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Electron Diffraction and X-Ray Investigation of Hydrothermally Vitrified 5 A Zeolite Containing Trapped Gases

R.-D. PENZHORN*

Institut für Radiochemie, Kernforschungszentrum Karlsruhe, 7500 Karlsruhe, Federal Republic of Germany

AND W. MERTIN

Institut für Anorganische und Analytische Chemie, Justus-Liebig-Universität, 6300 Giessen, Federal Republic of Germany

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The mechanism of gas fixation by hydrothermal treatment of zeolite type 5 A in the presence of a densified gas has been examined by electron diffraction and X rays. It is shown that gas trapping occurs in an X-ray amorphous phase which is formed within a broad spectrum of fixation conditions. The amorphous matrix recrystallizes at 850°C regardless of the parameter combination selected for vitrification. The recrystallization product consists essentially of anorthite and nepheline phases. In addition some $CaAl_2Si_2O_8$ was found. Observations made by X rays and by electron diffraction correlate well with leak rate data.

Introduction

Recently it was shown that the noble gases Ar, Kr, and Xe can be trapped efficiently and stably in a variety of type A zeolites containing cations such as Na^+, K^+, Cs^+, Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++} as well as in H or Na zeolones, when the original crystalline structure is hydrothermally destroyed in the presence of a densified gas (*1*, *2*). Based on this laboratory observation a technology is presently under development for the long-term storage of radioactive krypton, released during reprocessing of irradiated fuel from commercial nuclear reactors (*3*). Noble gas encapsulates in amorphous zeolites have also been employed to determine the neutron capture cross section in the 30-keV region of certain krypton isotopes. These measurements are relevant to the detailed analysis of the ^{85}Kr branching and the estimation of the neutron flux during s-process nucleosynthesis (*4*). The present investigation focuses attention on the mechanism of the fixation and characterization of the obtained products.

Experimental

Binderless K 154 zeolite 5 A pellets, as obtained from Bayer/Leverkusen, were loaded with krypton at constant pressure (900 or 1000 bar) and several temperatures, employing the equipment and procedures described with detail in previous publications (*1–4*). Prior to the fixation of a gas the

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* To whom correspondence should be addressed.

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zeolite samples were dehydrated under vacuum for several hours, at temperatures which depended upon the required amount of residual water.

To liberate the immobilized gas the loaded samples were heated up to 1100°C employing a fast temperature program. The amount of gas evolved was determined by a PVT procedure and its chemical composition analyzed by gas chromatography or mass spectrometry.

Representative unloaded and loaded samples were examined with an EM 400 Phillips electron microscope equipped with a high-magnification goniometer and a rotation holder (*5*). The acceleration voltage employed was 100 kV. Selected area diffraction was carried out with a camera length of 180 mm, at an aperture size of 10 μm.

Most samples were characterized by Guinier patterns at room temperature. In addition several samples were examined with a special Guinier camera, which continuously registers a powder pattern while the temperature varies according to a predetermined program (*6*). Some powdered samples were first slowly heated up to 890°C over a period of 25 hr and then cooled down over the same period of time, while continuously registering the X-ray pattern. For all X-ray diagrams Cu$K\alpha 1$ radiation (λ = 0.15405 nm) was used.

Results and Discussion

Fixation Parameters

The reversible adsorption of Kr by thoroughly dehydrated zeolite 5 A was investigated by Barrer *et al.* (*7*) up to temperatures of 450°C and pressures up to 90 bar. Such high temperatures were possible because the crystalline framework of dehydrated 5 A zeolite only begins to break down at temperatures above 700°C (*1*). If, however, a zeolite sample that contains some residual water in its cavities is heated in a closed vessel, a hydrothermal destruction of the crystalline structure takes place which, depending upon the prevailing conditions, may lead to a partial or even a complete loss of its adsorptive properties. If the structural collapse occurs while the cage system is permeated by a gas, then the guest molecules will be trapped in the amorphous solid produced (*2*). Figure 1 shows the Kr loading obtained at constant pressure of 900 bar when zeolite 5 A (Bayer K 154) containing about 0.8 wt% residual water was heated up to temperatures in the range 575–700°C. It is apparent, that at the conditions employed, loss of crystallinity with concomitant immobilization of adsorbed gas can be achieved only within a limited temperature interval. At temperatures above that interval and at high water fugacity, zeolite 5 A recrystallizes into some nonzeolitic phases of high density (ρ = 2.47 [g/cm^3]), which do not trap gas. If the initial water content is increased by an order of magnitude up to 9.5 wt%, the fixation temperature interval shifts down to 340–490°C (see Fig. 2). The concentration of mobile and chemisorbed water remaining in the latter samples after completion of each fixation experiment was determined by employing an NMR technique (*8*). The data obtained, shown in Fig. 2, reveal a var-

