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# The High Temperature Synthesis of $CsAlSiO_4$–ANA, a New Polymorph in the System $Cs_2O$–$Al_2O_3$–$SiO_2$

## I. The End Member of ANA Type of Zeolite Framework

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High temperature phase transformations of $Cs^+$ exchanged zeolites were investigated. Above 1000°C, Cs–X, Cs–Y (FAU), and Cs, ZK-4 (LTA) frameworks recrystallized in a pollucite phase. A $Cs^+$ loaded mordenite recrystallized at 1300°C in the orthorhombic $CsAlSi_5O_{12}$ phase. A $Cs^+$ exchanged zeolite A at 960°C recrystallized in a mixture of two polymorphic $CsAlSiO_4$ phases having different $(Al,Si)O_4$ frameworks. The unstable orthorhombic $CsAlSiO_4$–ABW phase has a topotactic transition at 1150°C into an ordered low $CsAlSiO_4$–ANA framework. Further calcination produces, at 1200°C, transformation of the low $CsAlSiO_4$–ANA phase to the more stable high $CsAlSiO_4$–ANA polymorph having cubic ($a_0$ = 13.6595 (5) Å) symmetry and an ordered Si–Al distribution. The crystal structure of high $CsAlSiO_4$–ANA, a new polymorph in the system $Cs_2O$–$Al_2O_3$–$SiO_2$, was determined using X-ray Rietveld analyses and $^{29}Si$ MAS NMR spectroscopy. © 1991 Academic Press, Inc.

## Introduction

Zeolites having open structures are very promising precursors in the synthesis of new materials by thermal transformations (*1–3*). It is observed that high temperature transformations of different zeolites are sensitive to the size and the degree of cation exchange. In such transformations the cation size determines the type of framework structure formed and its behavior. $Li^+$ exchanged LTA zeolite transforms into high conductive $\beta$-eucryptite, Na-LTA to less conductive nepheline, and the K-LTA form to the least conductive kaliophilite. One would then expect that $Cs^+$ exchanged LTA zeolite would likewise transform into a nonconductive phase.

Cesium aluminosilicate phases are of great interest as possible hosts for $^{137}Cs$ immobilization in radioactive waste management. In the system $Cs_2O$–$Al_2O_3$–$SiO_2$ only a few Cs aluminosilicate phases are known and well defined: $CsAlSiO_4$ has an ordered orthorhombic (*4, 5*) zeolite ABW framework; $CsAlSi_2O_6$ is known as the mineral pollucite having a cubic (*6*) ANA type zeolite (*7*) framework; $CsAlSi_5O_{12}$ with 5-membered rings of the Al and Si tetrahedra in the framework has orthorhombic (*8, 9*) symmetry.

The aim of this work was the study of transformation of $Cs^+$ loaded zeolites with different framework structure types and Si/Al ratios. During the course of investigations of thermal transformation of $Cs^+$ ex-



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changed LTA zeolite, two known polymorphic forms of $CsAlSiO_4$ having ABW and ANA types of tetrahedral framework were identified.

## Experimental

Zeolites A (framework code LTA), X and SK-40 (FAU) manufactured by Union Carbide and Mordenite (MOR) produced by Norton company were used. ZK-4 zeolite (LTA) was synthesized in our laboratory. $Cs^+$ exchanged forms of all zeolites were prepared by standard procedure. Chemical compositions of exchanged samples were analyzed using a Perkin–Elmer 380 atomic absorption spectrophotomer. Phase transformations and thermal behavior were investigated using a DuPont 1090 thermal analyzer equipped with high temperature DTA (1200°C) and DSC cells using a heating rate of 10°C $min^{-1}$. Before X-ray powder diffraction experiments, the samples were heated 3h to a constant temperature with an error of ±1°C. The X-ray powder diffraction (XRPD) patterns were obtained on a PHILIPS PW-1710 automated diffractometer, using a Cu tube operated at 40 kV and 35 mA. The instrument was equipped with a diffracted beam curved Graphite monochromator and a Xe-filled proportional counter.

Diffraction data for Rietveld (*10*) analysis were collected in the range $2\theta$-4 to 90°, counting for 4.85 sec in 0.02° steps. A fixed 1° divergence and 0.1° receiving slits were used. A silicon powder was used as a standard for calibration of diffractometer. All XRPD experiments were done at room temperature. The trial and error indexing program TREOR (*11*) and a program for the refinement of cell dimensions, LSUCRIPC (*12*), a version of the D. E. Appleman and H. T. Evans (*13*) program adapted for a personal computer, were used. Rietveld refinement was performed using the computer program (*14, 15*) DBW3.2S-8804.

$^{29}Si$ MAS NMR spectra were measured at 79.5 MHz with a Bruker MSL-400 multinuclear spectrometer. An Andrew–Beams probehead was used with rotors spinning at 5 kHz with air as the driving gas. Radio frequency pulses equivalent to 54° pulse angle were applied with a 12 sec recycle delay. $^{29}Si$ chemical shifts are quoted in ppm from external tetramethylsilane (TMS).

Infrared absorption spectra were obtained on a Perkin–Elmer model 983 grating spectrophotometer, using KBr pellets technique.

The electrical conductivity measurements were made as described earlier (*16*).

