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The Thermal Transformation of Na LiA Zeolites. A New Polymorph in the System $Li_2O–Al_2O_3–SiO_2$

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High-temperature phase transformations of A zeolite with various degrees of exchange of Na^+ with Li^+ ions were investigated. An increase in the number of Li^+ ions per unit cell accelerates the thermal transformation of the zeolite framework to the amorphous state. Above 730°C, four phases (carnegieite, nepheline, β-eucryptite, and a new phase—γ-eucryptite) were identified. Only γ- and β-eucryptite phases were obtained from pure LiA zeolite. γ-eucryptite is a new metastable polymorph in the system $Li_2O–Al_2O_3–SiO_2$. γ-eucryptite (a_0 = 7.231(3) Å, b_0 = 10.270(6) Å, c_0 = 12.054(7) Å) is transformed to β-eucryptite (a_0 = 10.533(5) Å, c_0 = 11.148(5) Å) above 840°C.

Introduction

The possibilities of obtaining new materials by thermal transformation of zeolites are very broad and are mostly conditioned by the structural characteristics of these systems. The thermal stability of zeolites depends upon zeolite type, SiO_2/Al_2O_3 ratio and cations (*1*). In most cases collapse of the framework takes place first, an amorphous phase is formed upon which there follows the growth of a new crystalline phases. For a certain SiO_2/Al_2O_3 ratio and zeolite type, the transformation zeolite amorphous state as well as the growth of new phases depend on the ionic radius of the cation (*2*). The thermal stability of A zeolite increases in the order LiA < NaA < KA which is obviously the consequence of the differences in ion mobility of the cations, well known from electric (*3*) and NMR measurements (*4, 5*). The presence of other cations (*4*) can also influence ion mobility in zeolite, so it was interesting to investigate the thermal stability of mixed ion forms. Upon collapse of the crystalline framework of A zeolite at higher temperatures, also depending on cation, new phases crystallize: β-eucryptite from LiA (*2*), carnegieite from NaA (*2, 6*), kaliophilite from KA (*2*), anorthite from CaA (*2*). It is not known whether, these or other phase would crystallize in mixed cationic forms of zeolites.

In the present paper high-temperature phase transformations of A zeolite with various degrees of exchange of the Na with Li ion were investigated.

Due to its multiple importance, the system $Li_2O–Al_2O_3–SiO_2$ has been more extensively investigated (*7–9*) as were some individual phases of that system (*9, 10*). β-

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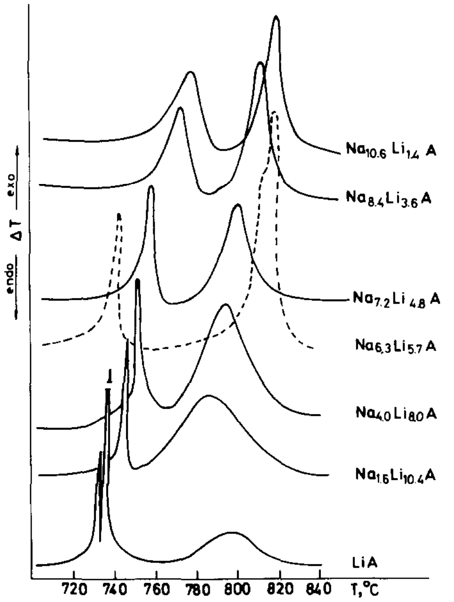

FIG. 1. DTA diagrams of dehydrated NaLiA zeolites.

Eucryptite was studied crystallographically in detail (*11–15*). Its structure enables good ionic conductivity at high temperatures (*16, 17*).

Experimental

The different NaLiA forms were obtained by ion exchange in 1 *N* LiCl at 373 K. The chemical analysis were performed by standard procedures, Al and Si were analyzed gravimetricaly and Li by atomic absorption.

The thermal analysis of samples previously dehydrated was performed on a Du Pont 990 thermal analyzer at a heating rate of 10°C/min in a flow of dry nitrogen. Before X-ray analysis the samples were heated at constant temperature with an error of ±1°C.

The X-ray powder diagrams were obtained on a Philips diffractometer (PW-1051) using Cu*Kα* radiation and a graphite monochromator at room temperature. The program POWDER (*25*) was utilized to calculate the unit cell dimensions.

