



# Thermal transformation of Cs-clinoptilolite to CsAlSi<sub>5</sub>O<sub>12</sub>

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## ABSTRACT

In this study we have investigated the protocol to produce CsAlSi<sub>5</sub>O<sub>12</sub> (CAS), a potential host for radioactive cesium, starting from clinoptilolite, a natural zeolite employed in cesium decontamination. A clinoptilolite-rich rock sampled in Sardinia (Italy) has been subjected to a beneficiation process, to obtain a powder with a higher zeolite content. The enriched material (90 wt% clinoptilolite) has been previously Na-, then Cs-exchanged. Both forms have been analyzed by ICP-AES and ICP-MS. Thermal treatments of 2 hours between 800 and 1250 °C have been performed on different aliquots of the Cs-exchanged material. Samples heated at  $T \geq 1150$  °C are composed basically only by CAS, as determined by XRD analyses, and their high crystallinity has been also confirmed by SEM observations. Ideally, the nucleation of CAS follows the reaction  $\text{Cs}_6\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot n\text{H}_2\text{O} \rightarrow n\text{H}_2\text{O} \uparrow + 6\text{CsAlSi}_5\text{O}_{12}$ . DTA analyses indicate that the transformation has occurred at 1145 °C. TG analyses, coupled with XRD data, lead to exclude a cesium volatilization during the synthesis of CAS.

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## 1. Introduction

The cesium aluminosilicate CsAlSi<sub>5</sub>O<sub>12</sub> (CAS-framework type) [1] is one of the crystalline phases proposed as potential hosts for radioactive cesium [2–5], along with pollucite [6,7] and ABW [8,9]. This material has refractory properties [2], ensure the immobility of cesium at high temperature and pressure [5,10], shows thermo-elastic stability and preserve its crystallinity at least up to 8.5 GPa and 1000 °C [5]. Furthermore, CAS exhibits a high resistance in acid media, even higher than pollucite.

CAS has been synthesized for the first time by Ito [11], by a slow cooling of a melt containing BaCO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. Afterward, CAS has been prepared from both chemical reagents [2,10,12] and synthetic zeolites like mordenite [13–16] and ferrierite, as well [4]. Conversely, attempts to obtain CAS from natural mordenite [14,17] and clinoptilolite [14,17,18], have failed. On the other hand, it would be worth an effort aimed to obtain CsAlSi<sub>5</sub>O<sub>12</sub> from natural zeolites, in particular from clinoptilolite. Indeed, this zeolite, like in the past, is still widely investigated, suggested and employed for environmental remediation purposes [19–23] and cesium decontamination [19,20,23–30]. In particular, after the Chernobyl disaster, clinoptilolite-rich rocks have been used to reduce cesium

radionuclide levels from potable waters, milk, chocolate and biscuits for children, soils, plants, sheep, chickens, and fruit juices [19]. Clinoptilolite has been used also after the Fukushima Accident, being a part of the first stage of the Cs-adsorption system [30,31]. To prevent Cs<sup>+</sup> release from spent clinoptilolite, temperatures up to 1000–1200 °C have been required to attain an almost complete cesium immobilization inside a glassy matrix [18,31–34]. The synthesis of crystalline phases like CsAlSi<sub>5</sub>O<sub>12</sub> should be preferable, because the leaching rate of Cs<sup>+</sup> from CAS is three orders of magnitude lower than from boro-silicate glass [5,14].

On the basis of the above mentioned considerations, the present research has been addressed to evaluate the possibility to obtain CAS through heating of a Cs-exchanged clinoptilolite.

## 2. Experimental

### 2.1. Starting material and beneficiation process

A clinoptilolite-rich rock collected in Sardinia (Italy), already characterized in previous studies (sample “LacBen” in Refs. [35–38]), has been used to develop the present research. The mineralogical composition of the material is: clinoptilolite 66 ± 4 wt.%; feldspars 18 ± 2 wt.%; opal-CT 13 ± 1 wt.%; quartz 3 ± 1 wt.%; traces of biotite [38]. The chemical formula and the theoretical Cation Exchange Capacity (CEC) of the clinoptilolite are Na<sub>0.50</sub>K<sub>0.86</sub>Ca<sub>1.57</sub>Mg<sub>0.70</sub>Si<sub>29.73</sub>Al<sub>6.31</sub>O<sub>72</sub> · 22.14H<sub>2</sub>O and 2.20 meq/g, respectively [36]. To obtain a material with a higher zeolite content,

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the rock has been subjected to a beneficiation process using the procedure proposed by Brundu et al. [39]. Briefly, the rock has been submitted to autogenous comminution and dry sieving. Then, the fraction below 100  $\mu\text{m}$  has been subjected to ultrasound attack and wet separation in deionized water.