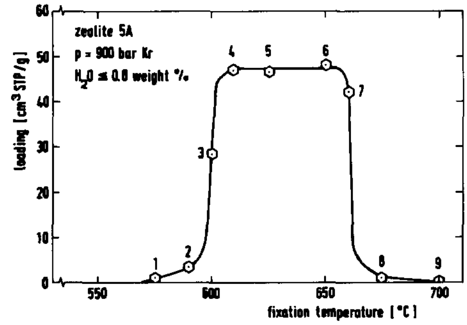

FIG. 1. Noble gas trapping as a function of the fixation temperature at constant pressure in zeolite having initially ≤0.8 wt% H_2O.

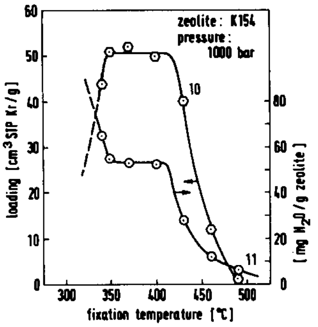

FIG. 2. Noble gas trapping (⊙) as a function of the fixation temperature at constant pressure in zeolite having initially 9.5 wt% H_2O. Also shown is the water content remaining in the various samples after completion of the fixation (⊙).

iable amount of water in crystalline 5 A (up to 25 wt%), a well-defined water content in the amorphous product, and essentially no water in the recrystallization product. It is apparent that, during vitrification, some of the water initially present in the matrix is trapped either as OH or H_2O (possibly to some extent in the small β-cavities) together with the noble gas.

During fixation the water fugacity can be estimated from the water content of the zeolite before and after the fixation, employing the fugacity coefficients obtained by Holser (*9*) (see Table I). The fugacities given in Table I are to be considered max. values, because some water may have condensed in the cold parts of the equipment (capillary high-pressure tubing, pressure sensor, etc.). From the results it is evident that the vitrification temperature can be considerably reduced by increasing the partial pressure of water over the zeolites.

The effect of temperature and initial water content on the formation of the gas-trapping matrix and the recrystallization product have been summarized in Fig. 3. In spite of an increase in water content by an order of magnitude and a variation in fixation temperature of more than 200°C, the Kr loading at 1000 bar appears to depend only little upon the choice of fixation parameters. To interpret this observation it is necessary to consider two opposing effects. On one hand, the sorption of Kr in fully dehydrated zeolite 5 A, which can be estimated to decrease in the order 90, 75.5, and 62.5 cm^3 STP/g at temperatures of 400, 520, and 650°C when the pressure is kept constant at 1000 bar (*10*). On the other, the experimental observation that, after noble gas fixation at temperatures in the range 400–650°C with increasing temperature, the loaded zeolite samples contain decreasing amounts of mobile and chemisorbed water. Since water will block part of the free volume in the zeolite cage system, an increase in sorption capacity is expected with raising temperatures. A shielding effect by water, due to clustering around the exchangeable cations that can interact with nonpolar sorbates, has also been described in the literature (*11*, *12*). However, the contribution of this effect is probably small because, at the high pressures employed in this work, the

TABLE I

WATER BALANCE DURING Kr FIXATION IN ZEOLITE 5 A (K 154)

Fixation temperature [°C]	Initial water content of zeolite [wt%]	Final water content of zeolite [wt%]			Calculated water fugacity [bar]
		Chemisorbed	Mobile	Total	
400	9.5	2.7	2.7	5.3	71.4
525	3.9	0.96	0.24	1.2	58.0
645	0.7	0.25	0.25	0.5	5.2