## Results

The high-temperature transformations of $Cs^+$ exchanged zeolites with different Si/Al ratios A (1.0), ZK-4 (1.5), X (2.3), Y (2.5), and mordenite (5.0) were investigated. Phase transitions in the range 900–1350°C were examined by DTA and followed by XRPD methods. Increasing Si/Al ratios (CsX and CsY sample results in a shift in the exothermal peak to higher temperatures. This is consistent with greater zeolite framework stability at higher Si/Al ratios. Generally, all $Cs^+$ exchanged zeolites were found on calcination to form amorphous precursors which recrystallize in pollucite phases above 1100°C. The $Cs^+$ exchanged mordenite sample is a double exception. It remained amorphous up to 1200°C and then recrystallized into a $CsAlSi_5O_{12}$ phase (*8*) above 1300°C, see Tables I and III.

The phase transition behavior of $Cs^+$ exchanged zeolite A is probably complex. The first endothermic peak (1000°C) in the DTA curve, Fig. 1, is assigned to transformation of the LTA framework into an amorphous form. The exothermal doublet (1160 and 1170°C) is likely a two step transformation similar to the recrystallization observed for $Li^+$ exchanged zeolite A (*1*). XRPD examination after firing at these temperatures con-

TABLE I

XRPD DATA FOR A HIGH-TEMPERATURE SYNTHESIZED $CsAlSi_5O_{12}$ PHASE (Cs-MORDENITE PRECURSOR AT 1300°C, 3hr) AND $CsAlSiO_4$–ABW POLYMORPH (Cs-LTA PRECURSOR AT 960°C; 3hr)

| $CsAlSi_5O_{12}$ phase, at 1350°C | | | | | | | $CsAlSiO_4$–ABW phase, at 960°C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $h$ | $k$ | $l$ | | $I/I_0$ | $d_0$ (Å) | $d_c$ (Å) | $h$ | $k$ | $l$ | | $I/I_0$ | $d_0$ (Å) | $d_c$ (Å) |
| 2 | 0 | 0 | | 3 | 6.8730 | 6.8890 | 0 | 1 | 1 | | 30 | 4.6818 | 4.6980 |
| 2 | 2 | 0 | | 2 | 5.3107 | 5.3163 | 2 | 1 | 0 | | 8 | 4.0235 | 4.0282 |
| 1 | 1 | 1 | | 4 | 4.5474 | 4.5398 | 1 | 2 | 1 | | 66 | 3.2971 | 3.3046 |
| 1 | 2 | 1 | | 44 | 4.1118 | 4.1081 | 2 | 2 | 0 | | 100 | 3.2460 | 3.2394 |
| 1 | 3 | 1 | | 100 | 3.6029 | 3.6004 | 0 | 0 | 2 | | 28 | 2.7034 | 2.7082 |
| 2 | 4 | 0 | | 61 | 3.5709 | 3.5733 | 0 | 2 | 2 | | 10 | 2.3485 | 2.3490 |
| 4 | 0 | 0 | | 27 | 3.4432 | 3.4445 | 2 | 0 | 2 | | 14 | 2.3165 | 2.3140 |
| 3 | 0 | 1 | R | 29 | 3.3820 | 3.3887 | 1 | 2 | 2 | | 6 | 2.2705 | 2.2714 |
| 4 | 1 | 0 | | 25 | 3.3696 | 3.3736 | 4 | 1 | 0 | | 4 | 2.1655 | 2.1675 |
| 3 | 1 | 1 | | 38 | 3.3233 | 3.3211 | 2 | 4 | 0 | | 9 | 2.0861 | 2.0854 |
| 4 | 2 | 0 | | 5 | 3.1835 | 3.1847 | 1 | 3 | 2 | R | 6 | 1.9935 | 2.0002 |
| 3 | 2 | 1 | | 7 | 3.1374 | 3.1404 | 1 | 4 | 2 | | 11 | 1.7461 | 1.7448 |
| 2 | 5 | 0 | | 11 | 3.0086 | 3.0081 | 3 | 3 | 2 | | 4 | 1.6885 | 1.6885 |
| 4 | 3 | 0 | | 10 | 2.9304 | 2.9300 | 2 | 1 | 3 | | 8 | 1.6500 | 1.6475 |
| 3 | 3 | 1 | | 12 | 2.8947 | 2.8954 | 4 | 4 | 0 | | 4 | 1.6193 | 1.6197 |
| 0 | 6 | 0 | | 4 | 2.7878 | 2.7864 | 2 | 3 | 3 | | 2 | 1.4762 | 1.4773 |
| 1 | 5 | 1 | | 7 | 2.7307 | 2.7278 | 6 | 2 | 1 | | 3 | 1.3705 | 1.3702 |
| 4 | 4 | 0 | | 2 | 2.6605 | 2.6581 | | | | | | | |
| 3 | 4 | 1 | | 4 | 2.6328 | 2.6322 | | | | | | | |
| 2 | 6 | 0 | | 4 | 2.5809 | 2.5831 | | | | | | | |
| 4 | 3 | 1 | | 6 | 2.5291 | 2.5306 | | | | | | | |
| 0 | 0 | 2 | | 6 | 2.5099 | 2.5102 | | | | | | | |
| 5 | 1 | 1 | | 6 | 2.3930 | 2.3908 | | | | | | | |
| 2 | 0 | 2 | | 4 | 2.3568 | 2.3585 | | | | | | | |
| 5 | 2 | 1 | | 6 | 2.3225 | 2.3207 | | | | | | | |
| 6 | 1 | 0 | | 3 | 2.2749 | 2.2750 | | | | | | | |
| 5 | 3 | 1 | | 1 | 2.2151 | 2.2164 | | | | | | | |
| 6 | 2 | 0 | | | | 2.2143 | | | | | | | |
| 3 | 6 | 1 | | 4 | 2.1524 | 2.1522 | | | | | | | |
| 0 | 4 | 2 | | | | 2.1519 | | | | | | | |
| 1 | 7 | 1 | | 3 | 2.1289 | 2.1308 | | | | | | | |
| 5 | 4 | 1 | | 4 | 2.0904 | 2.0915 | | | | | | | |
| 0 | 8 | 0 | | | | 2.0898 | | | | | | | |
| 1 | 8 | 0 | R | 2 | 2.0634 | 2.0661 | | | | | | | |
| 4 | 1 | 2 | | 3 | 2.0135 | 2.0139 | | | | | | | |
| 6 | 4 | 0 | | | | 2.0126 | | | | | | | |
| 7 | 1 | 0 | | 2 | 1.9540 | 1.9548 | | | | | | | |
| 1 | 8 | 1 | | 2 | 1.9091 | 1.9107 | | | | | | | |
| 6 | 5 | 0 | | 3 | 1.8924 | 1.8929 | | | | | | | |
| 6 | 4 | 1 | | 1 | 1.8668 | 1.8681 | | | | | | | |
| 7 | 0 | 1 | | 4 | 1.8321 | 1.8325 | | | | | | | |
| 4 | 7 | 1 | | 3 | 1.8285 | 1.8280 | | | | | | | |
| 7 | 2 | 1 | | 2 | 1.7903 | 1.7900 | | | | | | | |
| 4 | 5 | 2 | R | 2 | 1.7362 | 1.7344 | | | | | | | |
| 8 | 2 | 0 | | 3 | 1.6872 | 1.6868 | | | | | | | |
| 2 | 10 | 0 | | 2 | 1.6244 | 1.6247 | | | | | | | |
| 1 | 10 | 1 | | 3 | 1.5766 | 1.5758 | | | | | | | |
| 6 | 8 | 0 | | 1 | 1.5454 | 1.5456 | | | | | | | |
| 3 | 2 | 3 | | | | 1.5452 | | | | | | | |
| 8 | 5 | 0 | | 1 | 1.5316 | 1.5311 | | | | | | | |
| 7 | 6 | 1 | | | | 1.5311 | | | | | | | |
| 6 | 5 | 2 | | 2 | 1.5113 | 1.5114 | | | | | | | |

