Phys Chem Minerals (2016) 43:639–647
DOI 10.1007/s00269-016-0823-8

ORIGINAL PAPER

New insights on pressure, temperature, and chemical stability of $CsAlSi_5O_{12}$, a potential host for nuclear waste

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Received: 22 March 2016 / Accepted: 28 May 2016 / Published online: 13 June 2016

Abstract A Cs-bearing polyphase aggregate with composition (in wt%): $76(1)_{CsAlSi5O12} + 7(1)_{CsAlSi2O6} + 17(1)_{amorphous}$, was obtained from a clinoptilolite-rich epiclastic rock after a beneficiation process of the starting material (aimed to increase the fraction of zeolite to 90 wt%), cation exchange and then thermal treatment. $CsAlSi_5O_{12}$ is an open-framework compound with CAS topology; $CsAlSi_2O_6$ is a pollucite-like material with ANA topology. The thermal stability of this polyphase material was investigated by in situ high-*T* X-ray powder diffraction, the combined *P*–*T* effects by a series of runs with a single-stage piston cylinder apparatus, and its chemical stability following the "availability test" ("AVA test") protocol. A series of additional investigations were performed by WDS–electron microprobe analysis in order to describe the *P*–*T*-induced modification of the material texture, and to chemically characterize the starting material and the run products. The "AVA tests" of the polyphase aggregate show an extremely modest release of Cs^+: 0.05 mg/g. In response to applied temperature and at room *P*, $CsAlSi_5O_{12}$ experiences an unquenchable and displacive *Ama*2-to-*Amam* phase transition at about 770 K, and the *Amam* polymorph is stable in its crystalline form up to 1600 K; a crystalline-to-amorphous phase transition occurs between 1600 and 1650 K. In response to the applied $P = 0.5$ GPa, the crystalline-to-amorphous transition of $CsAlSi_5O_{12}$ occurs between 1670 and 1770 K. This leads to a positive Clapeyron slope (i.e., $dP/dT > 0$) of the crystalline-to-amorphous transition. When the polyphase aggregate is subjected at $P = 0.5$ GPa and $T > 1770$ K, $CsAlSi_5O_{12}$ melts and only $CsAlSi_2O_6$ (pollucite-like; dominant) and Cs-rich glass (subordinate) are observed in the quenched sample. Based on its thermo-elastic behavior, *P*–*T* phase stability fields, and Cs^+ retention capacity, $CsAlSi_5O_{12}$ is a possible candidate for use in the immobilization of radioactive isotopes of Cs, or as potential solid hosts for ^{137}Cs γ-radiation source in sterilization applications. More in general, even the $CsAlSi_5O_{12}$-rich aggregate obtained by a clinoptilolite-rich epiclastic rock appears to be suitable for this type of utilizations.

Keywords $CsAlSi_5O_{12}$ · $CsAlSi_2O_6$ · Clinoptilolite · Zeolites · Phase stability · High pressure · High temperature · Nuclear waste

Introduction

Cs-bearing minerals are rare in nature. Likely, the most common ones are represented by pollucite [(Cs, Na) $AlSi_2O_6 \cdot nH_2O$, e.g., Gatta et al. 2009a, b; Bellatreccia et al. 2012], pezzottaite [$Cs(Be_2Li)Al_2Si_6O_{18}$, e.g., Gatta et al. 2012a; Lambruschi et al. 2014], and londonite (Cs, K, Rb) $Al_4(Be,B)_4(B,Be)_{12}O_{28}$, e.g., Gatta et al. 2010, 2011]. On

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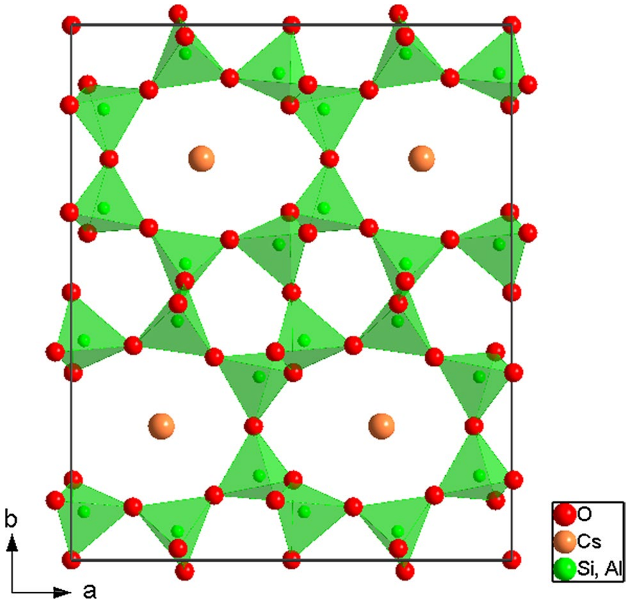