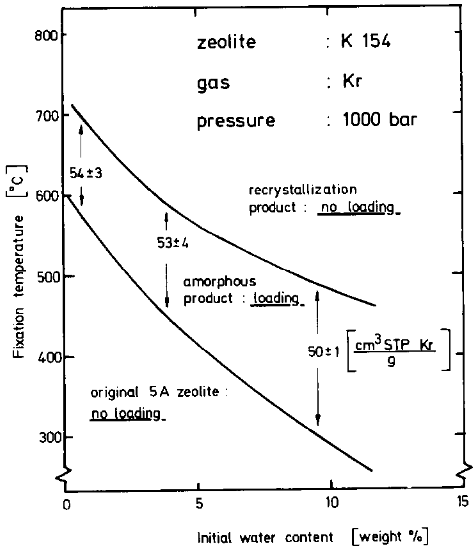

FIG. 3. Parameters for Kr fixation.

gas density outside the zeolite crystals is similar to that in sorbed state inside the crystals. The basis for the latter statement is the fact that, at equally high gas pressures, a similar Ar, Kr, and Xe loading is obtained in 5 A zeolite in spite of substantially different sorption affinities for these gases (*2, 7, 10*). Opposed to this, a Xe enrichment in the loaded gas is observed when the fixation of Xe : Kr = 1 : 1 or Xe : Ar = 1 : 1 mixtures is carried out at low excess pressures. For instance, whereas at a fixation pressure of 1500 bar of a 1 : 1 = Xe : Kr mixture the trapped gas shows a Xe/Kr ratio of 1.05, at 100 bar pressure this ratio increases up to 1.8 (*11*).

Electron Microscopical Results

To obtain more information on structure and chemical composition of the involved solid phases, first cubic zeolite 5 A was characterized by selected area diffraction and by high-resolution transmission electron microscopy (Fig. 4). The crystal was viewed along one of the ⟨100⟩ directions. Each bright dot of the high-resolution image in Fig. 4 originates from a α-cage of the 5 A molecular sieve structure (*12, 13*). The α-cages are separated from each other by a distance of 1.23 nm. This distance, which corresponds to the lattice constant of the zeolite pseudo-cell (*14, 15*), is also derivable from the electron microscope image. The crystal examined showed practically no structural faults but, as described by Bursill *et al.* (*13*), it was noticed that the electron beam induces extensive vitrification of the 5 A crystal, with the difference that a Ca-exchanged zeolite A is probably less sensitive toward electron bombardment than a Na-exchanged 4 A zeolite (*12*). Regions of amorphous material were particularly apparent at the edges of the examined crystals.

Next, a sample containing 37 cm³ STP Kr/g, that was obtained from a batch of Bayer 5 A K 154, conditioned at 200°C, and loaded with Kr at 520°C and 700 bar, was examined by selected area diffraction. It was found that a great portion of the starting material had become amorphous. All crystal flakes observed gave diffraction patterns that could be brought into mutual relation. From the resulting reciprocal lattice, which belongs to a hexagonal crystal system (see Fig. 5), the lengths of the unit cell sides were calculated to be $a = 0.532$ nm and $c = 1.505$ nm. Bearing in mind that these values were gained by electron diffraction without using a reference material, they match rather well those reported for the unit cell of hexagonal $CaAl_2Si_2O_8$, whose axial lengths are $a = 0.510$ nm and $c = 1.472$ nm (*16–18*). The experimental observation, that the recrystallization product binds essentially no water (see Fig. 2), is in line with the identified hexagonal compound.

A crystal of the hexagonal $CaAl_2Si_2O_8$, whose [011] zone axis happened to be parallel to the electron beam, was observed in the normal magnification mode at increasing electron beam intensities. No special details were recognizable at a primary mag-