*Note.* R—rejected lines.

firmed this interpretation. The amorphous $Cs_2O$–$Al_2O_3$–$SiO_2$ precursor after calcination at 960°C recrystallized into a mixture of two phases, Fig. 2 (continuous line). One of these, which has a strong doublet at $2\theta$ = 27.5° was identified as the $CsAlSiO_4$ phase,

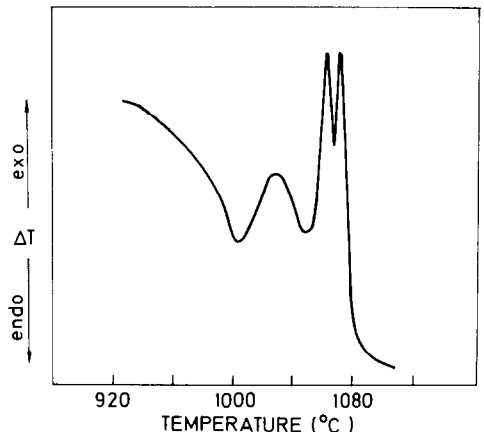


FIG. 1. DTA curve of $Cs^+$ exchanged LTA zeolite.

see Tables I and III, known from articles by R. M. Barrer and N. McCallum (*4*), T. V. Soloveva *et al.* (*17*), and S. A. Gallagher *et al.* (*5*). The second phase has strongest peaks at $2\theta = 26°$ and $2\theta = 30.6°$ and has been identified as a "pollucite-like" phase. Further clarification comes from studies in a temperature range 960–1200°C. From Fig. 2, it can be seen that orthorhombic (*5*) $CsAlSiO_4$ is unstable above 1000°C and recrystallizes in the pollucite-like phase. This conversion was followed quantitatively by XRPD analyses comparing the aforementioned strongest reflections, and is almost completed at 1050°C, see Fig. 2, (dashed line). Recrystallization of the orthorhombic $CsAlSiO_4$ phase (JCPDS file card 10-14) in a pollucite-like phase is a solid–solid transformation and the two phases are polymorphs. The formed pollucite-like phase in Fig. 3, (points line) is unstable with further increasing temperature and transformation to the pollucite pattern (1350°C) could be followed in Fig. 3 (dashed line). Measured XRPD patterns are presented in Table II. Obviously, the pollucite-like phase at 1150°C (Fig. 3, points line), has many superstructure reflections, Table II, which cannot be indexed on the standard pollucite unit cell with the cubic space group $Ia\bar{3}d$. The indexed interplanar spacings in Table II gave by least-