## 2.2. Preparation of Cs-clinoptilolite

To obtain a Cs-clinoptilolite, the material has been first Na-exchanged. The enriched powder has been contacted with a 1 M NaCl solution (VWR Prolabo salt; purity 99.9%) performing a sequence of eleven exchange cycles executed in batch at 65 °C under continuous stirring, with a solid/liquid ratio of 30 g/l. The Na-exchanged material has been rinsed with deionized water until complete removal of chloride solutions (test performed on elutes with  $\text{AgNO}_3$ ). The powder has been dried at 35 °C overnight in a ventilated drying oven, then rehydrated for 24 hours at 22 °C and  $53 \pm 2\%$  of relative humidity (monitored with an Ebro Data Logger EBI20-TH1) using a dessicator containing a saturated solution of  $\text{Ca}(\text{NO}_3)_2$ . The Na-clinoptilolite has been conducted in Cs-form using a 0.5 M CsCl solution (VWR Prolabo salt; purity 99.5%) and performing five exchanges cycles using the same conditions of Na-preconditioning. Once rinsed, the material has been dried and rehydrated as described above.

## 2.3. Chemical analyses

Chemical analyses of Na- and Cs-exchanged materials have been conducted at the Activation Laboratories Ltd (Ancaster, ON – Canada). Major elements have been determined after lithium metaborate/tetraborate fusion of the samples through Inductive Coupled Mass Atomic Emission Spectrometry (ICP-AES), performed with a Varian Vista 735 ICP. Cs contents have been determined by ICP Mass Spectrometry (ICP-MS; Perkin Elmer Sciex ELAN 9000) after sodium peroxide fusion of the samples.

## 2.4. Thermal treatments

Aliquots of 250 mg of the Cs-exchanged material have been submitted to thermal treatments of 2 hours at 800, 900, 1000, 1100, 1150, 1200 and 1250 °C, performed in a muffle furnace (Vittadini mod. FS.3) using high-alumina crucibles (Coors™). Further experiments have been performed at 1100 °C heating two aliquots of 250 mg of sample for 4 and 8 hours.

## 2.5. X-Ray diffraction (XRD)

The enriched material, the Na- and Cs-exchanged forms, and all heated samples have been investigated employing a Bruker D2-Phaser and the following conditions: 30 kV, 10 mA,  $\text{CuK}\alpha$  radiation, LynxEye detector with an angular opening of 5°,  $2\theta$  range 6–70°, step size 0.020°, time per step 2 s, spinner 15 rpm. Before the measurements, all the samples have been micronized using a Retsch MM400 mill ( $\text{ZrO}_2$  cups and balls). Only the enriched material has been analyzed by adding to the sample 20 wt.% of corundum as internal standard. All measurements have been performed using a low-background silicon crystal specimen holder (Bruker), except for the enriched material, placed in a larger standard sample holder. The XRD patterns have been evaluated using the software EVA 14.2 (Bruker DIFFRAC<sup>plus</sup> Package) coupled with the database PDF-2 (ICDD). Quantitative analysis of enriched material has been performed through the Rietveld method using the software Bruker Topas 4.2.

## 2.6. Thermal analyses

Thermogravimetric and Differential Thermal Analyses (TG-DTA) of Cs-exchanged material have been carried out using a TA-Instrument Q600 simultaneous thermal analyzer. Amounts of about 15 mg of sample have been heated up to 1300 °C in an alumina crucible at the following operating conditions: 10 °C/min; air flow 100 ml/min. Analyses have been replicated seven times to improve the statistic of observations. The software TA-Universal Analysis has been used to evaluate the results.

## 2.7. SEM observations

Morphological observations have been carried out on clinoptilolite-rich rock, zeolite-enriched material and heated samples. The materials, placed on aluminum stubs, have been gold coated (AGAR automatic sputter coater B7341) and observed using a ZEISS EVO LS-10 Scanning Electron Microscope.