Results

The results of differential thermal analysis of dehydrated NaLiA zeolites with different degrees of exchange of the Na ion with Li are presented in Fig. 1. There are several exothermal peaks at 700–900°C. The results of TG analysis indicate that there is no mass change in this temperature range. The number and shape of the DTA peaks depend on the ion exchange. Two peaks appear in all the systems, except for $Na_{6.3}Li_{5.7}A$ and LiA where three exothermal peaks appear. Increase of the degree of exchange leads to the peak shifting toward lower temperatures. The first peak becomes more narrow while the second high-temperature peak becomes broader with increasing exchange. The system $Na_{6.2}Li_{5.7}A$ is an exception. For LiA two very sharp peaks, close together, appear in the lower temperature range at 735 and 738°C. Between 850 and 1000°C there were no transformations that could be detected by the DTA method. On the basis of thermal analysis results it is obvious that in the system NaLiA zeolite several phase transformations take place, as shown and confirmed by X-ray analysis.

According to the lithium content and characteristic phase transformations, all the systems can be divided into three groups.

Systems with Low Lithium Content

$Na_{10.6}Li_{1.4}A$ and $Na_{8.4}Li_{3.6}A$ can be classified as systems with low lithium content. Carnegieite at low and nepheline at high-temperature regions were crystallized. The phase transformation of the A framework to the amorphous phase starts at 760°C. At temperatures higher than 770°C the carnegieite phase starts to form from the amorphous phase. The reaction is slower in the system having a lower lithium content, so that at 780°C in the system $\mathrm{Na_{10.6}Li_{1.4}A}$ the amorphous phase coexists with carnegieite, while in the system $\mathrm{Na_{8.4}Li_{3.6}A}$ only carnegieite appears. The carnegieite is not equally stable. At 800°C carnegieite originating from $\mathrm{Na_{8.4}Li_{3.6}A}$ zeolite starts to transform to nepheline. In both systems the only nepheline was identified in the temperature interval 850–1000°C.

Systems with Medium Lithium Content

The new phase is formed in the systems with $\mathrm{Li^+/Na^+}$ ratio 0.5–2. $\mathrm{Na_{7.2}Li_{4.8}A}$–$\mathrm{Na_{4.0}Li_{8.0}A}$ are considered systems with medium lithium content. Collapse of the crystalline framework is the fastest in the system $\mathrm{Na_{6.3}Li_{5.7}A}$: after 30 min at 740°C only the amorphous phase could be identified.

A new crystalline phase, which was not identified, forms in the temperature interval 745–770°C. That phase will, in this paper, be denoted as the γ-phase. In the $\mathrm{Na_{6.3}Li_{5.7}A}$ system it appears at lower temperatures than in other systems. In all systems with medium lithium content, carnegieite phase were also identified in the temperature interval 770–820°C. At a higher temperature range the γ-phase and carnegieite were transformed into β-eucryptite and nepheline, so that above 850°C only these two phases existed.

The $\mathrm{Na_{6.3}Li_{5.7}A}$ system also behaves unusually in this temperature interval, between 850 and 1000°C beside β-eucryptite and nepheline the stable carnegieite phase was also identified.

Systems with High Lithium Content

The property of system having a $\mathrm{Li^+/Na^+}$ ratio greater than 2 is that immediately after the transformation A framework → amorphous, γ-phase and β-eucryptite crystals start to grow.

The high lithium content considerably lowers the framework stability. In the case of LiA zeolite the transformation starts at 720°C and at 730°C the process is already very fast.