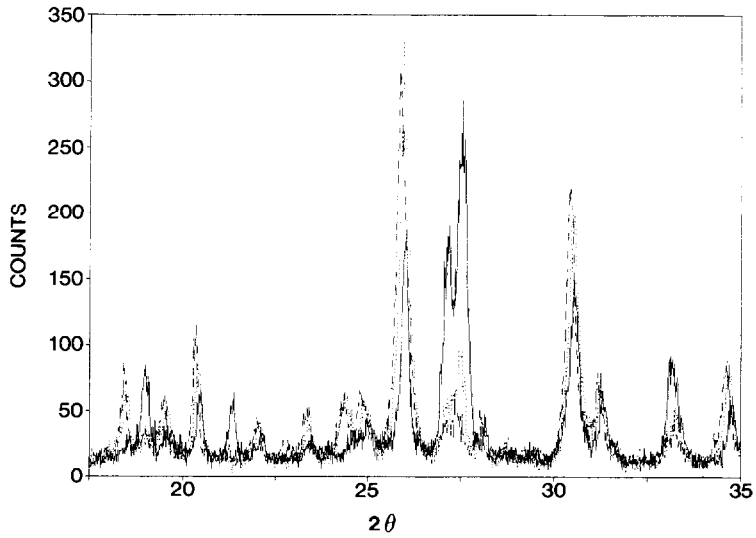


FIG. 2. XRPD traces of $Cs^+$ exchanged LTA zeolite precursor at different temperatures, showing solid–solid polymorphic transition of: $CsAlSiO_4$–ABW phase at 960°C, 3 hr (continuous line); over 1000°C, 3 hr (points line); to low $CsAlSiO_4$–ANA phase at 1050°C, 3 hr (dashed line).

TABLE II

XRPD DATA FOR A HIGH-TEMPERATURE SYNTHESIZED HIGH AND LOW FORMS OF $CsAlSiO_4$–ANA POLYMORPH (Cs-LTA PRECURSOR AT 1150°C, 3hr AND 1350°C, 3hr)

| Low $CsAlSiO_4$–ANA, 1150°C | | | | | | | High $CsAlSiO_4$–ANA, at 1350°C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $h$ | $k$ | $l$ | | $I/I_o$ | $d_o$ (Å) | $d_c$ (Å) | $h$ | $k$ | $l$ | $I/I_o$ | $d_o$ (Å) | $d_c$ (Å) |
| 2 | 2 | 0 | R | 2 | 9.3783 | 9.6698 | | | | | | |
| 3 | 1 | 0 | R | 1 | 8.0357 | 8.6489 | | | | | | |
| 3 | 2 | 1 | R | 1 | 7.5633 | 7.3097 | | | | | | |
| 4 | 2 | 2 | | 5 | 5.6052 | 5.5828 | 2 | 1 | 1 | 6 | 5.5642 | 5.5714 |
| 4 | 4 | 0 | R | 26 | 4.7855 | 4.8349 | 2 | 2 | 0 | 2 | 4.8193 | 4.8250 |
| 5 | 3 | 0 | | 6 | 4.6989 | 4.6905 | | | | | | |
| 6 | 1 | 1 | R | 21 | 4.5222 | 4.4368 | | | | | | |
| 6 | 2 | 0 | | 28 | 4.3416 | 4.3245 | | | | | | |
| 5 | 4 | 1 | R | 3 | 4.1664 | 4.2202 | | | | | | |
| 6 | 3 | 1 | | 12 | 4.0185 | 4.0326 | | | | | | |
| 6 | 4 | 0 | | 15 | 3.7967 | 3.7928 | | | | | | |
| 6 | 4 | 2 | | 11 | 3.6479 | 3.6548 | 3 | 2 | 1 | 44 | 3.6429 | 3.6473 |
| 7 | 3 | 0 | | 14 | 3.5779 | 3.5913 | | | | | | |
| 8 | 0 | 0 | | 100 | 3.4341 | 3.4188 | 4 | 0 | 0 | 100 | 3.4076 | 3.4118 |
| 8 | 2 | 0 | | 9 | 3.3022 | 3.3167 | | | | | | |
| 6 | 6 | 0 | | 14 | 3.2329 | 3.2233 | | | | | | |
| 7 | 5 | 0 | | 11 | 3.1710 | 3.1794 | | | | | | |
| 7 | 5 | 2 | | 6 | 3.1035 | 3.0968 | 4 | 2 | 0 | 4 | 3.0467 | 3.0516 |
| 6 | 6 | 4 | | 66 | 2.9271 | 2.9155 | 3 | 3 | 2 | 44 | 2.9072 | 2.9096 |
| 9 | 3 | 0 | R | 20 | 2.8559 | 2.8830 | | | | | | |
| 8 | 4 | 4 | R | 1 | 2.7585 | 2.7914 | 4 | 2 | 2 | 1 | 2.7831 | 2.7857 |
| 10 | 1 | 1 | | 5 | 2.7114 | 2.7081 | | | | | | |
| 10 | 2 | 0 | | 6 | 2.6822 | 2.6819 | 4 | 3 | 1 | 4 | 2.6763 | 2.6764 |
| 10 | 3 | 1 | | 30 | 2.5994 | 2.6077 | | | | | | |
| 10 | 4 | 0 | | 4 | 2.5308 | 2.5394 | | | | | | |
| 10 | 4 | 2 | | 4 | 2.4911 | 2.4967 | 5 | 2 | 1 | 6 | 2.4911 | 2.4916 |
| 11 | 2 | 1 | | 3 | 2.4429 | 2.4365 | | | | | | |
| 8 | 8 | 0 | | 7 | 2.4132 | 2.4174 | 4 | 4 | 0 | 22 | 2.4110 | 2.4125 |
| 10 | 6 | 0 | | 6 | 2.3493 | 2.3453 | | | | | | |
| 10 | 6 | 2 | | 2 | 2.3145 | 2.3115 | | | | | | |
| 12 | 1 | 1 | | 5 | 2.2688 | 2.2635 | | | | | | |
| 12 | 2 | 2 | | 3 | 2.2130 | 2.2184 | 6 | 1 | 1 | 12 | 2.2143 | 2.2138 |
| 12 | 3 | 1 | R | 6 | 2.1919 | 2.2039 | | | | | | |
| 10 | 8 | 0 | | 4 | 2.1342 | 2.1357 | 6 | 2 | 0 | 1 | 2.1576 | 2.1578 |
| 10 | 6 | 6 | | 5 | 2.0890 | 2.0854 | | | | | | |
| 12 | 4 | 4 | | 6 | 2.0616 | 2.0616 | | | | | | |
| 12 | 6 | 2 | | 6 | 2.0135 | 2.0163 | 6 | 3 | 1 | 6 | 2.0106 | 2.0121 |
| 10 | 9 | 3 | | 3 | 1.9803 | 1.9842 | 4 | 4 | 4 | 5 | 1.9708 | 1.9698 |
| 12 | 8 | 0 | R | 10 | 1.9009 | 1.8964 | 6 | 4 | 0 | 1 | 1.8916 | 1.8925 |
| 14 | 4 | 0 | R | 5 | 1.8742 | 1.8784 | | | | | | |
| 14 | 5 | 1 | R | 2 | 1.8417 | 1.8356 | 6 | 3 | 3 | 10 | 1.8562 | 1.8571 |
| 15 | 2 | 1 | R | 1 | 1.8071 | 1.8034 | 6 | 4 | 2 | 1 | 1.8235 | 1.8237 |
| 15 | 3 | 2 | R | 3 | 1.7659 | 1.7728 | | | | | | |
| 12 | 10 | 2 | | 10 | 1.7365 | 1.7367 | 6 | 5 | 1 | 12 | 1.7337 | 1.7332 |
| | | | | | | | 8 | 0 | 0 | 3 | 1.7068 | 1.7059 |
| 16 | 2 | 2 | | 2 | 1.6825 | 1.6833 | 8 | 1 | 1 | 1 | 1.6795 | 1.6798 |
| | | | | | | | 8 | 2 | 0 | R 1 | 1.6529 | 1.6549 |
| | | | | | | | 6 | 5 | 3 | 1 | 1.6318 | 1.6311 |
| 14 | 10 | 0 | R | 3 | 1.5846 | 1.5897 | 7 | 5 | 0 | 1 | 1.5855 | 1.5864 |
| 14 | 10 | 4 | | 5 | 1.5487 | 1.5484 | 7 | 5 | 2 | 3 | 1.5445 | 1.5452 |
| 16 | 8 | 0 | R | 4 | 1.5305 | 1.5289 | 8 | 4 | 0 | 3 | 1.5260 | 1.5258 |
| 17 | 5 | 4 | | 3 | 1.5058 | 1.5056 | | | | | | |
| 18 | 4 | 0 | | 2 | 1.4823 | 1.4833 | 9 | 2 | 1 | 2 | 1.4725 | 1.4716 |
| 18 | 5 | 1 | R | 1 | 1.4606 | 1.4619 | | | | | | |
| 19 | 3 | 0 | | 1 | 1.4243 | 1.4219 | 9 | 3 | 0 | 1 | 1.4384 | 1.4385 |
| | | | | | | | 9 | 3 | 2 | 2 | 1.4083 | 1.4076 |
| 19 | 6 | 1 | R | 4 | 1.3720 | 1.3709 | 8 | 4 | 4 | 1 | 1.3931 | 1.3928 |
| 20 | 0 | 0 | R | 4 | 1.3691 | 1.3675 | 10 | 1 | 1 | 3 | 1.3521 | 1.3513 |