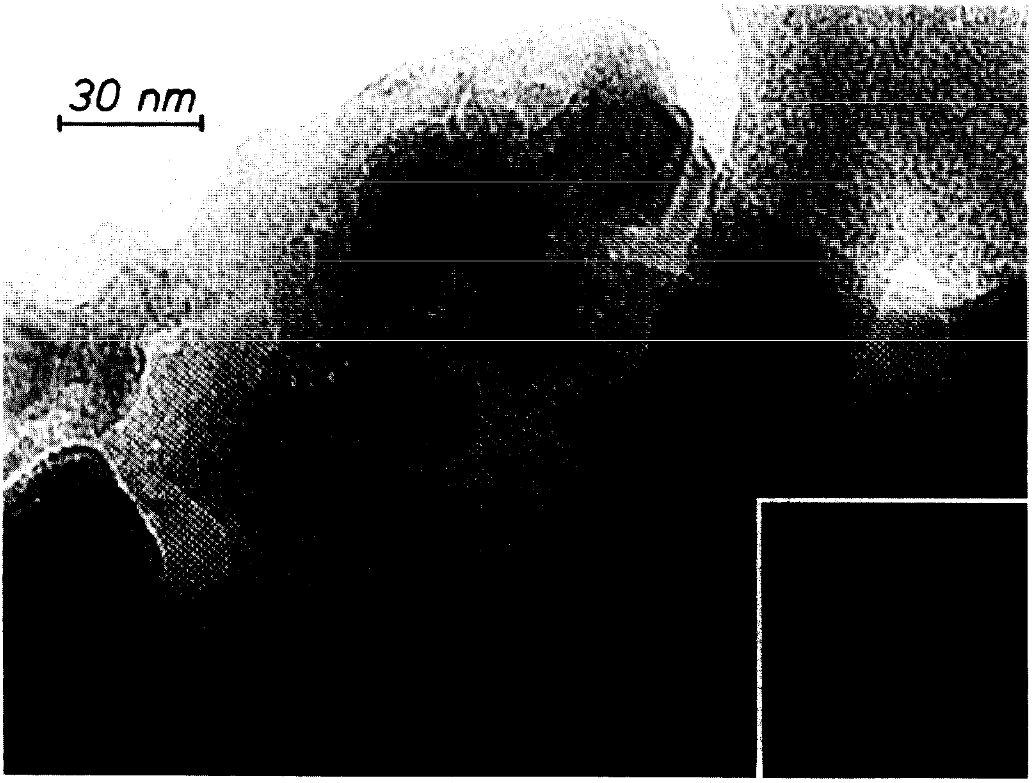

FIG. 4. High-resolution transmission electron microscopy view of a zeolite 5 A crystal along a ⟨100⟩ axis (insert gives the corresponding diffraction pattern).

nification of 165,000 times. But at a magnification of 440,000 times the increased intensity of the electron beam caused the formation of bright spots, which vesicularly enlarged and finally opened (Fig. 6). This formation of blebs is distinctly different from the behavior of unloaded zeolite. After a certain irradiation the diffraction pattern could no longer be detected and the crystal flake became amorphous.

Additional information was obtained from samples of batches of Bayer K 154 loaded at the experimental conditions given in Fig. 1. For instance, examination of sample 5 (Fig. 1) by selected area diffraction revealed essentially vitrified particles. The crystals found gave diagrams that could be interrelated with one another and belonged to the cubic lattice of zeolite 5 A. A high-resolution electron microscopical image showed zones of undisturbed zeolite structure. No crystals of another lattice type were found in this sample. Sample 9 (Fig. 1) was also inspected employing the same technique. This sample contained no krypton because heating was carried out at a temperature above the fixation interval. The crystals examined showed diffraction patterns that stem from a structure with lattice constants as known for nepheline. This compound, whose composition is $Na_2Al_2Si_2O_8$, has a density of 2.62 g/cm^3. The presence of Na ions in the recrystallization product can readily be explained by the fact that commercial zeolite 5 A is an incompletely Ca-exchanged 4 A zeolite.