## 2.8. Thermal treatments of CAS-“doped” material

In order to check the effect of seed  $\text{CsAlSi}_5\text{O}_{12}$  crystals on the CAS synthesis, a further experiment has been performed. A mixture containing 90 wt.% of Cs-exchanged material and 10 wt.% of CAS (previously synthesized) has been treated for 2 hours at 1100 °C. The XRD pattern of the heated mixture has been compared with the XRD pattern of a mixture prepared with 90 wt.% of Cs-exchanged powder previously heated for 2 hours at 1100 °C, and 10 wt.% of CAS.

# 3. Results and discussion

The beneficiation process has allowed to obtain a powder with a clinoptilolite content of about 90 wt.% (Table 1). Notwithstanding the size of clinoptilolite crystals in the bulk rock is below 10  $\mu\text{m}$  (Fig. 1), the mechanical stress induced by the beneficiation process does not allow to observe the same euhedral morphologies in the zeolite-enriched powder. It is noteworthy that the increase in zeolite grade has been obtained by a cheap and replicable method.

The chemical compositions of the Na- and Cs-exchanged materials are reported in the Table 2. The high cesium content, along with the low sodium, potassium, calcium and magnesium contents, indicate that a near end-member of Cs-clinoptilolite has been obtained.

The XRD patterns of the Na- and Cs-exchanged materials are reported in Fig. 2. The  $\text{Cs}^+$  uptake influenced the XRD pattern of clinoptilolite, with a general lowering of the intensity of the diffracted radiation. In particular, the peak at  $2\theta \approx 9.8^\circ$  (i.e.  $d \approx 9.00 \text{ \AA}$ ), which is very strong in the Na-form, becomes very weak in the Cs-form. This Bragg peak is “cation-sensitive” because the channel system of clinoptilolite is parallel to (010), the diffraction plane that governs the intensity of this peak [19].

The TG-DTA curves of the Cs-exchanged material are reported in Fig. 3, where it is evident the reproducibility of the analysis. The majority of the dehydration occurred below 250 °C, through two endothermic reactions at about 65–70 °C and 185–190 °C. In the

**Table 1**

Mineralogical composition of the enriched material (wt.%, e.s.d. = estimated standard deviation).

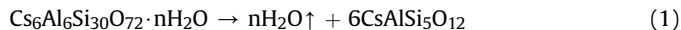
	Clinoptilolite	Quartz	Biotite	Feldspars	Opal-CT	Amorphous
Content	89.5	0.4	1.4	3.2	1.2	4.3
e.s.d.	$\pm 2.0$	$\pm 0.1$	$\pm 0.2$	$\pm 0.3$	$\pm 0.2$	$\pm 0.5$

DTA curves, the “knee” at about 850 °C should correspond to the beginning of the amorphization process of Cs-clinoptilolite. Finally, a wide endothermic peak is detectable between 1240 and 1258 °C (mean value = 1251(6) °C). The onset temperature of this endothermic reaction is located at 1145 °C, as shown in Fig. 4 along the derivative of the DTA curve.

The XRD patterns of the heated samples, reported in Fig. 5, show that a heating process of 2 hours at 800 °C basically does not affect the structure of the Cs-clinoptilolite, whereas only a weak reduction of the peak intensity/background ratio occurs after a 900 °C treatment. These observations validate the indication obtained from the DTA curve concerning the beginning of the amorphization at 850 °C. However, beside an amorphous fraction, the structure of Cs-clinoptilolite is still recognizable on the XRD pattern of the sample heated for 2 hours at 1000 °C, whereas to attain the complete breakdown a treatment of 2 hours at 1100 °C is required (Fig. 5). These data confirm the high thermal stability of the cesium form of this zeolite, and the temperature needed to obtain its vitrification [34,37]. On the other hand, the experiments here performed demonstrate how, by increasing of only 50 °C the temperature of the thermal treatment, a crystalline matrix can be obtained (Fig. 5). All samples heated for 2 hours between 1150 and 1250 °C exhibit an XRD pattern with sharp peaks and flat background, thus corresponding to a material that is, basically, completely crystalline. In particular, the structure of the orthorhombic phase  $\text{CsAlSi}_5\text{O}_{12}$  (CAS), described by Ito [11] and Araki [40], is clearly recognizable in the XRD pattern and matches all peaks (Fig. 6).

