003) 1.
10. M. BELLOTTO and C. CRISTIANI, *Mater. Sci. Forum* **79–82** (1991) 745.
11. A. F. GUALTIERI and G. ARTIOLI, *Powder Diffraction* **10** (1995) 269.
12. A. C. LARSON, R. B. VON DREELE, in "*GSAS: General Structure Analysis System LANSCE*" (MS-H805; Los Alamos National Laboratory: Los Alamos, NM, 1998).
13. M. C. MASCOLO, G. DELL'AGLI, C. FERONE, M. PANSINI and G. MASCOLO, *J. Europ. Cer. Soc.* **23** (2003) 1705.
14. C. FERONE, S. ESPOSITO, G. DELL'AGLI, R. PALMACCIO and M. PANSINI accepted for publication on *J. Amer. Ceramic Soc.*
15. C. SILIGARDI, F. ANDREOLA, T. MANFREDINI, C. FERONE and M. PANSINI to be submitted.
16. J. E. DAVIDSON, M. D. INGRAM, A. BUNDE and K. FUNKE, *J. Non Cryst. Sol.* **203** (1996) 246.
17. J. E. KIM, S. J. KIM, K. OHNSHIMA, Y. H. HWANG and Y. S. YANG, *Mater. Sci. Eng. A* **375–377** (2004) 1255.
18. R. BALAJI RAO, GOPAL N. O. and N. VERAAIAH, *J. Alloys and Comp.* **368** (2004) 25.

Received 24 January
and accepted 24 June 2005