*Note.* R—rejected lines.

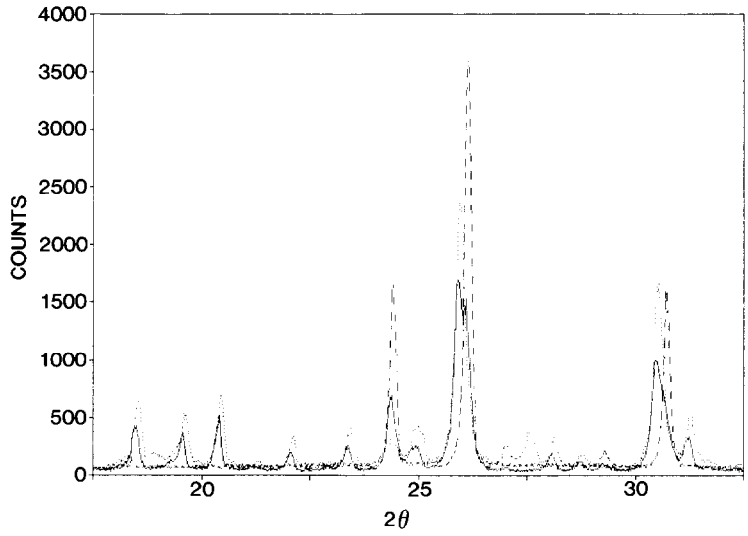


FIG. 3. XRPD traces of $Cs^+$ exchanged LTA zeolite in the temperature range 1150°C, 3 hr to 1350°C, 3 hr showing conversion of low $CsAlSiO_4$–ANA (points line) over 1200°C, 3 hr (continuous line) to high $CsAlSiO_4$–ANA phase (dashed line).