In Table 3 are indicated the chemical compositions of Cs-exchanged material, reported on anhydrous base, and of CAS, the latter calculated on the basis of chemical formula  $\text{CsAlSi}_5\text{O}_{12}$ . With a simple proportion is possible to calculate that the percentage of CAS (pure) theoretically obtainable from the Cs-exchanged material corresponds to 91.6 wt.%. Obviously, if the CAS structure tolerates some substitutions of Si with Al (and  $\text{Fe}^{III}$ ), and admits K (as reported for boropollucite - [41]) and Na traces, the percentage of CAS (impure) could be slightly higher. For example, if, with the same Si/Al ratio of the starting clinoptilolite (4.71, i.e. silica/alumina = 5.55), all sodium and potassium atoms present in the material were admitted in the structure of nucleated CAS, this phase could reach 92.6 wt.%. Actually, in the samples heated at  $T \geq 1150$  °C the pervasive presence of nucleated crystals can be observed by SEM, and tabular morphologies, from 10 to 20  $\mu\text{m}$  in length, are often recognizable (Fig. 7).

In the formula  $\text{CsAlSi}_5\text{O}_{12}$  the proportion between silicon and aluminum atoms is 5:1, thus, by considering a Cs-clinoptilolite having the same Si/Al ratio, the reaction that leads to CAS formation can be summarized as:



However, a perfect stoichiometric composition is not mandatory to obtain a zeolite with the structure of CAS. Indeed, it has been obtained with Si/Al ratio from 4.95 to 6.06 [10,12], and Tomiyama et al. [16] report the nucleation of CAS even from a synthetic mordenite with a Si/Al ratio of 10.7. Clinoptilolite has the same framework topology of heulandite, and the Si/Al ratio of these two species varies almost continuously between 2.6 and 5.7, where clinoptilolite is defined as the series with  $\text{Si}:\text{Al} \geq 4.0$  [42]. The clinoptilolite used in this work has a Si/Al ratio of 4.71, thus rather close to that expected for the CAS one, that is 5. Once Cs-exchanged and thermally treated at 1150 °C, this clinoptilolite has resulted in a matrix substantially composed only by CAS crystals. From a practical point of view, it could be interesting to investigate which are

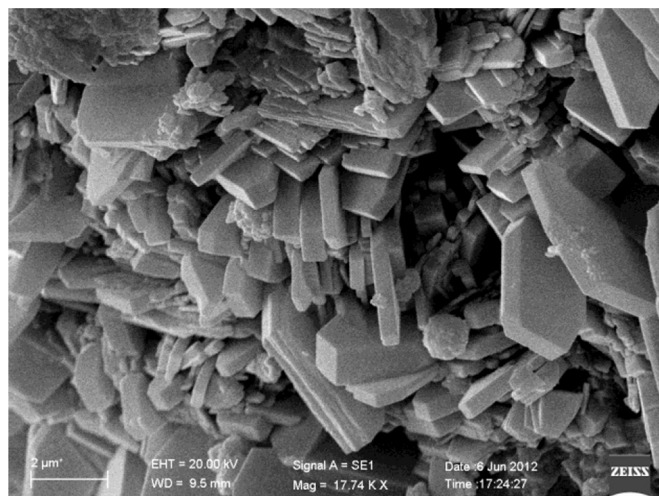


Fig. 1. SEM image (in secondary electrons) of clinoptilolite crystals in the bulk rock (sample “LacBen”, Sardinia, Italy).

the upper and lower limits of the Si/Al ratio, and the highest tolerable content of chemical impurities, that permit to obtain the same result.

Another critical aspect in the nucleation of CAS is the temperature. The presence of some incipient peak of this compound in the XRD pattern of the sample heated for 2 hours at 1100 °C (Fig. 8) suggested us to check the effect of longer thermal treatments at the same temperature. It can be observed, in Fig. 8, how the peaks of the  $\text{CsAlSi}_5\text{O}_{12}$  become more pronounced with the heating time; however, even after 8 hours, the amorphous fraction is still well recognizable. The slow kinetic of the nucleation at 1100 °C, in contrast with the fast crystallization recorded at 1150 °C, leads us to conclude that the threshold temperature corresponds to 1145 °C, as previously inferred from the derivative of the DTA curve (Fig. 4).

