JOURNAL OF MATERIALS SCIENCE 23 (1988) 4081–4084

Li^+ ion mobility in eucryptite phases

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The two polymorphs of $LiAlSiO_4$, β and γ eucryptite, were studied by X-ray and thermal methods. The β-eucryptite originated from different precursors that obtained from LiA zeolite is presented. It is shown that the electric conductivity of β-eucryptites increased as the unit cell parameter, c_0, increased. These results correlate well with chemical compositions and thermal investigations. The conductivity in mixed systems depends on the ratio β/γ eucryptites which indicates a higher Li^+ mobility in the γ-phase.

1. Introduction

It has been recognized for some time that a compound having framework structures would be a good ionic conductor. One of these inorganic materials is β-eucryptite which exhibits interesting properties related to its hexagonal β-quartz type structure. The electric conductivity is anisotropic $\sigma_{\parallel c} = 10^{-1}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and $\sigma_{\perp c} = 2 \times 10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ while in glass and glass ceramics a decrease in conductivity of a few orders of magnitude was found [1, 2]. Investigations on the monocrystal have shown that the second-order phase transition at about 480° C had no effect on ionic conductivity [3]. In the crystal structure of β-eucryptite, the order–disorder of lithium [4, 5] is known, but the aluminium and silicon tetrahedra are strongly ordered [6].

Using conventional preparation methods, only β-eucryptite phase was obtained. The high-temperature transformation of lithium-exchanged zeolite A gives two polymorphs, β- and γ-eucryptites [7]. A second phase γ-eucryptite is a new polymorph modification of which electrical and other characteristics are not known. It might be excepted that this phase would also be a good ionic conductor.

2. Experimental details

Zeolite A, manufactured by Union Carbide, was used after a standard ion-exchanged procedure. The lithium ion-exchanged gels (Li-exchanged gel) were prepared from A zeolite precursor. The reaction mixture ($SiO_2/Al_2O_3 = 2$, $Na_2O/Al_2O_3 = 2.0$ to 3.5) of sodium silicate and sodium aluminate was reacted for a few minutes at 90° C. The samples were filtrated, washed and then the ion exchange reaction $Na^+ \rightarrow Li^+$ proceeded. Other types of gel were prepared by mixing aqueous solutions of lithium hydroxide, silica sol, aluminium chloride and ammonium dihydrogen phosphate in different ratios. Aluminium chloride ($SiO_2/Al_2O_3 = 2$) or aluminium chloride and ammonium dihydrogen phosphate ($SiO_2/P_2O_5 = 4 - 0.2$) were added drop by drop to hot mixtures of lithium hydroxide–silica sol ($Li_2O/SiO_2 = 1.25$). The gels were filtrated, washed and analysed after drying at 400° C. After that these amorphous precursors were thermally treated in the programmed conditions.

The chemical compositions of the samples examined in this paper are presented in Table I. All samples were analysed using an atomic absorption spectrophotometer Perkin–Elmer 380. Phase transformation as well as thermal behaviour were investigated using a Du-Pont 1090 thermal analyser equipped with high-temperature DTA (1200° C) and DSC cells, at a heating rate of $10^\circ\,\mathrm{C\,min^{-1}}$. Before X-ray analysis, the samples were heated to a constant temperature with an error of $\pm 1^\circ$ C.

The X-ray powder diagrams were obtained using a Philips diffractometer, PW-1051, with $CuK\alpha$ radiation and a graphite monochromator, at room temperature. A fully automatic programme [8] for finding the symmetry and a programme for the refinement [9] of cell dimensions from powder data were used to calculate the unit cell dimensions of β-eucryptites.

The electrical conductivity measurements were made as described earlier [10].