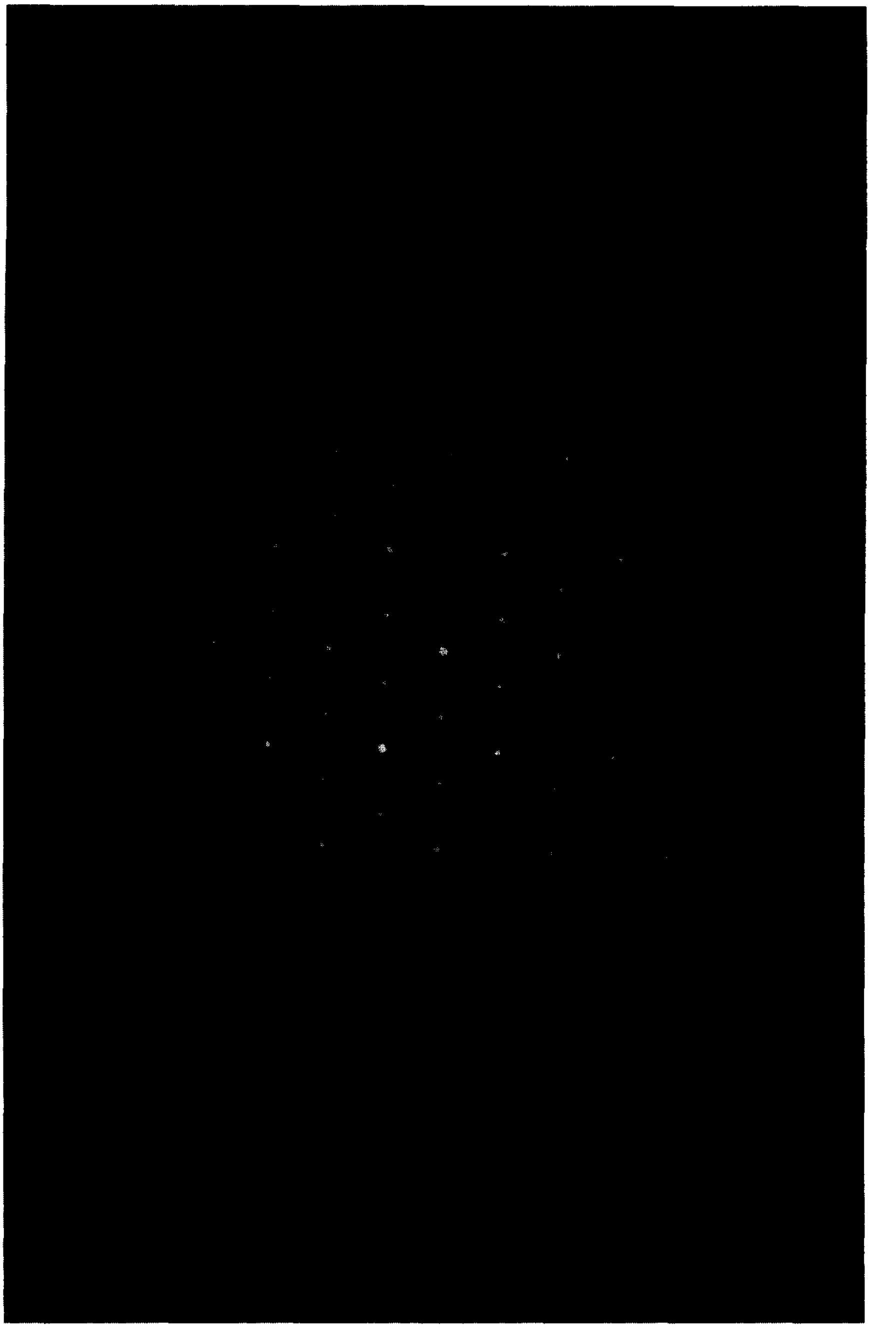

FIG. 5. Selected area diffraction pattern of a crystal from the hexagonal recrystallization product ([001] zone).