Fig. 1 The crystal structure of $CsAlSi_5O_{12}$ viewed down [001], based on the structure model of Gatta et al. (2008b)

the other hand, a number of synthetic Cs-aluminosilicates have been synthesized in the last decades in search for crystalline compounds potentially usable for immobilization of radioactive isotopes of Cs, or as potential solid hosts for ^{137}Cs γ-radiation source in sterilization applications (e.g., Vance and Seff 1975; Firor and Seff 1977; Gallagher et al. 1977; Araki 1980; Adl and Vance 1982; Komarneni and Roy 1983; Vance et al. 1984; Taylor et al. 1989; Mellini et al. 1996; Drábek et al. 1998; Klika et al. 2006; Bubnova et al. 2007; Sanchez-Valle et al. 2010; Gatta et al. 2008a, 2012b; Cappelletti et al. 2011; Hwang et al. 2015). The synthesis conditions and the crystal structure of $CsAlSi_5O_{12}$ were first reported by Ito (1976) and Araki (1980). This material is an open-framework aluminosilicate, with CAS-type topology (Bearlocher et al. 2001). Its crystal structure was solved in the space group *Ama*2. The structure is built by the secondary building unit (SBU) 5-1 (Bearlocher et al. 2001) and contains one system of 8-membered ring (8mR) channels, running along [001], where the extra-framework Cs sites lie (Fig. 1). Several additional studies have been devoted to the crystal chemistry of this compound (e.g., Annehed and Fälth 1984; Hughes and Weller 2002; Fisch 2007; Fisch et al. 2008, 2010; Gatta et al. 2008b; Brundu and Cerri 2015; Rampf et al. 2015). Fisch et al. (2008) described the high-temperature behavior of $CsAlSi_5O_{12}$ by in situ X-ray powder and single-crystal diffraction experiments, showing a *T*-induced displacive phase transition at 770 K (at room *P*) from the acentric low-temperature space group *Ama*2 to the centrosymmetric *Amam*. Data were collected up to 970 K. The volume thermal expansion coefficient of the low-*T* polymorph is $\alpha \sim 6.5 \times 10^{-5}$ K^{-1}, with a decrease down to $\alpha \sim 2.2 \times 10^{-5}$ K^{-1} for the high-*T* polymorph. An additional in situ Raman experiment was conducted by Fisch et al. (2008) up to 1270 K, showing the stability of $CsAlSi_5O_{12}$, in its high-*T* crystalline polymorph, under such conditions. Later, Fisch et al. (2010) reported the high Cs retention of $CsAlSi_5O_{12}$ by treating the powdered compound in boiling 1 M NaCl solution, showing that only 16 mol% of Cs in $CsAlSi_5O_{12}$ was exchanged by Na after 35 days and that the zeolite remained anhydrous even after partial Na-exchange in aqueous solution. Gatta et al. (2008b) described the elastic behavior and the *P*-induced structural evolution (at the atomic level) of $CsAlSi_5O_{12}$ by in situ single-crystal X-ray diffraction with a diamond anvil cell. $CsAlSi_5O_{12}$ was found to be stable at least up to 8 GPa (i.e., the maximum pressure achieved in the experiment), showing a compressional behavior described with a bulk modulus (obtained by a third-order Birch–Murnaghan equation of state fit): $K_{T0} = 20(1)$ GPa and $\partial K_{T0}/\partial P = 6.5(7)$, with an anisotropic compressional scheme: $K_{T0a}:K_{T0b}:K_{T0c} = 1:1.50:2.36$. The stability at high *T* (at room *P*) and at high *P* (at room *T*) is surprising, if we consider the microporous nature of this material, with a ceramic-like character that deserves further investigations.

The aim of this study is: (1) to extend the previous knowledge on the *T* stability of $CsAlSi_5O_{12}$ at $T > 1270$ K (by in situ X-ray powder diffraction), (2) to investigate the combined effect of *P* and *T* (via single-stage piston cylinder experiments) on the stability field of this technological material, (3) to check the chemical stability of $CsAlSi_5O_{12}$, in order to evaluate the effective immobilization of Cs. The experiments of this study have been performed using a natural starting material, following the protocol recently reported by Brundu and Cerri (2015).

Experimental

$CsAlSi_5O_{12}$-rich material and its amorphous counterpart (a Cs-aluminosilicate glass) were prepared at the University of Sassari, Italy, following the protocol reported by Brundu and Cerri (2015). Briefly, a clinoptilolite-rich rock from Logudoro (northern Sardinia, Italy; sample labelled as "LacBen" in Cerri et al. 2001), was subjected to a beneficiation process as described by Cerri et al. (2016). The resulting powder (grain size: < 80 µm), containing about 90 wt% of clinoptilolite (along with residual fractions of glass, feldspars, quartz, biotite, and opal-CT) was initially Na-exchanged, and then Cs-exchanged to the final chemical composition (by ICP-AES/MS): SiO_2 55.05 wt%, TiO_2 0.16 wt%, P_2O_5 0.03 wt%, Al_2O_3 10.29 wt%, Fe_2O_3 0.61 wt%, MnO 0.01 wt%, MgO 0.33 wt%, CaO 0.26 wt%, Na_2O 0.13 wt%, K_2O 0.29 wt%, Cs_2O 23.85 wt%, LoI