3. Results

3.1. β-eucryptite

The lithium forms of zeolites with six-membered rings as common building units are recrystallized into the β-eucryptite [11]. The same phase is formed from amorphous gels. Fig. 1 shows typical DTA

TABLE I Chemical composition of the investigated eucryptites

Used precursor	Designation of β-eucryptite	Chemical formula
LiA zeolite	E-AZ	$Li_{1.01}(AlO_2)_{0.90}(SiO_2)_{1.02}$
Li-exchanged gel	E-EG	$Li_{0.99}(AlO_2)_{1.02}(SiO_2)_{1.13}$
Li-gel	E-Gl	$Li_{1.01}(AlO_2)_{1.03}(SiO_2)_{1.16}$
Li-P-gel	E-PG	$Li_{0.81}(AlO_2)_{1.03}(SiO_2)_{0.93}(PO_2)_{0.2}$

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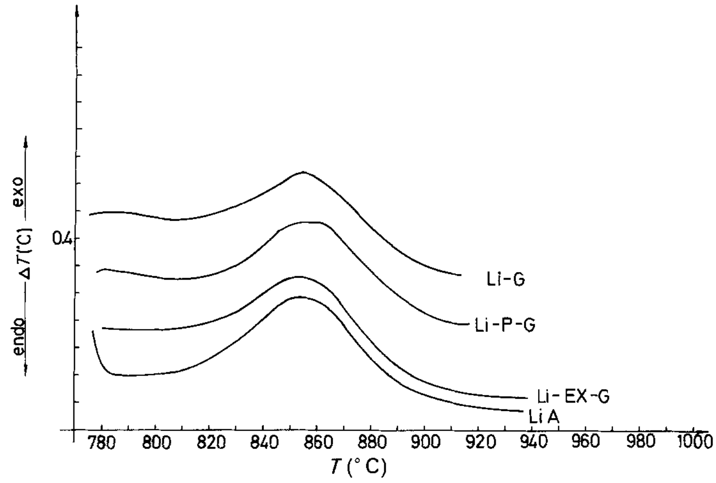

Figure 1 DTA crystallization curves of the investigated β-eucryptites.

crystallization curves. It is evident that positions of the maxima are at 850 to 860° C but the shapes of peaks are not similar. The mechanism of crystallization is probably not the same. All the investigated gels are transformed in β-eucryptite. The only traces of unidentified phases appearing in the system (lithium gel and Li–P-gel) are recrystallized.

The X-ray powder diffraction patterns of pure β-eucryptites (Table II) obtained from different precursors show the typical expected reflections. The characteristic of all powder patterns investigated from Table II, is a displacement to lower interplanar spacings. The unit cell parameters calculated from indexed d-values are given in Table III.

β-eucryptite has a second-order phase transition at 480° C [12]. We have also found the same transition in the β-phase originating from LiA zeolite. In DSC curves of other investigated β-eucryptite samples the new endothermal peaks at 459° C (E-EG), 472° C (E-GL) and 556° C (E-PG) are seen (Fig. 2).

The electrical conductivity of the β-phases is shown in Fig. 3. It is obvious that the conductivity of the E-AZ sample (curve d) is one order of magnitude higher than that of E-EG and E-GL eucryptites (curve f). The ionic conductivity of sample E-GL was similar to E-EG, and only results for E-EG are presented in Fig. 3. The conductivity of β-eucryptite originating from Li–P-Gel is also showed in Fig. 3 (curve e).

3.2. γ-eucryptite

The new polymorph in the system Li_2O–Al_2O_3–SiO_2 was described in a previous paper [11]. The β-eucryptite was obtained from LiA zeolite. It was also shown that this phase recrystallized into β-eucryptite above 840° C.