The possibility to synthesize  $\text{CsAlSi}_5\text{O}_{12}$  in 2 hours at 1100 °C by doping the Cs-clinoptilolite with a 10% of CAS (previously synthesized) has been verified. The presence of seed crystals of CAS did not produce any advantage.

Data here reported indicate that during the synthesis of  $\text{CsAlSi}_5\text{O}_{12}$  from clinoptilolite, cesium volatilization has not occurred. Indeed, the stability of the zeolite at 800 °C (Fig. 5), and the absence of weight losses above this temperature up to 1300 °C (Fig. 3), lead to exclude this problem. Conversely, cesium volatilization has been recorded in the synthesis of  $\text{CsAlSi}_5\text{O}_{12}$  from chemicals [2], but also of  $\text{CsBSi}_5\text{O}_{12}$  (isostructural with CAS) obtained from boropollucite [43].

The production of a ceramic matrix, basically composed only by CAS, starting from clinoptilolite, is here reported for the first time. Clinoptilolite has actually been used to reduce cesium radionuclide levels in contaminated waters [19,20,30,31], unlike to the synthetic zeolites mordenite and ferrierite. Furthermore, clinoptilolite has been transformed in  $\text{CsAlSi}_5\text{O}_{12}$  at lower temperatures (1150 °C) with respect to ferrierite and mordenite (1200–1300 °C; [13–16]). Finally, clinoptilolite is the most common among natural zeolites, and high-grade deposits are distributed worldwide [20]. Obviously, in attempting the synthesis of CAS from a zeolite-rich rock, a chemical and mineralogical characterization is mandatory.

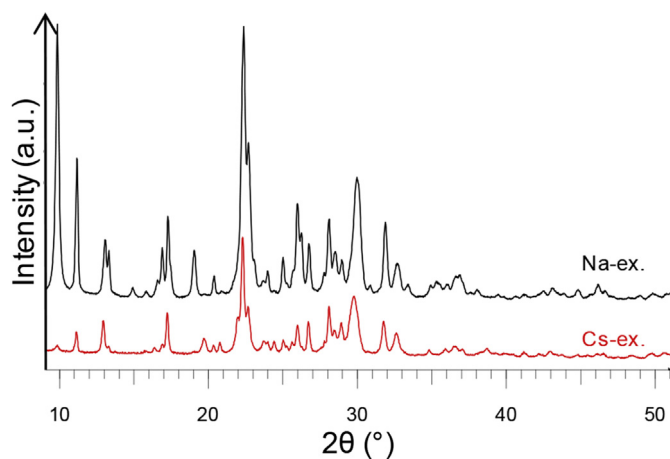
Future developments of this research relate:

- 1) The chemical analysis (by electron microprobe analysis in energy and/or wavelength dispersive X-Ray spectroscopy) and the structural refinement of the CAS obtained (by Rietveld method);

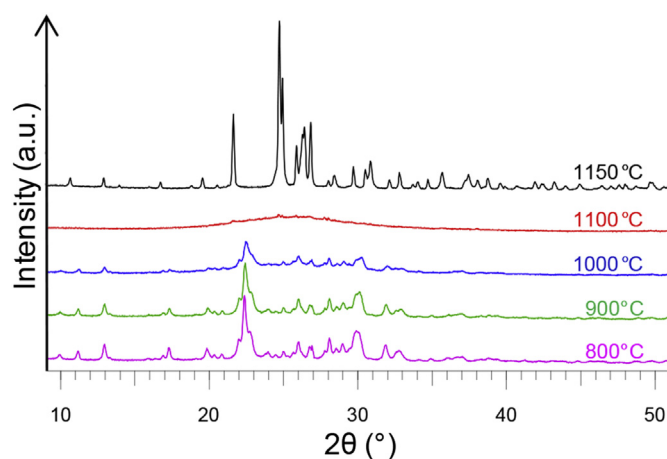
**Table 2**  
Chemical composition of Na- and Cs-exchanged materials (wt.%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Cs <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Loi	TOT
Na-ex.	65.26	12.11	0.50	<0.01	0.51	0.35	5.85	0.43	<sup>a</sup>	0.18	0.05	14.80	100.00
Cs-ex.	55.05	10.29	0.61	0.01	0.33	0.26	0.13	0.29	23.85	0.16	0.03	9.09	100.01