9.09 wt% (Brundu and Cerri 2015). Cs-aluminosilicate glass and $CsAlSi_5O_{12}$-rich material were then obtained by a heating process of the Cs-exchanged clinoptilolite in high-alumina crucibles (Coors™) for 2 h at 1320 and 1470 K, respectively. About 500 mg of glass and 2 g of $CsAlSi_5O_{12}$-rich material (hereafter CAS-RM) were produced. The transformation of Cs-clinoptilolite to CAS-RM leads to an increase in density of 10.9 %, being 2.57(1) g/cm^3 of the unheated powder and 2.85(2) g/cm^3 after the thermal treatment (density measured with a helium pycnometer AccuPyc 1340). The white color of the Cs-clinoptilolite powder changed to reddish-brown in the CAS-RM.

The cation retention capacity of the CAS-RM and its amorphous counterpart (the aforementioned "Cs-aluminosilicate glass") were evaluated by the so-called availability test ("AVA test", Van Der Sloot and Kosson 1995) at the Department of Chemical, Materials Engineering and Industrial Production, University of Napoli Federico II. This test is a measure of the fraction of an element present in the material that is not tied up in poorly soluble mineral phases and can potentially be released into environment. Accordingly, powder samples of CAS-RM and its amorphous counterpart were contacted with distilled water (solid-to-liquid weight ratio equal to 1:50). In a first stage, lasted 3 h, the pH of the contact solution was kept constant at 7.0 by adding suitable amounts of a 1 M HNO_3 solution. The treatment was then replicated on the solid recovered from the mother solution, at the same conditions as above, except pH, which was fixed to 4.0. Moreover, the samples were also subjected to back-exchange with NaCl solution, in order to check the possible presence of exchangeable cations in the two phases. Accordingly, 100 mg of each powdered sample was treated for 24 h with 50 ml of a 1 M NaCl solution, under continuous stirring and at 298 K. Cation content in the final solution was analyzed, after liquid separation from solid phase, by inductively coupled plasma optical emission spectrometry (ICP–OES).

Synchrotron X-ray powder diffraction data of CAS-RM were collected at the ID09 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble (France), in transmitting geometry. Data have been collected with a MAR555 flat panel detector, using a monochromatic beam of 0.4140 Å. Data reduction was performed with the FIT2D software (Hammersley et al. 1996) and the Rietveld full-profile fit was carried out using the GSAS package (Larson and Von Dreele 1994). The whole diffraction pattern was fitted using the pseudo-Voigt profile function of Thomson et al. (1987), and the background curves were refined with a Chebyshev polynomial (with 16 coefficients). In order to estimate the amorphous content (by Rietveld/RIR method, e.g., Gualtieri 2000), a fraction of 20 wt% of standard corundum was added to the polycrystalline sample (Fig. 2). The employed structure models were: $CsAlSi_5O_{12}$ reported by Gatta et al. (2008b), $CsAlSi_2O_6$ by Gatta et al. (2009a), corundum by Ishizawa et al. (1980).

In situ high-temperature X-ray powder diffraction experiments were conducted with a θ–θ geometry Philips X'Pert diffractometer (Cu$K\alpha$ radiation), equipped with an Anton Paar heating chamber (HTK 16 MSW) and a Pt heating strip, at the Earth Sciences Dept.—University of Milan (DST-MI). Data were collected in the 2θ-range 5–80° (with a step-size of 0.03° 2θ and a counting time of 1 s/step) at