squares optimization (*11*, *12*) the unit cell dimensions in Table III. Rietveld refinement results, Tables IV–VI and Fig. 4, of the phase formed at 1350°C confirmed pollucite crystal structure. The starting parameters used in the refinement of T (Si,Al) and O atomic positions were taken from the structure given by R. Beger (*6*). In the first stage of refinement, only framework parameters were refined. When the refinement converged, Fourier and difference syntheses were used to locate the sites of extra framework cations involved. Subsequent refinements and Fourier syntheses gradually resolved the detailed distribution of $Cs^+$ cations in three different positions. Most of the Cs atoms (14.3) occupy 16 *b* positions of *Ia3d* cubic space group. The rest of the $Cs^+$ and 2–3 $Na^+$ cations (from results of chemical analyses 1–1.5 $Na^+$ cations per unit cell of zeolite A were not exchanged) are statistically distributed over: 24 *c* and 48 *g* (coordinate $x = 0.053$) Wyckoff positions. Numerous attempts to refine temperature and site population factors of the cations at these positions gave unrealistic values. Another feature of the pollucite formed at 1350°C is ordered Si and Al tetrahedral framework

TABLE III

UNIT CELL DIMENSIONS OF HIGH-TEMPERATURE SYNTHESIZED PHASES FROM THE $Cs_2O$–$Al_2O_3$–$SiO_2$ SYSTEM

| Sample | $a_o$ (Å) | $b_o$ (Å) | $c_o$ (Å) | $V_o$ (Å)$^3$ |
|---|---|---|---|---|
| $CsAlSiO_4$–ABW | 8.908(8) | 9.440(11) | 5.416(2) | 455.4(8) |
| $CsAlSi_5O_{12}$ | 13.778(9) | 16.718(13) | 5.0205(2) | 1156.4(5) |
| low $CsAlSiO_4$–ANA | 27.35(2) | | | 20459(39) |
| high $CsAlSiO_4$–ANA | 13.647(3) | | | 2452(2) |

TABLE IV

DATA COLLECTION AND REITVELD REFINEMENT PARAMETERS FOR HIGH $CsAlSiO_4$–ANA

| | | |
|---|---|---|
| No. data points | | 4301 |
| No. contributing reflections | | 180 |
| No. atomic variables | | 8 |
| Total no. variables | | 13 |
| $2\theta$ range (°) | | 4–90 |
| pseudo-Voigt profile coefficients: | $U$ | 0.50(3) |
| | $V$ | −0.17(2) |
| | $W$ | 0.039(3) |
| asymmetry parameter | | 0.62(6) |
| zero point (°) | | 0.031(1) |
| unit cell $a_o$ (Å) | | 13.6595(4) |
| final residuals[a] | $R_p$ | 7.24 |
| | $R_{wp}$ | 9.79 |
| | $R_B$ | 5.21 |
| | $R_E$ | 6.25 |

[a] $R_p$, unweighted profile residual; $R_{wp}$, weighted profile residual; $R_B$, integrated intensity residual; $R_E$, expected $R_{wp}$.

deduced by means $^{29}Si$ MAS NMR experiment, Fig. 5.

In Fig. 6, infrared absorption spectra of a cubic pollucite phase derived from Cs–Y zeolite calcined at 1300°C (curve (a)) and the pollucite-like phase obtained after calcination of Cs–A zeolite at 1150°C (curve (b)) are presented. IR spectra of pollucites obtained from Cs–X, Cs, ZK-4 and Cs–A zeolites after treatment at 1350°C are the same as presented by curve (a) in Fig. 6. All of these spectra are typical for the ANA type of zeolite framework (*18*). As can be seen from Fig. 6, on comparing curves (a) and (b) there are significant differences in the regions 420–470 $cm^{-1}$ and 670–690 $cm^{-1}$. Two well defined bands at 425 and 465 $cm^{-1}$ and at 670 and 680 $cm^{-1}$ appeared in the spectrum of the pollucite-like phase previously calcinated at 1150°C.

The electrical conductivity of cubic pollucite produced from a Cs–Y precursor and the pollucite-like phase obtained from Cs–A zeolite precursor are shown in Fig. 7. It is clear there are no significant differences in the conductivities of these two phases.

## Discussion

The framework of pollucite structure (*6*) consists of single 4-ring, single 6-ring, and single 8-ring, which define large cavities with 12 oxygen atoms appropriately placed for coordinating $Cs^+$ cations. The same framework topology is adopted by analcime (*19, 20*), leucite (*21*), and many additional compositional variants (*7, 22*). A common characteristic of all variants with the same ANA framework is that Si/Al ratios are $\geq 2$. The anionic framework charge associated with the framework must be balanced by extra framework cations. Structural data for ANA (*23*) framework materials (*24, 25*) show 16 cations statistically distributed near three different site positions of $Ia\bar{3}d$ cubic space group. We can consider then the structural reasons for the significant differences in XRPD patterns of pollucite-like phases at 1150 and 1350°C produced from a Cs–A pre-