TABLE I

POWDER DIFFRACTION DATA FOR THE γ-EUCRYPTITE PHASE

I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)
3	1	0	1	6.1393	6.2010
12	1	1	2	4.2518	4.2207
100	0	0	3	4.0235	4.0179
100	1	2	1	3.9459	3.9550
70	0	2	3	3.1680	3.1644
10	2	0	2	3.1139	3.1005
20	1	0	4	2.7809	2.7816
4	1	1	4	2.6848	2.6848
	2	0	3		2.6876
3	0	4	0	2.5763	2.5675
30	0	4	1	2.5179	2.5112
10	1	4	0	2.4227	2.4195
8[a]	3	1	0	2.3352	2.3467
10	2	3	2	2.2932	2.2981
	1	0	5		2.2869
3	1	4	2	2.2449	2.2454
6[a]	2	3	3	2.1273	2.1140
3	0	5	1	2.0265	2.0248
	3	1	3		2.0264
6	1	5	0	1.9741	1.9759
	0	1	6		1.9716
12	1	0	6	1.9388	1.9356
6	3	3	2	1.8761	1.8733
	1	5	2		1.8775
3	4	2	1	1.6903	1.6884
4	1	6	0	1.6690	1.6657
5	2	0	7	1.5554	1.5546
12	1	3	7	1.5043	1.5046
12	3	3	6	1.4069	1.4069
	5	0	2		1.4063
4	2	6	4	1.3759	1.3763
5	5	1	4	1.2934	1.2935

[a] Reflections not included in the refinement.

From the amorphous phase at 735°C in the case LiA, β-eucryptite and the γ-phase probably start to grow simultaneously. Both phases are stable in the temperature interval 745–770°C. The powder X-ray diffraction pattern of the γ-phase obtained upon heating LiA zeolite for several hours at 750°C is given in Table I.

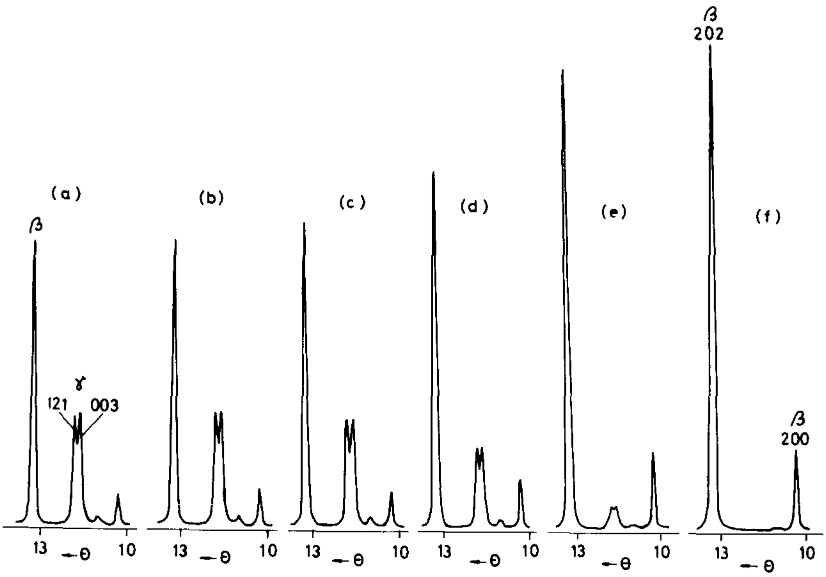

FIG. 2. Changes of X-ray powder diffraction traces of the most intense reflections of β-eucryptite and γ-phase at (a) 770°C, 1 hr; (b) 830°C, 1 hr; (c) 845°C, 1 hr; (d) 890°C, 1 hr; (e) 910°C, 1 hr; (f) 970°C, 1 hr.

By following changes in the LiA system between 760 and 950°C, it was determined that the γ-phase transforms to β-eucryptite (Fig. 2). Only the β-eucryptite phase was identified above 950°C and Table II contains the X-ray powder diffraction pattern of this β-eucryptite. The results obtained for unit cell dimensions of the γ-phase and β-eucryptite, calculated on the basis of X-ray powder diffraction patterns (Tables I and II) by the least-squares method are given in Tables III and IV.

In the system $Na_{1.6}Li_{10.4}A$ at 770°C all three phases were identified. Also in the higher temperature range nepheline and β-eucryptite existed together.

Discussion

The crystal structure of Li_9Na_3A zeolite is known (*18*), but there is no data concerning the structures of the other mixed NaLiA forms. The exact location of cations during ion exchange is not clear, however, it is known that Na^+ in the S6R ring is exchange first, and then in all the other positions. The results obtained in this paper show that the increase in the number of Li ions per unit cell accelerates the process of thermal transformation of the A framework to the amorphous state, so the stability increases in the series:

$$Na_{10.6}Li_{1.4}A > Na_{8.4}Li_{3.6}A > Na_{7.2}Li_{4.8}A > Na_{4.0}Li_{8.0}A > Na_{1.6}Li_{10.4}A > LiA$$

In the system $Na_{6.3}Li_{5.7}A$ the thermal stability is the same order of magnitude as LiA zeolite. These results are, beside the known greater ionic mobility of Li^+ relative to Na^+ (*3*, *4*), also a consequence of structural differences.