TABLE II Powder diffraction data for the investigated β-eucryptites

I/I_0	hkl	E-EG		E-GL		E-PG	
		d_{obs} (nm)	d_{calc} (nm)	d_{obs} (nm)	d_{calc} (nm)	d_{obs} (nm)	d_{calc} (nm)
20	2 0 0	0.45544	0.45515	0.45451	0.45444	0.45138	0.45346
100	2 0 2	0.34943	0.34976	0.34889	0.34969	0.34893	0.35002
8	2 2 0	0.26277	0.26278	0.26202	0.26237	0.26079	0.26180
2	2 0 4	0.23423	0.23430	0.23429	0.23450	0.23507	0.23531
8	4 0 0	0.22747	0.22758	0.22697	0.22722	0.22622	0.22673
7	4 0 2	0.21006	0.21009	0.20969	0.20987	0.20929	0.20965
30	2 2 4	0.18946	0.18942	0.18931	0.18942	0.18947	0.18971
2	4 0 4	0.17476	0.17488	0.17470	0.17484	0.17468	0.17501
2	4 2 0	0.17196	0.17203	0.17154	0.17176	0.17104	0.17139
15	4 2 2	0.16404	0.16409	0.16383	0.16389	0.16346	0.16364
2	6 0 0	0.15165	0.15172	0.15139	0.15148	0.15083	0.15115
7	4 2 4	0.14559	0.14559	0.14547	0.14550	0.14528	0.14549
10	4 0 6	0.14221	0.14223	0.14219	0.14229	0.14271	0.14265
4	6 0 4	0.13280	0.13265	0.13251	0.13254	0.13237	0.13249
5	2 0 8			0.13107	0.13106		
5	4 4 0	0.13139	0.13139			0.13074	0.13090
3	4 2 6	0.12505	0.12508	0.12498	0.12508	0.12517	0.12526
5	6 2 2	0.12297	0.12299	0.12273	0.12283	0.12250	0.12261
6	2 2 8	0.12121	0.12123	0.12128	0.12136		
2	6 2 4	0.11459	0.11460	0.11447	0.11449	0.11427	0.11439
1	8 0 0	0.11375	0.11379	0.11363	0.11361	0.11334	0.11336
1	2 0 10					0.10691	0.10700
1	4 4 6	0.10656	0.10657	0.10652	0.10652		
1	6 4 2	0.10256	0.10256	0.10238	0.10242		
2	6 0 8	0.10154	0.10153				
1	8 2 2			0.09755	0.09758		
1	6 4 4	0.09758	0.09754			0.09732	0.09731
1	8 0 6	0.09648	0.09651	0.09645	0.09645	0.09641	0.09645
1	8 2 4	0.09333	0.09335				

TABLE III Unit cell parameters for the investigated β-eucryptites

Designation of β-eucryptite	a_0 (nm)	c_0 (nm)	V_0 (nm^3)
E-AZ	1.0533(5)	1.1148(5)	1.0711
E-PG	1.0473(8)	1.0983(12)	1.0433
E-GL	1.0495(3)	1.0951(4)	1.0445
E-EG	1.0511(2)	1.0932(3)	1.0459

In this work the transformations of partially crystallized A zeolite into the eucryptite phases were investigated. The pure β-phase is formed from amorphous gel (Li-exchanged gel, Fig. 1d). The partially crystallized LiA zeolite was transformed in the mixture of both phases γ and β. The ratio γ/β phase increases as the amount of A zeolite increases. The X-ray diffractogram of γ and β phases obtained from well-crystallized LiA zeolite is shown in Fig. 4a.

The effect of the cation positions in zeolite type A on crystallization of γ-phase was also investigated. It was found that the γ-eucryptite appears if Li^+ exchanged more than two Na^+ cations per unit cell in NaA zeolite. This phase was not formed if Na^+ exchanged more than four Li^+ per unit cell in LiA zeolite. In these systems γ-eucryptite coexists with β-carnegieite. One typical X-ray diffractogram of the mixture β-eucryptite carnegieite is given in Fig. 4b.

We had no success in separating γ-eucryptite from the other phases. The electrical conductivity of these mixtures is also shown in Fig. 3. The γ–β-eucryptite mixtures originating from LiA zeolite heated at 770, 845 and 910° C are represented by curves a and b, and c, respectively. The curves g, h and j in Fig. 3 correspond to the mixtures carnegieite-γ-eucryptite originating from Li_8Na_4A, Li_6Na_6A and Li_4Na_8A, respectively. It is obvious from Fig. 3 that γ-eucryptite increases the conductivity in the system.