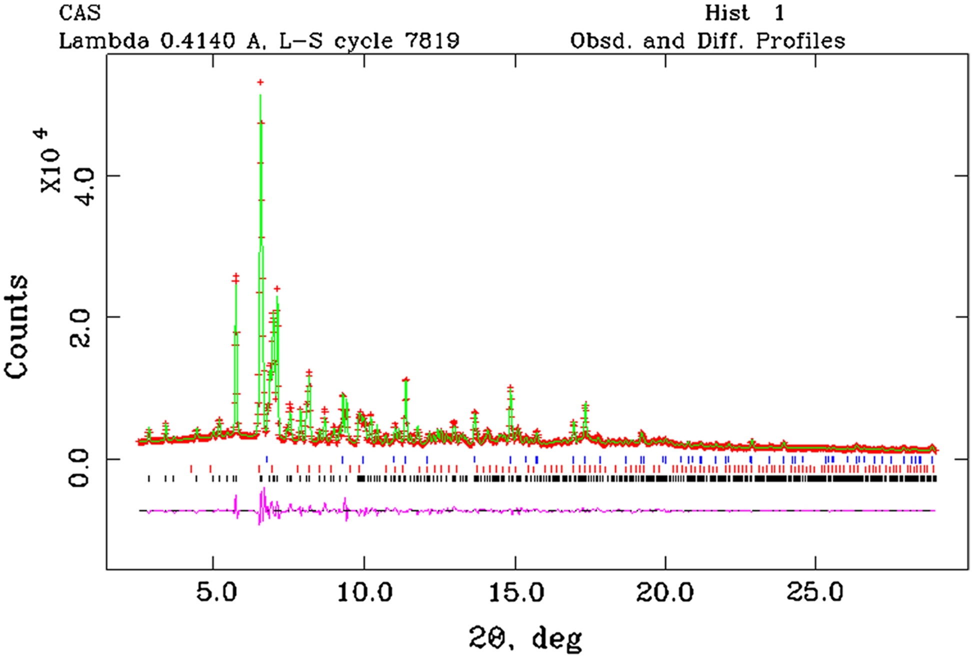

Fig. 2 Experimental (*crosses*) and calculated (*solid line*) synchrotron X-ray powder diffraction pattern for CAS-RM. Calculated peak positions ($CsAlSi_5O_{12}$ in *black*, $CsAlSi_2O_6$ in *red*, and corundum in *blue*) and difference *plots* are shown at the *bottom*. $Rp = 4.12$ %, $wRp = 5.89$ %

298, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1650, and 1700 K (Fig. 3).

In order to evaluate the stability of $CsAlSi_5O_{12}$ under the combined effect of pressure and temperature, additional experiments were performed in a single-stage piston cylinder at the DST-MI. The treatment at non-ambient conditions was carried out at 0.5 GPa and at 1170, 1570, 1670, and 1770 K, respectively, using salt–Pyrex–MgO assemblies up to 1570 K, and talc–silica glass–MgO assemblies for the higher temperatures (Fig. 4). Straight graphite heaters were used and temperature was measured with S-type thermocouple and considered accurate to ± 5 K (see Fumagalli et al. 2009 for further details). An initial pressure of about 0.1–0.2 GPa was first applied, then the sample was heated to 670 K to soften the Pyrex, compressed to the final pressure and then heated at 100 K/min up to the experimental temperature. Run durations ranged from 1 to 24 h. The starting CAS-RM was loaded in a ~4-mm-long Pt capsule, with 3 mm of outer diameter and cold-welded. It is worth to report that a first attempt to use an Au capsule resulted in the contamination of the material and the formation of different type of Cs-aurides. The untreated CAS-RM and the *P*–*T*-treated samples were investigated by X-ray powder diffraction and with a JEOL JXA-8200 Superprobe at the DST-MI, in order to collect BSE images (Fig. 5) and to perform analyses in wavelength-dispersive mode (EPMA–WDS). EPMA–WDS data were collected operating at 15 kV and 15 nA; natural and synthetic materials were used as standards, following the same protocol adopted by Gatta et al. (2009a). All standards were calibrated within 0.5 % at 1σ. Raw data were corrected using a Phi–Rho–Z routine of the Jeol suite of programs.

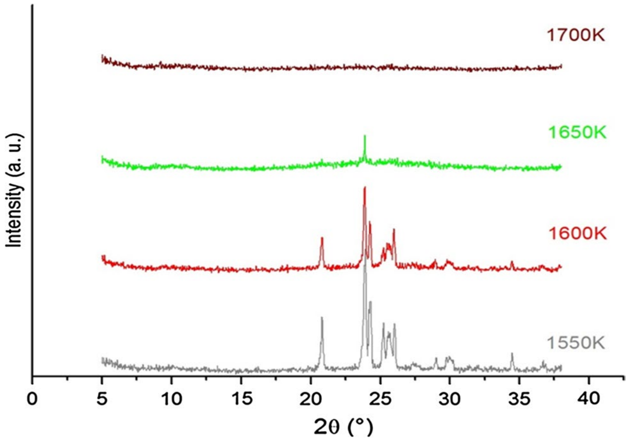

Fig. 3 In situ X-ray powder diffraction patterns collected at $T \geq 1550$ K (and at room *P*) at DST-MI