The rearrangement of amorphous states to crystalline phases obviously depends upon the cation ratio and, probably, upon their positions at high temperature. When the number of Li^+ per unit cell is greater than 8, the stable β-eucryptite phase ap-

TABLE II

POWDER DIFFRACTION DATA FOR THE β-EUCRYPTITE PHASE

I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)
20	2	0	0	4.5620	4.5608
1s	2	0	1	4.2197	4.2212
1s,b	1	1	2	3.8822	
100	2	0	2	3.5233	3.5298
1s,b	2	1	2	2.9662	
8	2	2	0	2.6328	2.6332
2	2	0	4	2.3713	2.3782
8	4	0	0	2.2799	2.2804
7	4	0	2	2.1102	2.1106
27	2	2	4	1.9106	1.9141
2	4	0	4	1.7623	1.7649
2	4	2	0	1.7249	1.7238
14	4	2	2	1.6466	1.6469
2	6	0	0	1.5211	1.5203
7	4	2	4	1.4651	1.4661
10	4	0	6	1.4374	1.4405
5	2	0	8	1.3336	1.3327
5	4	4	0	1.3169	1.3166
3	4	2	6	1.2619	1.2637
6	2	2	8	1.2331	1.2317
2	6	2	4	1.1516	1.1519
1	8	0	0	1.1409	1.1402
2	6	0	8	1.0274	1.0273
1	8	2	2	0.9794	0.9798
1	8	0	6	0.9713	0.9718
2	4	2	10	0.9360	0.9361

Note. Broad (b) reflections were not included in the refinement; s = superstructure reflections.

TABLE III

UNIT CELL PARAMETERS FOR THE γ-EUCRYPTITE PHASE AND γ-Galloeucryptite

	γ-Eucryptite	γ-Galloeucryptite (M. Behruzi and T. Hahn (1971))
a(Å)	7.231(3)	7.192(7)
b(Å)	10.270(6)	10.203(2)
c(Å)	12.054(7)	12.030(10)
V(Å)	895(1)	882.8

pears ay 735°C. This same phase is obtained by the transformation of γ-phase if the Li^+/Na^+ ratio is greater than 0.5. The unit cell dimensions of β-eucryptite powder, which are formed at 735°C and above 830°C, are the same. The results (Tables II and IV) indicate that the β-eucryptite formed corresponds to the one identified by Roy *et al.* (*8, 10*) and Winkler (*11*). The X-ray powder diffraction pattern given by Berger *et al.* (*2*), for the transformation of LiA zeolite to β-eucryptite differs considerably from these results. It is well known that β-eucryptite has a negative thermal expansion coefficient (*19*), a consequence of Li^+ disorder processes which are reversible (*20*) with temperature. Also, long thermal treatment of β-eucryptite produce irreversible disorder of Si and Al atoms in the crystal lattices.

Comparing our results with unit cell data of β-eucryptite given by Schulz (*20*) and other authors (*12, 15, 22–24*) (Table IV) it is probable that β-eucryptite transformed from LiA zeolite has a disordered structure.

All mixed systems in which the Li^+/Na^+ ratio is above 0.5 by transformation of the amorphous phases, yield a metastable phase which we were unable to identify and which we named the γ-phase. From quantitative X-ray analysis is clear that the γ-phase is stable beside β-eucryptite in the temperature interval 770–830°C (Figs. 2a,b). After that, the γ-phase starts to transform to β-eucryptite and this process