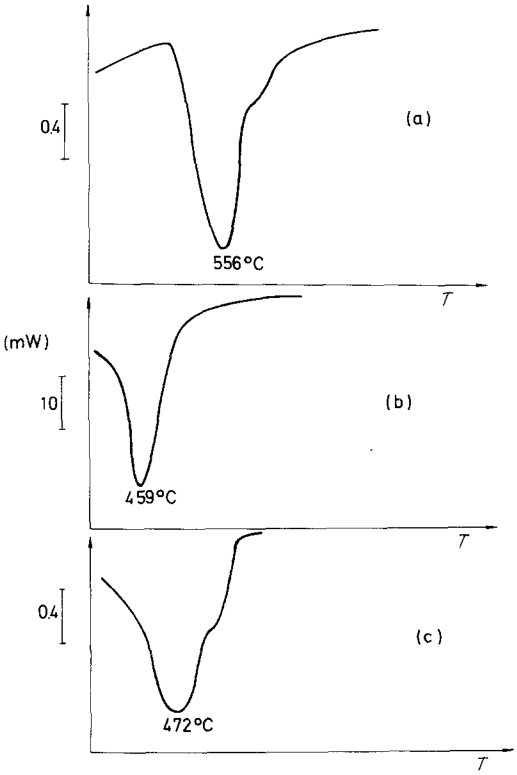

Figure 2 DSC curves of the investigated eucryptites (a) E-PG; (b) E-EG; (c) E-GI.

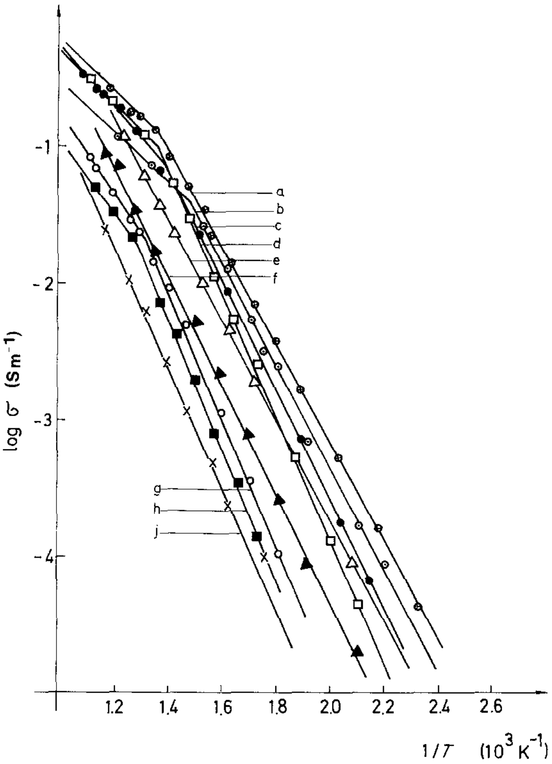

Figure 3 Temperature dependence of electrical conductivity of the investigated eucryptites: Curves a, b and c correspond to mixtures of β/γ obtained at 770, 845 and 910° C, respectively. Curve d, E-AZ; curve e, E-PG; curve f, E-EG; curves g, h and j, mixtures β-eucryptite and carnegieite.

4. Discussion

In the system Li_2O–Al_2O_3–SiO_2 the polymorphs β- and γ-eucryptite are known. The β-eucryptite is chemically expressed as a stuffed high-quartz solid solution [13] of the general composition $LiAlSi_{n/2}O_{n+2}$, ($n = 2$). β-eucryptite is a good one-dimensional ionic conductor. The high Li^+ mobility along the c_0 axes in the channels and two possible sites is available [3–6]. The electrical conductivity of monocrystal β-eucryptite is higher than in the powdered form. Our measurements of electrical conductivity of polycrystalline β-phases originating from different precursors lay between the conductivity along the c_0 and a_0 crystallographic axes. In all samples investigated the Li^+ mobility is one order of magnitude higher than in β-eucryptite produced from the glass [2]. The electrical conductivity curves of β-phases are shifted one to another (Fig. 3). The appropriate endothermal peaks on the DSC curves (Fig. 2) are not at the same positions. These differences could not be explained solely by chemical composition (Table I) except for the E-PG sample. They may result from the structural state of the samples investigated.