TABLE V

POSITIONAL ($x$, $y$, $z$), ISOTROPIC THERMAL ($B$), AND SITE OCCUPANCY ($N$) PARAMETERS FOR HIGH $CsAlSiO_4$–ANA

| Atom | Site | $x$ | $y$ | $z$ | $B$(Å) | $N$ |
|---|---|---|---|---|---|---|
| $T_1$ (Si,Al) | 48 *g* | 0.125 | 0.1626(2) | 0.4126 | 0.8(1) | 1.0 |
| $O_1$ | 96 *h* | 0.1028(3) | 0.1332(3) | 0.7198(4) | 1.9(1) | 1.0 |
| $Cs_1$ | 16 *b* | 0.125 | 0.125 | 0.125 | 2.4(2) | 0.89 |

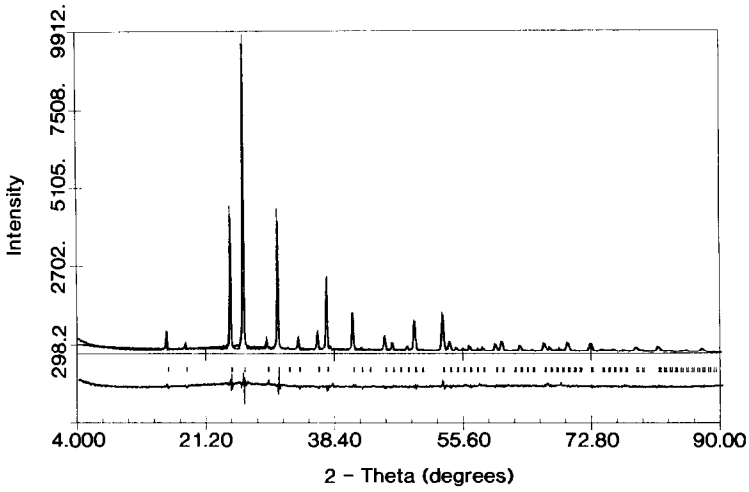


FIG. 4. Final Rietveld X-ray profile plot of high $CsAlSiO_4$–ANA phase. The upper curves show the observed and calculated profiles, the lower ones show the difference.

cursor and the cubic pollucite (*6*). We presume that both pollucite-like phases synthesized at 1150 and at 1350°C have an ordered tetrahedral ANA type of framework in which the Si/Al ratio is unity, and hence the framework composition is $(Al_{24}Si_{24}O_{96})$. The structural formula of the pollucite-like phases synthesized at 1150 and at 1350°C would then be $Cs_{24}Al_{24}Si_{24}O_{96}$ or $CsAlSiO_4$. Results of structural refinement and $^{29}Si$ MAS NMR spectroscopy of the phase formed at 1350°C

TABLE VI

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED DEVIATIONS IN PARENTHESES FOR HIGH $CsAlSiO_4$–ANA

| Linkage[a] | Multiplicity | Distance/angle |
|---|---|---|
| $T^b$–$O^{31}$ | 2 | 1.654 (5) Å |
| $T_1$–$O^{11*}$ | 2 | 1.624 (9) |
| $O^{45*}$–$O^{11*}$ | 2 | 2.707 (17) |
| $O^{45*}$–$O^{31}$ | 1 | 2.604 (29) |
| $O^{31}$–$O^{11*}$ | 2 | 2.728 (17) |
| $O^{11*}$–$O^{14*}$ | 1 | 2.579 (18) |
| $Cs_1$–$O^{45*}$ | 6 | 3.372 (3) |
| $Cs_1$–$O^{31}$ | 6 | 3.561 (3) |
| $O^{31}$–$T_1$–$O^{11*}$ | 2 | 112.6 (6) (°) |
| $O^{31}$–$T_1$–$O^{14*}$ | 2 | 111.3 (6) |
| $O^{31}$–$T_1$–$O^{45*}$ | 1 | 103.8 (7) |
| $O^{11*}$–$T_1$–$O^{11*}$ | 1 | 105.1 (7) |

[a] Superscript numbers indicate the number of the symmetry operator that has been applied (*35*). * indicates that the body centering operation 1/2, 1/2, 1/2 has also been applied.

[b] $T$ = Si,Al

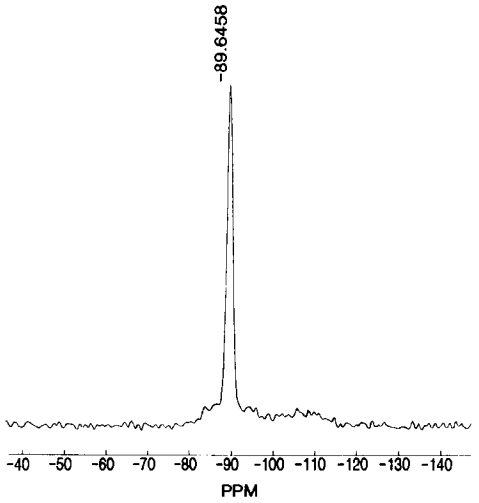


FIG. 5. $^{29}Si$ MAS NMR spectra of high $CsAlSiO_4$–ANA phase.