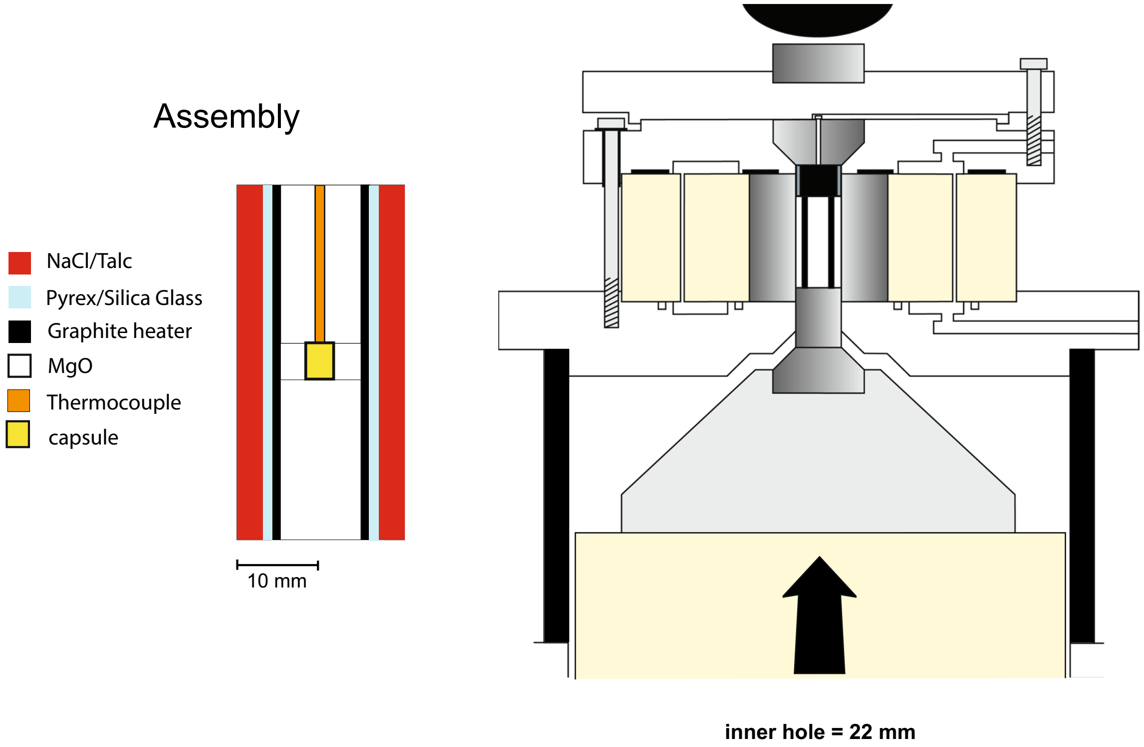

Fig. 4 Schematic diagram of the single-stage piston cylinder used for the high *P*–*T* experiments conducted at the DST-MI. The configuration of the salt–Pyrex–MgO assemblies used for experiments up to 1570 K, and talc–silica glass–MgO assemblies for higher temperatures, is shown

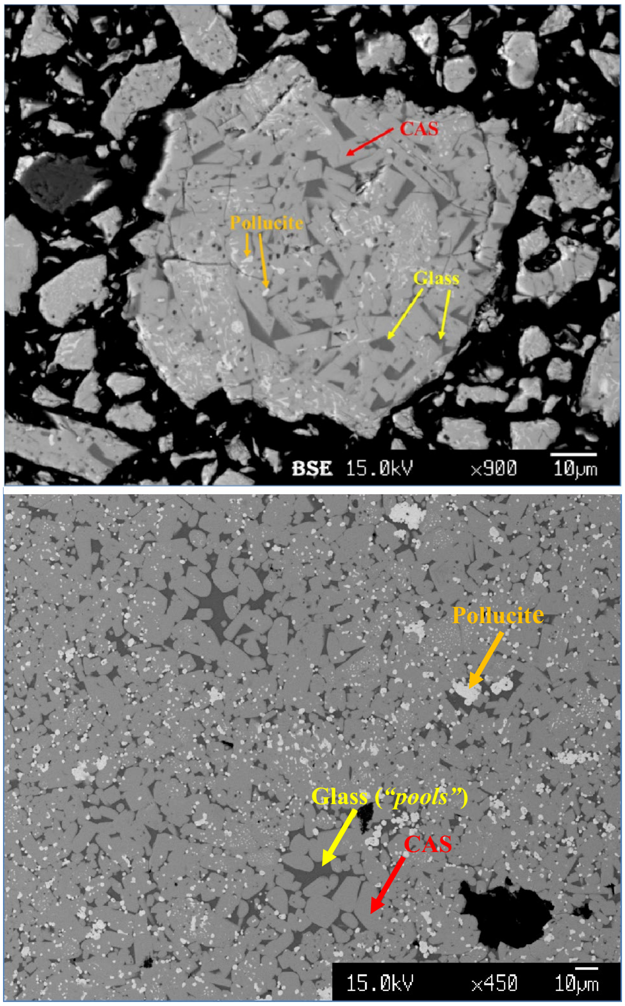

Fig. 5 BSE images of the untreated CAS-RM (*above*) and of the sample treated at 1570 K and 0.5 GPa (*below*). *CAS* $CsAlSi_5O_{12}$, *pollucite* $CsAlSi_2O_6$

Results

Reverse-exchange tests showed that the Cs-aluminosilicate glass releases 1.10 mg/g of Cs^+, whereas CAS-RM does not release any Cs^+ at significant level (i.e., below L.O.Q). The "AVA tests" showed that the amorphous Cs-aluminosilicate glass releases 1.94 mg/g of Cs^+, whereas the CAS-RM releases 0.05 mg/g of Cs^+.

