*Thermochimica Acta*, 135 (1988) 365–370
Elsevier Science Publishers B.V., Amsterdam



# KINETICS AND MECHANISM OF β-EUCRYPTITE CRYSTALLIZATION IN NON-ISOTHERMAL CONDITIONS

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*Abstract*

The crystallization of β-eucryptite from different precursors was studied. The zeolites ( LiA, LiZK-4 ) and gels ( lithium exchanged gel, lithium alkoxid gel ) were employed as a parent materials. It was shown that precursors are involved on the crystallization kinetics. Particular relevance in the present work is the occurrence of silicium and aluminium disorder in the β-eucryptite framework.

*Introduction*

The tectosilicate β-eucryptite is a good high-temperature ionic conductor. The ion $Li^+$ mobility results from specific structural characteristics. Due to an ordered[1] arrangement of Al and Si atoms in alternating layers perpendicular to the hexagonal $c_0$ axis, the $Li^+$ ions are located in structural channels running parallel to $c_0$. However, it was observed that conductivity and unit cell parameters of polycrystalline β-eucryptite are changed with the used precursors. This effect could be related with disordered arrangement of Al and Si in the framework[2,3]. From that aspect it is very interesting to consider the role of ordering phenomena to the mechanisms and kinetics of β-eucryptite crystallization. The influence of precursors should be taken into account in the studies of nucleation and growth processes. In the present study, the crystallization kinetics of β-eucryptite created from different parent materials was discussed.

*Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988*
0040-6031/88/$03.50 

*Experimental*

The precursor signed as LiZK-4 was obtained from zeolite ZK-4 with ratio Si:Al = 1.5 . The procedure given by Kerr[4], was applied. The sample was treated with LiCl and fully ion-exchanged and after that was calcinated in air at 550°C . The hydrolysis-polycondensation reactions of metal alkoxides have been used in preparation of precursor designate as Li-AG. The alkoxides $Si(OCH_3)_4$ ( Alfa Ventron), $Al(OC_4H_9)_3$ (Aldrich Chem) and ethanol solution of LiCl were mixed at 60°C. The mixture aged 20h at 60°C and then slowly hydrolyzed in air to give a monolith gel. The preparation of β-eucryptite from LiA zeolite and gels (Li-EG , Li-G ) was described by an earlier study [2]. DTA curves were recorded on Du-Pont 1090 thermal analyzer equipped with a high temperature cell (1200°C), the heating rate was $20°min^{-1}$. Before X-ray analyses the samples were programmely heated up to constant temperature, cooled down and examined at room temperature. The X-ray powder diffraction patterns (XRPD) were obtained on Philips diffractometer, PW-1051, using Cuk-alpha radiation and graphite monochromator . The fully automatic program[5] for finding the symmetry and a program for the refinement[6] of cell dimensions from powder data were utilized . All the computations necessary to evaluate the kinetic data were carried out on IBM-AT-PC. MAS/NMR $^{27}$Al and $^{29}$Si spectra were recorded by Bruker CXP- 200 spectrometer.

*Results and Discussion*

The β-eucryptite have been prepared from melts[7] or from various solid precursors[2,3]. The amorphous and crystalline phases with Si/Al ratio between 1-1.5 could be a perspective β-eucryptite precursors . The zeolites (LiA, LiZK-4) and a few types of amorphous gels ( Li-EG, Li-G, Li-AG ) were used as parent materials. The samples were programmely heated and analyzed at room temperature. The precursors phases were identified by XRPD analysis before transition into the β-eucryptite. Powder patterns of all the samples thermally treated up to 1100°C indicated the presence of β-eucryptite,

The DTA curves of the investigated transformations are presented in Fig.1. The exothermal peaks ( curve a, e ) belong to recrystallization of $\gamma$-eucryptite into $\beta$-eucryptite. It is interesting the appearance of the endothermal peak in the same transformation of $\gamma$-eucryptite come from Li-A(BW), curve f in Fig.1. The crystallization of $\beta$-phase from amorphous gels is shown also in Fig. 1. (curves b and c).

The zeolite LiZK-4 was identified after heating at 800°C. The kinetics of transformation was established only from high temperature peak at 950°C ,see curve d in Fig.1.