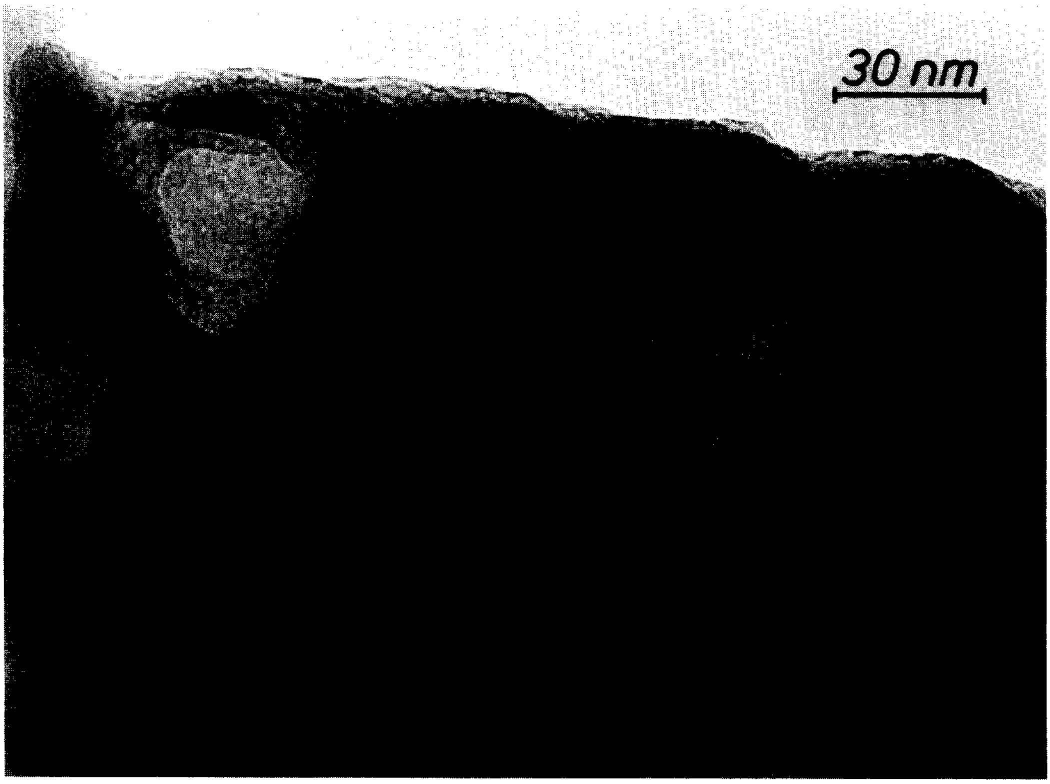

FIG. 6. High-resolution electron microscopy view of a formerly hexagonal $CaAl_2Si_2O_8$ crystal after intensive irradiation by electrons: formation of bubbles within the amorphous substance.

X-Ray Powder Patterns

Samples from Kr-fixation experiments were also characterized by Guinier powder patterns. The sample containing 37 cm^3 STP Kr/g, loaded with Kr at 520°C and 700 bar after conditioning at 200°C, revealed only weak reflexions. This indicates, in accordance with electron diffraction observations, that a substantial portion of the original structure has become vitreous during the immobilization of Kr. Moreover, the Guinier pattern shows lines that can be assigned to anorthite (see Fig. 7). Anorthite, which has the lattice parameters $a = 0.82$ nm, $b = 1.28$ nm, $c = 1.42$ nm, $\alpha = 93.2°$, $\beta = 115.9°$, and $\gamma = 91.2°$, is characterized by a Guinier diagram rich in lines so that certain reflexes coincide with the relatively few possible ones of hexagonal $CaAl_2Si_2O_8$.

The latter compound, which makes up only a minor portion of the sample, seems to occur as better and more characteristic crystals than anorthite. This may explain why they were incidentally selected for electron diffraction examination. Anorthite itself can be recognized by its characteristic triplet line at $2\theta = 28°$ (see Fig. 7). The hydrothermally produced anorthite phase seems to be somewhat modified because the triplet has degenerated into a doublet and all lines are a bit diffuse, indicating poor crystallinity. The formation of $CaAl_2$ Si_2O_8 is in line with the results of other workers, who observed that the Ca-exchanged form of zeolite A may transform

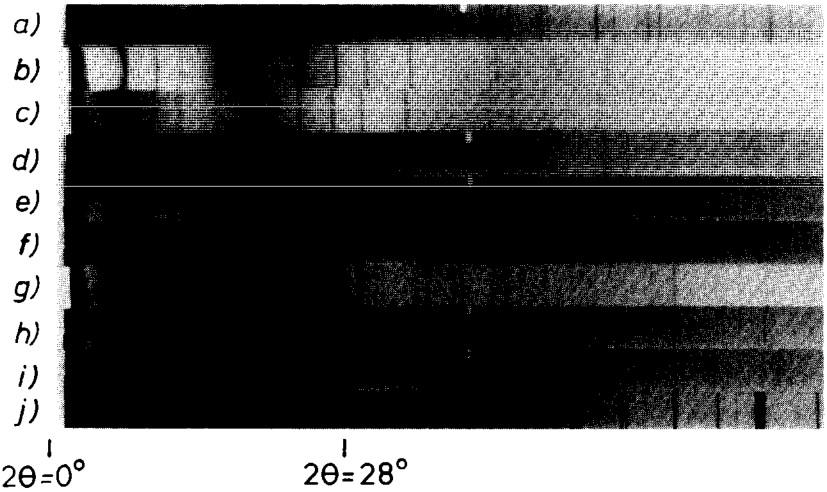

FIG. 7. Guinier pattern of (a) the original 5 A zeolite (K 154), (b) sample 1 in Fig. 1, (c) sample 3 in Fig. 1, (d) sample 5 in Fig. 1, (e) sample 6 in Fig. 1, (f) sample 8 in Fig. 1, (g) sample 9 in Fig. 1, (h) nepheline, (i) anorthite, (j) low quartz.

hydrothermally into a feldspar of the anorthite type at temperatures above 210°C (*12*). In general it is concluded that the sample examined was subjected to hydrothermal conditions that exceeded those recommendable for the achievement of high thermal stability with concomitant maximum loading.