The high-quality Rietveld full-profile fit (*R*p 4.12 %, *wR*p 5.89 %) of the synchrotron powder diffraction pattern of CAS-RM, modelled with the co-presence of three crystalline phases (i.e., $CsAlSi_5O_{12}$, pollucite-like $CsAlSi_2O_6$, and corundum added as internal standard, Fig. 2), leads to the following wt% fractions:

$$76(1)_{\mathrm{CsAlSi5O12}} + 7(1)_{\mathrm{CsAlSi2O6}} + 17(1)_{\mathrm{amorphous}}.$$

This result is consistent with the experimental findings based on the BSE images (see below).

The in situ X-ray powder diffraction patterns collected at high *T* (at DST-MI) show that $CsAlSi_5O_{12}$ maintains its crystalline form up to 1600 K (at room *P*). At 1650 K, the material appears being completely amorphous, as shown in Fig. 3. Diffraction data were collected up to 1700 K. Diffraction patterns collected decreasing temperature show that the *T*-induced crystalline-to-amorphous transformation is completely irreversible.

The average composition of $CsAlSi_5O_{12}$, pollucite-like compound, and Cs-rich glass obtained by EPMA–WDS are reported in Table 1. The BSE images obtained from the (untreated) CAS-RM and from the material run at 1570 K and 0.5 GPa (Fig. 5; Table 2), in a piston cylinder, show the occurrence of $CsAlSi_5O_{12}$, pollucite-type compound (ideally $CsAlSi_2O_6$), and a small fraction of Cs-rich glass. $CsAlSi_5O_{12}$ crystals are elongated and euhedral, with an average size of ~10 μm. Some $CsAlSi_5O_{12}$ crystals are poikilitic and contain several inclusions of few μm-sized pollucite. Glass often forms pools, and $CsAlSi_5O_{12}$ crystals that coexist with glass show well developed crystal faces toward the liquid (Fig. 5). Comparing the untreated CAS-RM with the *P*–*T*-treated samples, which do not encompass melting, no relevant textural and chemical changes have been detected (Fig. 5). This scenario is preserved up to 1660 K and 0.5 GPa, as deduced on the basis of the ex situ X-ray diffraction data (Table 2). The run conducted at 1770 K and 0.5 GPa shows that $CsAlSi_5O_{12}$ experiences a crystalline-to-amorphous state transformation between 1670 and 1770 K (at 0.5 GPa), and at 1770 K and 0.5 GPa only a pollucite-like compound as dominant phase, along with a subordinate amorphous phase, occurs (Table 2).

Discussion and conclusions

This study shows, for the first time, how a Cs-bearing ceramic-like material, able to preserve its crystallinity in response to extreme *P*–*T* conditions and its chemical integrity even under acid attack, can be obtained starting from a natural material, following the protocol of Brundu and Cerri (2015), here briefly described:

1. Raw material: clinoptilolite-rich epiclastic rock from Sardinia (60–70 wt% of zeolite);
2. Beneficiation process toward a 90 wt% of clinoptilolite;
3. Cation-exchange processes: first to a Na form and then to a Cs form, obtaining a material rich in $Cs_6Al_6Si_{30}O_{72}\cdot nH_2O$ (i.e., Cs-clinoptilolite);
4. Transformation process by thermal treatment at 1423 K for 2 h:

Table 1 Average wavelength-dispersive (EPMA–WDS) chemical analysis of crystalline phases and glass in the starting material (i.e., untreated CAS-RM) and in experimental products obtained after treatment at 0.5 GPa and 1570 K

Oxides (wt%)	CAS untreated material	CAS @ 0.5 GPa, 1570 K
Al_2O_3	10.51 (0.18)	10.78 (0.26)
SiO_2	64.44 (0.68)	66.80 (0.61)
Cs_2O	22.44 (0.74)	19.51 (0.63)
FeO	0.19 (0.09)	0.02 (0.02)
Na_2O	0.05 (0.04)	0.01 (0.04)
CaO	0.06 (0.01)	0.00 (0.00)
K_2O	0.25 (0.07)	0.20 (0.05)
Total	97.94	97.32
Oxides (wt%)	**Pollucite untreated material**	**Pollucite @ 0.5 GPa, 1570 K**
Al_2O_3	15.57 (0.89)	17.29 (1.34)
SiO_2	47.02 (0.97)	44.27 (1.26)
Cs_2O	33.32 (0.65)	36.10 (3.24)
FeO	0.23 (0.07)	0.07 (0.07)
Na_2O	0.13 (0.04)	0.08 (0.08)
CaO	0.11 (0.07)	0.05 (0.05)
K_2O	0.86 (0.36)	0.74 (0.06)
Total	97.24	98.60
Oxides (wt%)	**Glass untreated material**	**Glass @ 0.5 GPa, 1570 K**
MgO	2.98 (0.26)	2.58 (0.08)
Al_2O_3	16.95 (1.58)	16.50 (0.38)
SiO_2	58.28 (2.10)	60.84 (0.93)
Cs_2O	10.60 (0.92)	11.33 (2.22)
FeO	3.00 (0.44)	3.67 (0.73)
Na_2O	1.09 (0.07)	0.82 (0.08)
CaO	2.19 (1.09)	1.89 (0.27)
K_2O	1.05 (0.21)	0.81 (0.06)
Total	96.14	98.44