The measurement of d values (Table II) by means of the Visser programme did not confirm the suggestions of other authors [14, 15] concerning a possible lowering of the symmetry. A comparison of our results with the corresponding data cited in the literature shows a significant difference in c_0 and V_0 parameters. All β-eucryptites examined have a c_0 parameter less than that cited. In addition, it is clear that there is a tendency

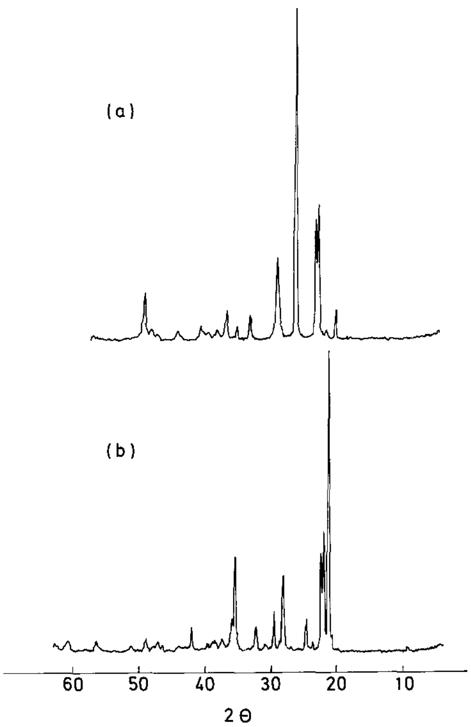

Figure 4 X-ray diffractograms of (a) β and γ-eucryptite mixture, (b) γ-eucryptite and carnegieite mixture.

for c_0 parameters to decrease one to another, which could be well correlated with electrical conductivity measurements.

In our opinion, a significant decrease in the c_0 parameter for sample E-AZ could be a consequence of primary disordered silicon and aluminium atoms in the framework as considered by Schulz [16, 17]. However, disorder phenomena of silicon and aluminium atoms in the framework of aluminosilicates which have the ratio $\mathrm{Si:Al} = 1:1$ is the opposite to Loewenstein's rule [18].

The situation for samples E-EG and E-GL eucryptites is also complicated. The ratio of oxides of silicon and aluminium (Table I) is somewhat greater than unity in both cases. This means there is more silicon in the topology of framework and contemporary their disorder in the channels running parallel to the c_0 axes. From crystal structure studies of β-eucryptite it is known that Li^+ cations have two different coordinations with the oxygens from the walls of the channels. It is possible that the disorder of silicon and aluminium atoms creates new lithium sites. This could be explained by the decrease in the ionic conductivity of E-EG and E-GL eucryptites.

Interpretation of results in the case of β-eucryptite synthesized from Li–P-gel is more complicated and several factors need to be taken into account to explain the decrease of c_0 parameter. Our results are in good agreement with those of Perrota and coworkers [19, 20] who measured a variation of unit cell parameters of β-$LiAlSiO_4$–$AlPO_4$ solid solutions. The substitution of the smaller P^{5+} for Si^{4+} cations in the framework of β-eucryptite synthesized from Li–P-gel, normally produced a small decrease in the unit cell parameters, but we believe that the reason for the changes in c_0 and ionic conductivity is the same in all samples investigated. However, before any definite conclusion is drawn, it is necessary to undertake a single crystal structural study and to measure the ^{29}Si and ^{27}Al MAS NMR spectra. For the γ-phase, the hypothesis is given that crystallization of γ-eucryptite depends on the positions of the cations and Si,Al ordering in the precursor. This phase is formed only from A zeolite in which silicon and aluminium atoms are strongly ordered [21, 22]. It has been confirmed that the γ-phase can readily be formed only when A zeolite with lithium ions in the privileged position are recrystallized. The γ-eucryptite coexists with β-eucryptite (LiA zeolite) or with β-carnegieite ($Na_{12-x}Li_xA$, $x = 2$ or $Li_{12-y}Na_yA$, $y = 4$, zeolites) after high-temperature transformation.

The ionic conductivity of γ-eucryptite was measured together with that of β-eucryptite and β-carnegieite, Fig. 3. From these results it is clear that the presence of γ-eucryptite increases the ionic conductivity of the mixtures. This means that Li^+ has a greater mobility in γ than in the β-eucryptite.

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Received 27 April
and accepted 6 July 1987