More revealing were the samples obtained at progressively increasing fixation temperatures. Samples 1, 3, and 5 in Fig. 1 show Guinier patterns typical of zeolite 5 A (Fig. 7). The positions of the reflexion lines of these samples do not exactly coincide. Therefore, their lattice parameters cannot be identical. Moreover, with increasing fixation temperature the sharpness of the lines diminishes, suggesting an increase in the degree of vitrification. Sample 6 in Fig. 1 was found to be completely amorphous, indicating optimal fixation conditions. The fixation products denoted by numbers 8 and 9 in Fig. 1 yield reflexions of nepheline and anorthite. The lines of anorthite are much

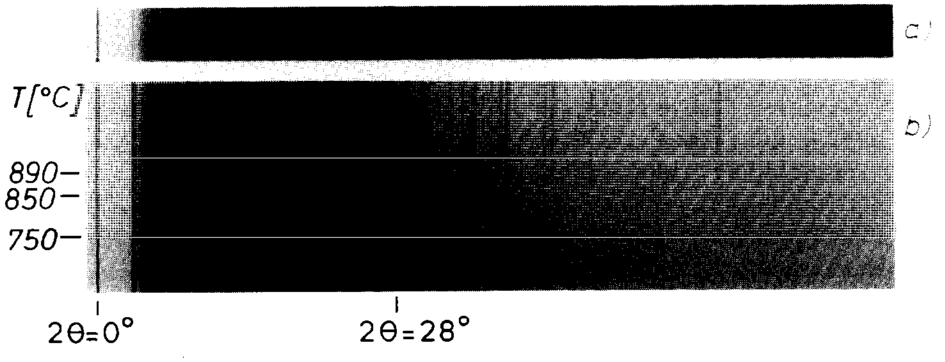

FIG. 8. (a) Guinier pattern of sample 11 in Fig. 2, showing lines of nepheline and the anorthite phase. (b) Guinier pattern of sample 10 in Fig. 2. Shown is a section of a continuously recorded pattern obtained while applying a slow temperature program.

more diffuse than those of nepheline and slightly shifted with respect to those of pure anorthite (see Fig. 7), probably because the anorthite phase is not as well crystallized as the nepheline phase. Since well-crystallized fragments were preferred for the electron diffraction examination, it is readily understood why only nepheline crystals were observed. Finally it should be remarked that, in contrast to the usual nepheline, the recrystallization product gives 100 and 110 reflexions of considerable intensity, possibly because calcium ions are present and therefore the composition of the product differs from that of pure nepheline.

Some samples were examined with a special Guinier camera which registered the X-ray pattern while the samples were subjected to the temperature program described above. During these measurements the probes were not sealed off from the ambient atmosphere. The results show that by slow isobaric water desorption, zeolite 5 A transforms irreversibly at 850°C into nepheline and anorthite. When amorphous samples loaded with noble gas at either 430 or 650°C (sample 10 in Fig. 2 or sample 6 in Fig. 1) were heated by the same procedure while recording the X-ray pattern it was noticed that these samples also convert into nepheline and anorthite at the same temperature, that is 850°C (see Fig. 8). This observation, as well as all X-ray and electron microscopical data reported above, are in excellent agreement with results from gas-leakage experiments shown in Fig. 9. For instance, an incompletely vitrified sample (sample 3 in Fig. 1) is characterized by a large fractional leakage at $\vartheta < 850°C$. Thoroughly amorphous samples instead (sample 6 in Fig. 1) will liberate the trapped gas only when the phase-transformation temperature (~850°C) is reached. Below that temperature very slow diffusion through the amorphous matrix takes place (*1*, *2*).

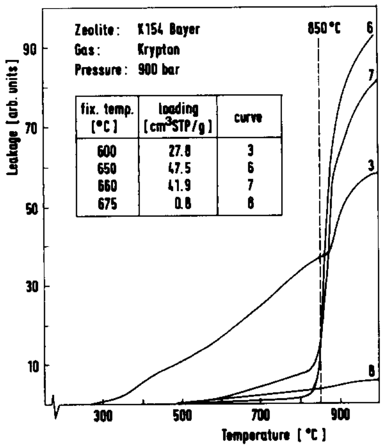

FIG. 9. Gas release rates from several samples in Fig. 1 as a function of temperature at a heating rate of 30°C/min.

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