Values in parentheses: 1σ *e.s.d.*. CAS: $CsAlSi_5O_{12}$; pollucite: $CsAlSi_2O_6$

Table 2 Run conditions for the high *P*–*T* treatments of the CAS-RM by single-stage piston cylinder

Run#	*P* (GPa)	*T* (K)	Run time (h)	Capsule	Assembly	Run products
Cas1	0.5	1070	22	Au	Salt–Pyrex–MgO	$CsAlSi_5O_{12}$, $CsAlSi_2O_6$, Cs-aurides (+glass)
Cas2	0.5	1570	24	Pt	Salt–Pyrex–MgO	$CsAlSi_5O_{12}$, $CsAlSi_2O_6$ (+glass)
Cas3	0.5	1770	1	Pt	Talc–silica glass–MgO	$CsAlSi_2O_6$ (+glass)
Cas4	0.5	1670	2	Pt	Talc–silica glass–MgO	$CsAlSi_5O_{12}$, $CsAlSi_2O_6$ (+glass)

$$Cs_6Al_6Si_{30}O_{72} \cdot nH_2O \rightarrow 6CsAlSi_5O_{12} + nH_2O \uparrow$$

This protocol shows how a natural clinoptilolite can be used to capture Cs dispersed in a solution, on the basis of the high affinity of this zeolite for Cs (e.g., Pabalan and Bertetti 2001 and references therein). This is the typical scenario occurring when Cs, in different isotopic configurations and its ionic form, is concentrated in heavy water of the primary circuit of pressurized water reactor, or dispersed in soils or hydrologic systems after nuclear testing or nuclear accidents, as the Chernobyl disaster (in 1986) or, more recently, the Fukushima Daiichi nuclear disaster (in 2011). There have been dozens of accidents at nuclear power plants documented worldwide (more than 90 are listed by Sovacool 2010), and further details about the recent accidents are reported in the webpage of the International Atomic Energy Agency (IAEA) (http://www-pub.iaea.org/books/IAEABooks/Publications_on_Accident_Response).

Before the experiments of Brundu and Cerri (2015), $CsAlSi_5O_{12}$ was reported as obtainable by a synthesis process only, under hydrothermal conditions, starting from chemicals. Several experiments aimed to describe the crystal structure, and the *P*–*T*-induced behaviors of this material were based on the use of $CsAlSi_5O_{12}$ obtained by hydrothermal synthesis (listed in Gatta et al. 2008b). The transformation process of an highly available mineral commodity (i.e., clinoptilolite-rich rock), which can spontaneously capture Cs^+ and transforms to $CsAlSi_5O_{12}$ by a thermal treatment at room *P*, led to a change of the scenario on the potential use of $CsAlSi_5O_{12}$ as a host for nuclear waste. The experimental findings of this manuscript extend the previous results of Fisch et al. (2008, 2010) and Gatta et al. (2008b) toward a more complete characterization of the high pressure, high temperature, and chemical stability of $CsAlSi_5O_{12}$, which are mandatory for the use of a given compound in nuclear technology. However, the use of a natural raw material leads to the formation of a Cs-bearing polyphase material made by: $CsAlSi_5O_{12}$ (dominant), pollucite-like compound (subordinate), and Cs-rich amorphous phase (subordinate). This forced us to investigate the *P*–*T* behavior and chemical stability of the polyphase aggregate.

Average EPMA–WDS data of $CsAlSi_5O_{12}$ and pollucite-like compound of this study show total values of the chemical composition ranging between 97.2 and 98.6 wt% (Table 1). This deficiency might be explained by the potential low fraction of zeolitic H_2O in $CsAlSi_5O_{12}$ and pollucite-like compound, spontaneously adsorbed by the environment as usually occurs in this class of open-framework materials. The limited size of glass pools (of few micrometers of size) can, on the other hand, explain the deficiency reported for the analyses of the glass fraction (Fig. 5; Table 1).

If we combine the experimental findings of this study (i.e., by in situ high-*T* X-ray powder diffraction and single-stage piston cylinder at high *P*–*T*) and those previously reported by Fisch et al. (2008) and Gatta et al. (2008b), we can have a better picture about the *P*–*T* phase stability of $CsAlSi_5O_{12}$:

- In response to applied pressure and at room *T*, this compound is stable in its crystalline form at least up to 8.5 GPa (Gatta et al. 2008b);
- In response to applied temperature and at room *P*, this compound experiences an unquenchable and displacive *Ama*2-to-*Amam* phase transition at about 770 K, and the *Amam* polymorph is stable in its crystalline form up to 1600 K; $CsAlSi_5O_{12}$ experiences a *T*-induced crystalline-to-amorphous phase transition between 1600 and 1650 K (Fig. 3);
- In response to the applied $P = 0.5$ GPa, the crystalline-to-amorphous transition occurs between 1670 and 1770 K. This leads to a positive Clapeyron slope (i.e., $dP/dT > 0$), as schematically shown in Fig. 6. We can expect a positive slope even for the *Ama*2-to-*Amam* phase transition.