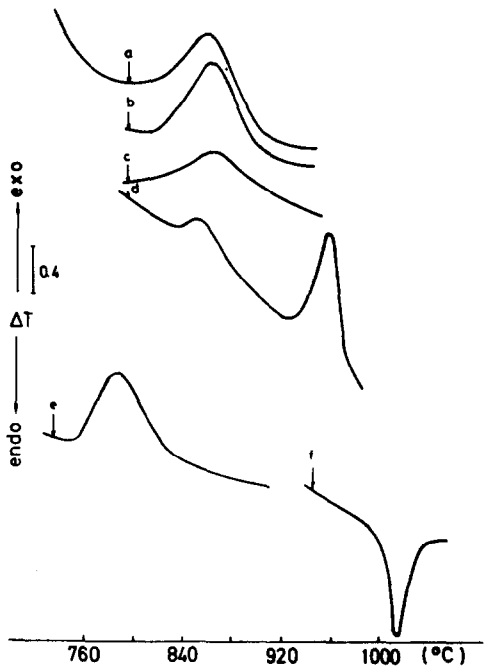


Figure.1. DTA curves of various $\beta$-eucryptite precursors
(a) $\gamma$-eucryptite(LiA);(b) amorphous(EG);
(c) amorphous(LiG)
(d) Li-ZK4; (e) $\gamma$-eucryptite(Li-AG);
(f) $\gamma$-eucryptite(LiABW)

The kinetic parameters of crystallization processes have been evaluated from DTA peaks using the equations of the solid state reactions in non-isothermal conditions. The kinetics and mechanism were investigated by the methods suggested by Satava[8] and Sestak-Bergen[9] . To the first approximation the function logg($\alpha$) vs. 1/T should be straight line for the correct mechanism. The different types of mechanism were tested. The results are shown in Table 1. The most probably reaction mechanism in the $\beta$-eucryptite crystallization is random nucleation. As can be seen in Table 1. the crystallization from metal alkoxid is exception .

TABLE 1. Effects of Used Precursors on the Crystallization of $\beta$-eucryptite

| Parent material | Precursor | Rate controlling step | E (kcal/mol) iso. | non-iso. |
|---|---|---|---|---|
| LiA | $\gamma$-eucryptite | $-\ln(1-\alpha)=kt^3$ | 44.5 | 34.2 |
| Li-EG | amorphous | $-\ln(1-\alpha)=kt^3$ | | 36.4 |
| Li-G | amorphous | $-\ln(1-\alpha)=kt^3$ | | 38.9 |
| Li-ZK4 | LiZK4 ? | $-\ln(1-\alpha)=kt^3$ | | 68.5 |
| Li-AG | $\gamma$-eucryptite | $-(1-\alpha)=kt^3$ | | 23.1 |
| LiA(BW)[10] | $\gamma$-eucryptite | $-\ln(1-\alpha)=kt^3$ | | 70.5 |

The used rate equations are valid for values of $\alpha$ in the interval 0.05 to 0.955 . It was noticeable that used method yield almost perfect straight lines with correlation coefficient higher then 0.998. The activation energies are also presented in Table 1. The recrystallization of $\gamma$-eucryptite originated from LiA zeolite in isothermal conditions was investigated. The changes of XRPD traces of the most intense reflections of $\gamma$-eucryptite (121) and $\beta$-eucryptite (202) after heating at: 770°, 830°, 845°, 860°, 910° and 970°C were measured. The random nucleation was well correlated with experimental results obtained from X-ray experiment. The evaluated activation energy is shown in Table 1.

The activation energies increase from 34.2 to 70.5 kcal/mol if the rate controlling step was random nucleation. The crystallization process of $\beta$-phase ( Li-AG ) is probably enhanced by polymerization of alkoxid.

As can be seen from Table 1., the transformation of $\gamma$-eucryptite is followed by significant differences of activation energies.

The regarding role in this systems could be played by disorder of Al and Si atoms and Li ions in precursors and in the framework of finally formed $\beta$-eucryptite, too. The additional arguments can be found in the results of MAS/NMR spectra Fig.2, and unit cell dimensions of $\beta$-eucryptites , Table 2. The observation that, obtained $\beta$-eucryptite may have different unit cell parameters is also verified in this study.