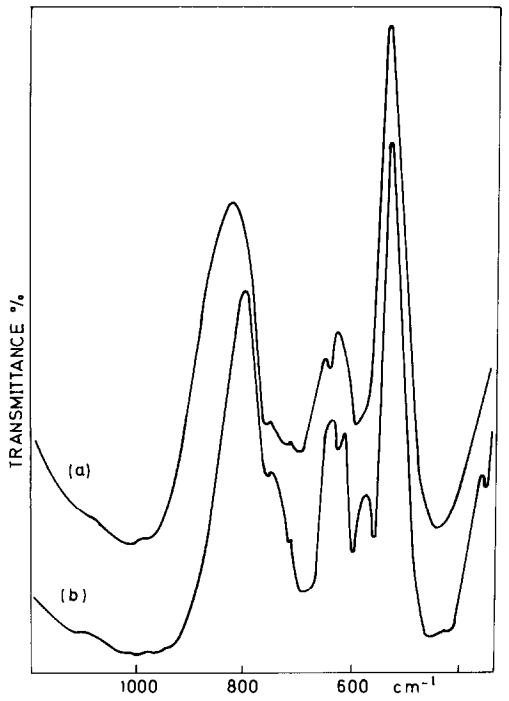


FIG. 6. IR absorption spectra of: (a) pollucite originated from Cs–Y zeolite precursor at 1300°C, 3 hr and (b) low $CsAlSiO_4$–ANA phase at 1150°C, 3 hr originated from $Cs^+$ exchanged LTA zeolite precursor.

confirmed our presumptions about the infer T mark. We would then designate the phases synthesized at 1150° and at 1350°C from $Cs^+$–LTA precursor as $CsAlSiO_4$–ANA (low and high temperature form). A solid–solid polymorphic transformation of a $CsAlSiO_4$–ABW phase (*5*) into $CsAlSiO_4$–ANA (low and high temperature form) phases can be readily explained structurally. Both frameworks (*28*) are (4;2)-connected regular 3*D* nets having tetrahedral single 4-rings and single 6-rings. The differences between them lies in the presence of double zigzag (zz) chains in ABW as opposed to twisted-square (ts) chains in ANA frameworks. This partial structural relationship allows the possibility of a topotactic (*33, 34*) transformation of ordered (*5*) tetrahedral ABW to ANA framework, which is in the case of $CsAlSiO_4$ polymorphs irreversible, but in the case of $Rb^+$ and $K^+$ exchanged zeolite A precursor, the transition is reversible (*29*). The $CsAlSiO_4$–ANA phases synthesized at 1150 and 1350°C (low and high form) are new polymorphs in the system $Cs_2O$–$Al_2O_3$–$SiO_2$ and properly to the Loewenstein (*26*) rule this is the first synthesis of an ordered ANA type of zeolite framework (*27*) with a Si/Al ratio equal to unity.

In Fig. 3 (points and dashed lines) it can be seen that there are significant differences in the number and intensities of the (low and high) $CsAlSiO_4$–ANA. These possibly result from redistribution of $Cs^+$ cations at about 1200°C. Figure 3 (continuous line) shows a splitting of the strongest reflection at $2\theta = 26°$ with increasing temperature. Numerous efforts to index the low $CsAlSiO_4$–ANA powder pattern, Table III, based on tetragonal (*21*) or orthorhombic (*20*) symmetry, according to the results of K. Hirao *et al.* (*30*), D. Taylor and C.

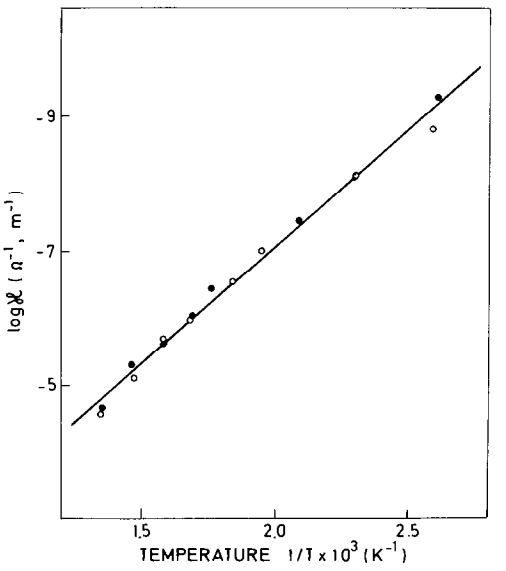


FIG. 7. Electrical conductivity curves of: (○) pollucite originated from Cs–Y zeolite precursor at 1300°C, 3 hr and (●) high $CsAlSiO_4$–ANA phase at 1350°C, 3 hr originated from $Cs^+$ exchanged LTA zeolite precursor.

Henderson (*31*), and A. Kosorykov and L. Nadel (*32*) were without success. Indexing based on doubled 13.6 Å cubic unit cell, which would be expected for certain cation orderings (*27*) within the aluminosilicate framework is given in Table II and Table III. Details of X-ray Rietveld analysis and $^{29}Si$ and $^{27}Al$ solid state MAS NMR results of low $CsAlSiO_4$–ANA will be published separately.

Results of infrared absorption examination, Fig. 6, and electrical conductivity measurements given in Fig. 7, also speak in favor of slight reorientation of cations at about 1200°C.

## Conclusion

The syntheses and characterization of $CsAlSiO_4$–ANA (low and high) materials with an ordered zeolite ANA framework have been described. This study demonstrates conditions of polymorphic transformations in the system $Cs_2O$–$Al_2O_3$–$SiO_2$. The topotactic transition of unstable $CsAlSiO_4$–ABW to stable $CsAlSiO_4$–ANA framework is complete at 1150°C. Further calcination induces conversion of low $CsAlSiO_4$–ANA to the final high $CsAlSiO_4$–ANA product at 1350°C. The framework geometry of the ordered high $CsAlSiO_4$–ANA phase is similar to that described for pollucite. Results obtained from this and our earlier studies confirm calcination of cation exchanged zeolites as a method for syntheses of new materials.

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