TABLE IV

UNIT CELL PARAMETERS FOR THE β-EUCRYPTITES

Authors	a (Å)	c (Å)
Pillar and Peacor (1973)	10.497 (3)	11.200 (5)
Tscherry and Schulz (1970)	10.4918(3)	11.1749(7)
Scöhnerr and Schedler (1977)	10.4948(9)	11.189 (1)
Schulz (1974)		
Non-heat-treated	10.5015(8)	11.185 (3)
heat-treated	10.5088(6)	11.147 (2)
This work	10.533 (5)	11.148 (5)

is finished at 970°C (Figs. 2c,d,e,f). A metastable γ-phase which was defined by X-ray analysis (Tables I and III) represent a new phase in the $Li_2O-Al_2O_3-SiO_2$ system. It is the third polymorphic modification of the composition $LiAlSiO_4$ beside the already known α- and β-eucryptites. The crystallographic properties of this phase are similar to those for γ-galhoeucryptite described by Behruzi und Hahn (*21*). An interesting problem arises as to why the γ-phase has not been identified in the course of numerous investigations of the $Li_2O-Al_2O_3-SiO_2$ system (*7–9*). The reason could be the narrow stability range of this phase. It is also possible that in the metastable amorphous phases which result from the collapse of the A framework, there are such cation positions which enable arrangement to a structure of this type.

The results obtained for systems with high lithium content confirm this. In these systems, parallel to the stable β-phase, the metastable γ-phase also appears, which could be named γ-eucryptite.

References

1. K. B. Mac Daniels and P. K. Meier, *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS monograph, Amer. Chem. Soc., Washington (1976). p. 347.

2. A. S. Berger, T. I. Samsonova, and L. K. Yakovlev, *Izv. Akad. Nauk SSSR, Ser. Khim.* **10,** 2129 (1971).

3. V. Vučelić, N. Juranić, S. Macura, and M. Šušić, *J. Inorg. Nucl. Chem.* **37,** 1277 (1975).

4. D. Freude, H. Herden, H. Pfeifer, H. Schmidel, and R. Schöllner, *Z. Phys. Chem. (Leipzig)* **259,** (1978).

5. R. Schöllner, and H. Herden, *ACS Symp. Ser.* **40,** 357 (1977).

6. A. S. Berger and L. K. Yakovlev, *Zh. Prikl. Khim. (Leningrad)* **6,** 1240 (1965).

7. R. A. Hatch, *Amer. Mineral.* **28,** 471 (1943).

8. R. Roy, D. M. Roy, and E. F. Osborn, *J. Amer. Ceram. Soc.* **33,** 152 (1950).

9. D. London and D. M. Burt, *Amer. Mineral.* **67,** 483 (1982).

10. T. Isaacs and R. Roy, *Geochim. Acta* **15,** 213 (1958).

11. H. G. F. Winkler, *Acta Crystallogr.* **1,** 27 (1948).

12. W. W. Pillars and D. R. Peacor, *Amer. Mineral.* **58,** 681 (1973).

13. H. Schulz and V. Tscherry, *Acta Crystallogr. Sect. B* **28,** 2168 (1972).

14. H. Schulz and V. Tscherry, *Acta Crystallogr. Sect. B* **28,** 2174 (1972).

15. W. Press, B. Renker, H. Schulz, and H. Böhm, *Phys. Rev. B: Condens. Matter* **21,** 1250 (1980).

16. U. v. Alpen, H. Schulz, and G. H. Talat, *Solid State Commun.* **23,** 914 (1977).

17. U. v. Alpen, E. Schönherr, H. Schulz, and G. H. Talat, *Electrochim. Acta* **22,** 805 (1977).

18. Z. Jirak, V. Bosacek, S. Vratislav, H. Herden, R. Schöllner, W. J. Mortier, L. Gellens, and J. B. Uytterhoeven, *Zeolites* **3,** 255 (1983).

19. F. H. Gillery and E. A. Bush, *J. Amer. Ceram. Soc.* **42,** 175 (1959).

20. H. Schulz, *J. Amer. Ceram. Soc.* **57,** 313 (1974).

21. M. Behruzi and T. Hahn, *Z. Kristallogr.* **133,** 405 (1971).

22. E. Schönherr and E. Schedler, *J. Cryst. Growth* **42,** 289 (1977).

23. V. Tscherry and H. Schulz, *Naturwissenschaften* **57,** 194 (1970).

24. M. Behruzi and T. Hahn, *Naturwissenschaften* **54,** 643 (1967).

25. O. Lindqvist and F. Wengelin, *Ark. Kemi* **28,** 179 (1968).