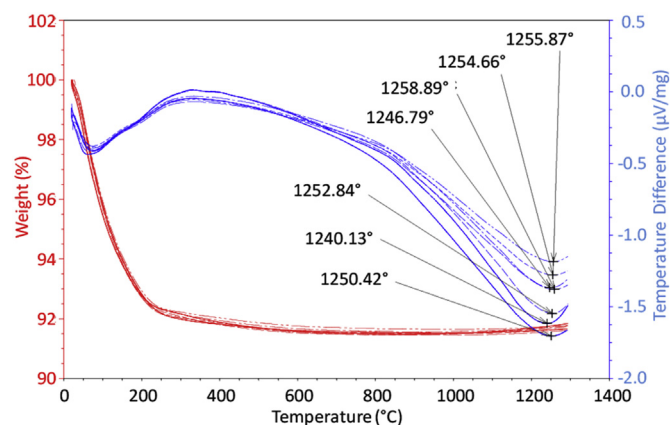
<sup>a</sup> Cs content = 0.93 ppm.



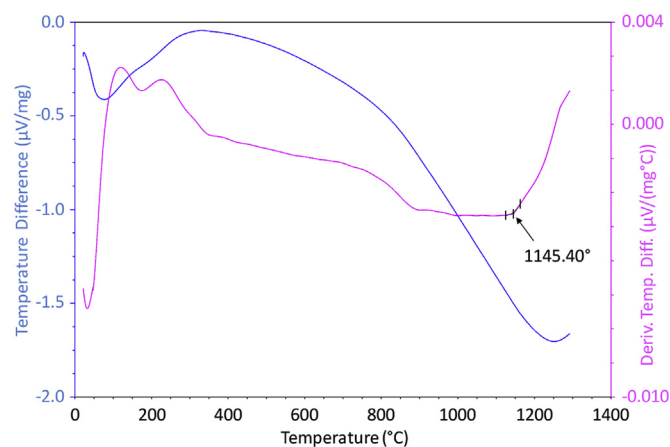
**Fig. 2.** XRD patterns of the Na- and Cs-exchanged materials.



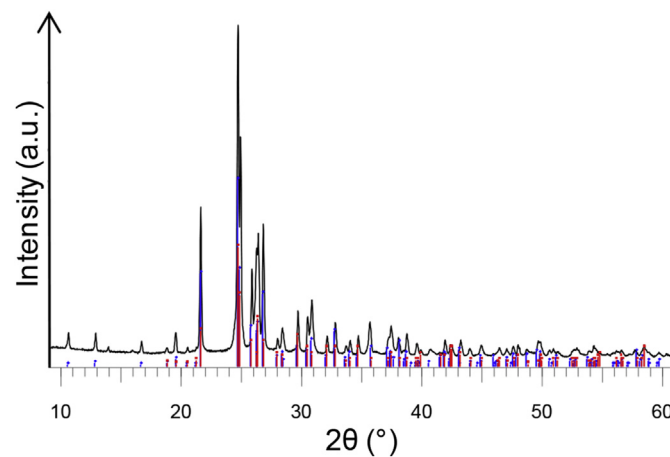
**Fig. 5.** XRD patterns of samples heated from 800 to 1150 °C.



**Fig. 3.** TG-DTA curves of the seven analyses performed on the Cs-exchanged material.



**Fig. 4.** DTA and derivative of DTA of the Cs-exchanged material.



**Fig. 6.** XRD pattern of sample heated at 1150 °C compared with that reported for CAS (red bars: PDF Number 29-0406, [11]; blue bars: 01-083-1314, [40]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2) The comparison between the cesium leaching from the CAS with respect to the leaching from the glass obtained using the same Cs-clinoptilolite heated at 1100 °C.