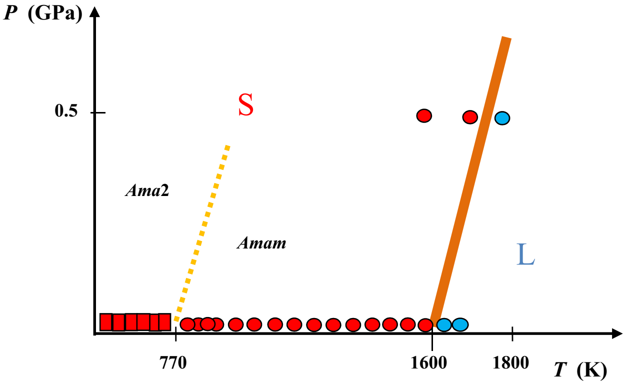

Fig. 6 Schematic *P*–*T* phase diagram of $CsAlSi_5O_{12}$ on the basis of the experimental findings of this study and of the previous ones (Fisch et al. 2008; Gatta et al. 2008b). *Solid symbols* represent the experimental data points

If we consider the microporous nature of $CsAlSi_5O_{12}$, which is a nominally zeolitic material, its *P*–*T* stability is surprising. Such a behavior is typical for a ceramic material, rather than for an open-framework compound. We believe that the “unusual” thermo-elastic behavior of $CsAlSi_5O_{12}$ and its *P*–*T* phase stability are somehow governed by the absence of extra-framework H_2O molecules, which usually make zeolites highly unstable materials at high *T* in response to dehydration processes (zeolites can contain up to 20 wt% of H_2O).

The reverse-exchange and the “AVA” tests provided excellent results in terms of Cs^+ retention capacity of the CAS-RM, which are typical of a ceramic compound rather than for an open-framework compounds (Liguori et al. 2013). These experimental findings corroborate the first results on the chemical stability of $CsAlSi_5O_{12}$ reported by Komarneni and Roy (1983) and by Fisch et al. (2010). The retention capacity for Cs^+ in $CsAlSi_5O_{12}$ can be explained on the basis of the bonding configuration of Cs in the 8mR channels running along [001]. As discussed by Gatta et al. (2008b), the Cs-site lies off-center in the 8mR channel, with a coordination number CN = 13, and Cs–O_{max} ~3.609 and Cs–O_{min} ~3.490 Å. The oxygens belonging to the opposite part of the channel wall, with respect to the Cs atom, are not bonded to it. With this configuration, the bond strength is superior if compared with that of a cation site potentially located in the center of the 8mR channel. Similarly, the high Cs-retention capacity of pollucite is governed by the short free diameter (~2.86 Å) of the 6-membered ring channels along [111], which implies a high coordination number of Cs (CN = 12, Gatta et al.

2009a, b) and relatively short Cs–O bond distances (six Cs–O bond distances of ~3.397 Å and six of ~3.555 Å, Gatta et al. 2009a, b). Likely, the synthetic counterpart of pollucite is the best open-framework material so far known for its high-*T* stability and for its retention capacity of Cs^+ (e.g., Komarneni and White 1981; Komarneni and Roy 1983; Kobayashi et al. 1997, 2006; Gatta et al. 2009a, b). In this light, the presence of a pollucite-like compound as dominant phase obtained at 1770 K and 0.5 GPa (i.e., at *T* above the stability field of $CsAlSi_5O_{12}$) is a positive result.

On the basis of its thermo-elastic behavior, *P*–*T* phase stability fields, and Cs^+ retention capacity, $CsAlSi_5O_{12}$ is a possible candidate for use in the immobilization of radioactive isotopes of Cs, or as potential solid hosts for ^{137}Cs γ-radiation source in sterilization applications. The $CsAlSi_5O_{12}$-rich material obtained by a clinoptilolite-rich epiclastic rock, following the protocol of Brundu and Cerri (2015), appears to be suitable for this type of utilizations.

Acknowledgments GDG acknowledges the Italian Ministry of Education, MIUR-Project: "Futuro in Ricerca 2012—ImPACT-RBFR12CLQD". The authors thank Marco Merlini for the data collected at ESRF. GC acknowledges the support of Fondazione Banco di Sardegna, 2011, Project: "Synthesis of ceramic materials of environmental and industrial relevance from zeolitic precursors". Martin Fisch (Bern) and an anonymous reviewer are thanked for the revision of the manuscript.

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