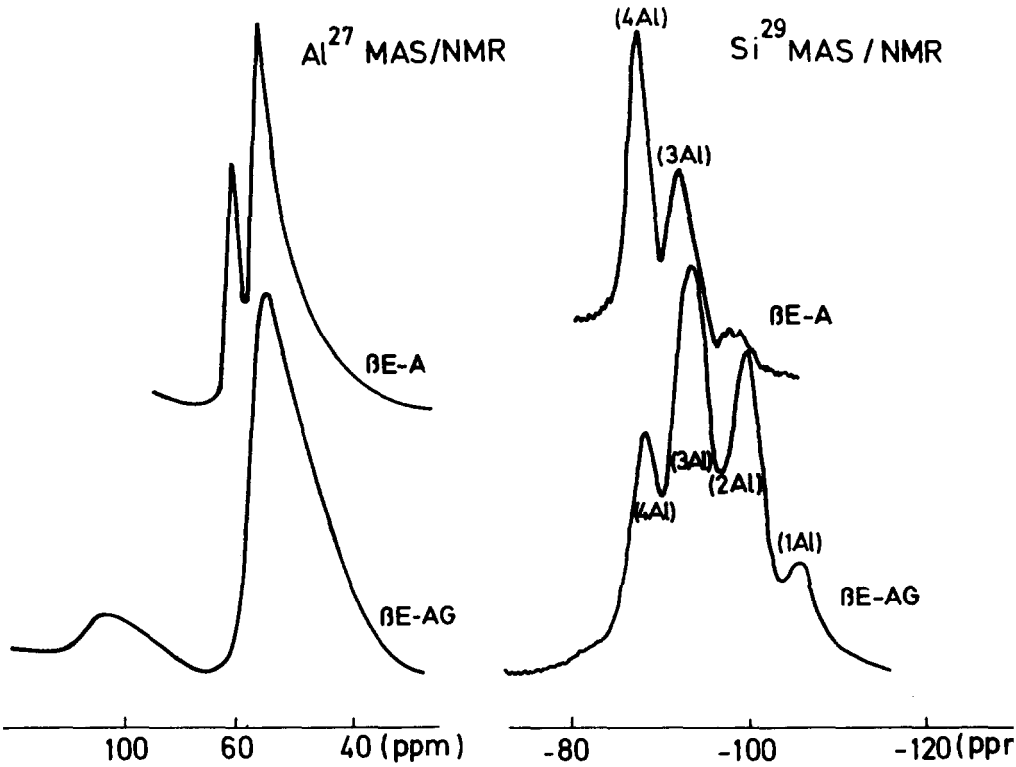


Fig.2. MAS/NMR $^{27}$Al and $^{29}$Si spectra of $\beta$-eucryptites

Table 2. Unit Cell Parameters for β-eucryptites

| Designation of β-eucryptite | ao(Å) | co(Å) | Vo( Å$^3$) |
|---|---|---|---|
| E-A | 10.533(5) | 11.148(5) | 1071.1 |
| E-EG | 10.511(2) | 10.932(3) | 1045.9 |
| E-G | 10.495(3) | 10.951(4) | 1044.5 |
| E-ZK4 | 10.428(17) | 11.021(12) | 1037.9 |
| E-AG | 10.500(11) | 11.124(9) | 1062.1 |
| E-(BW)[10] | 10.512(6) | 11.147(5) | 1066.8 |

β-eucryptites originated from LiA zeolite and Li-EG have been characterized by $^{27}$Al and $^{29}$Si MAS/NMR spectra. The particular relevance of this work is the occurrence of silicium and aluminum disorder in the framework. Two lines, Si(4Al) and Si(3Al) appeared in the MAS/NMR spectrum of β-eucryptite come from LiA zeolite . Four types of Si: Si(4Al), Si(3Al), Si(2Al) and Si(1Al) were assigned in the spectra of β-eucryptite prepared from amorphous gel. It is possible that disorder of Si and Al atoms creates new Li sites, what could be indication for different Li+ ion mobility.

*Acknowledgement*
*The autors are grateful to P.Norby for the sample γ-eucryptite.*

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