#### 4. Conclusions

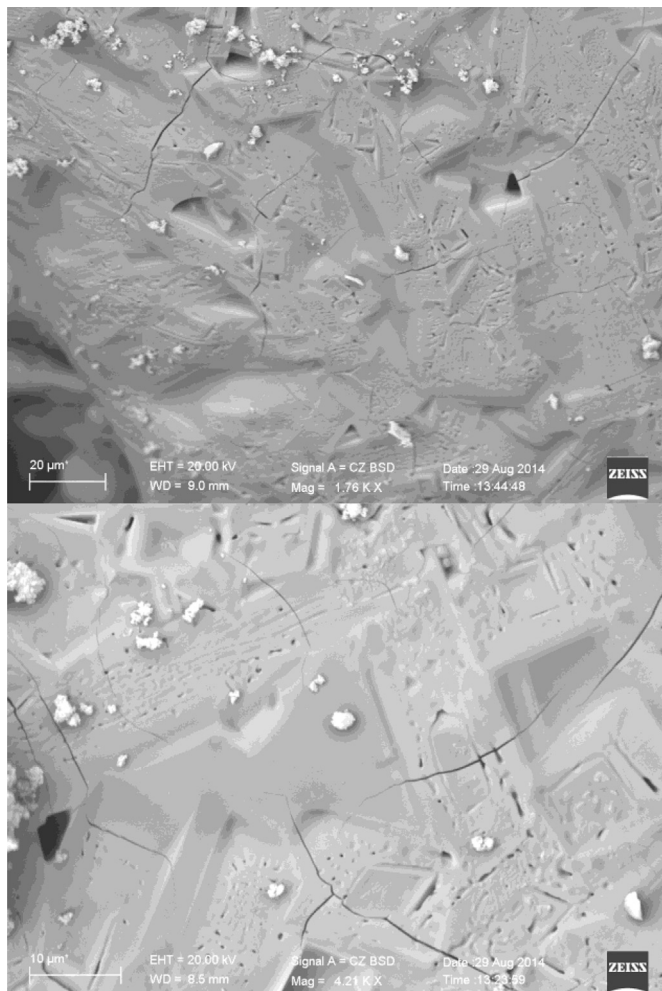
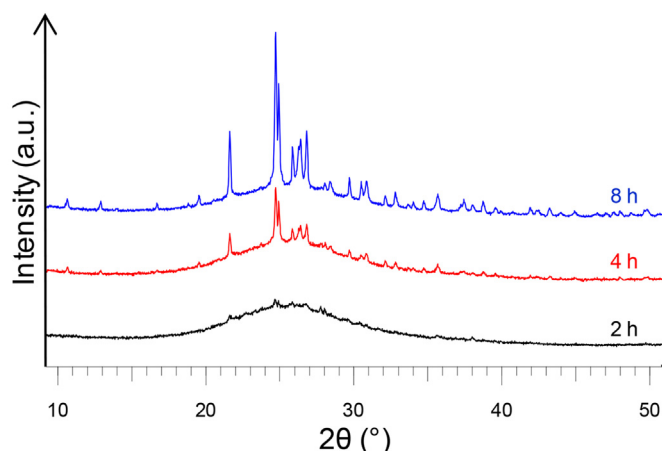
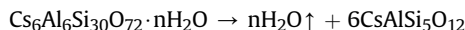
This research shows, for the first time, the production of a crystalline matrix, basically constituted only by CsAlSi<sub>5</sub>O<sub>12</sub>, from clinoptilolite, a natural zeolite employed for cesium decontamination.

Ideally, the reaction that leads to CAS formation by thermal treatment of a Cs-clinoptilolite is the following



**Table 3**Chemical compositions (wt.%) of Cs-exchanged material (anhydrous basis) and CAS (calculated on the basis of chemical formula  $\text{CsAlSi}_5\text{O}_{12}$ ).

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	$\text{Cs}_2\text{O}$	Tot
Cs-ex	60.48	11.31	0.67	0.01	0.36	0.29	0.14	0.32	0.18	0.03	26.21	100.00
CAS	61.02	10.36	—	—	—	—	—	—	—	—	28.62	100.00

**Fig. 7.** SEM images (in back-scattered electrons) of sample heated at 1250 °C.**Fig. 8.** XRD patterns of samples heated at 1100 °C.

and a heating of two hours at 1150 °C is sufficient to complete the transformation. The reaction is fast and, except for  $\text{H}_2\text{O}$ , does not imply mass loss. These findings can provide useful information for the management of spent clinoptilolite exploited in cesium decontamination.

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