JOURNAL OF SOLID STATE CHEMISTRY 86, 129–130 (1990)

Order–Disorder in Rock Salt-Like Phases and Solid Solutions, $Li_2(Ti_{1-x}Zr_x)O_3$

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Received September 27, 1989; in revised form January 19, 1990

Ordered rock salt structures are formed by a variety of complex oxides containing >1 cation. Different cation-ordering sequences occur for different stoichiometries, e.g., $LiFeO_2$, Li_2TiO_3, Li_3NbO_4 (*1*). Different ordering sequences are also possible within the same overall stoichiometry, e.g., Li_2TiO_3 and Li_2ZrO_3 have different structures. With increasing temperature, cation disorder becomes more prevalent, to give structures with partial or complete cation disorder. For example, the cations in Li_2TiO_3 disorder completely above 1213°C to give the cubic rock salt structure (*2*).

We report here the results of a phase diagram study of the join Li_2TiO_3–Li_2ZrO_3. This shows that Li_2ZrO_3 also has a cubic, rock salt-like polymorph at high temperatures and that a complete range of solid–solution forms between Li_2TiO_3 and Li_2ZrO_3. The low temperature polymorphs, with different crystal structures, form only limited solid–solution ranges.

Mixtures of Li_2CO_3, TiO_2, and ZrO_2 in 5- to 10-g amounts were reacted in Pt crucibles in a muffle furnace, initially at ~700°C for a few hours to expel CO_2 and then at 900–1000°C for 12–24 hr. For the phase diagram study and to determine the products under conditions of thermodynamic equilibrium, small samples wrapped in Pt foil envelopes were heated for times ranging from 0.25 to 12 hr and for temperatures in the range 900 to 1500°C after which they were quenched to room temperature by dropping into Hg. Checks were made to ensure that, for the results used in constructing the phase diagram, equilibrium had been reached and loss of lithia from the samples by volatilization had not occurred. Products were analyzed by X-ray powder diffraction, Hägg Guinier camera, and Cu$K\alpha_1$ radiation.

The phase diagram constructed from the data is shown in Fig. 1. Data points indicate compositions and temperatures studied and for which no change in phase assemblage during quenching was deduced to have occurred.

The diagram shows a complete range of

0022-4596/90 $3.00

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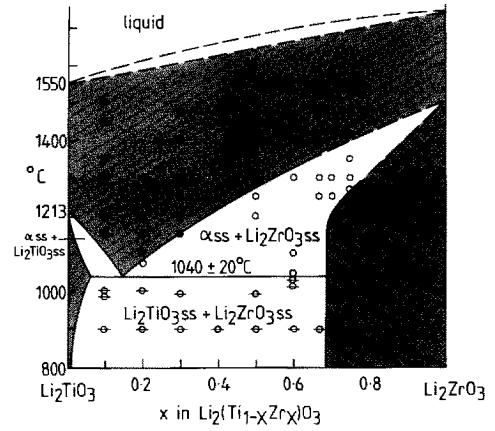

FIG. 1. Phase diagram for the join Li_2TiO_3–Li_2ZrO_3. Results indicated are for ●, single-phase products; ○, ⊖, two-phase mixtures.

disordered, cubic solid–solutions at high temperatures. Li_2TiO_3 is known from previous work to form this polymorph (*2*), even though it cannot be quenched as such to room temperature. This disordered α phase also cannot be quenched to room temperature for Li_2ZrO_3 and solid–solutions containing <40% Li_2TiO_3; it can be quenched over the range ~95 to 45% Li_2TiO_3. The existence of the α polymorph of Li_2ZrO_3 was deduced from an extrapolation of the phase boundaries for more

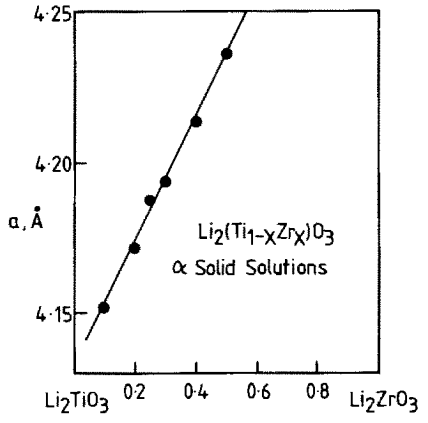

FIG. 2. Lattice parameter of the cubic α solid–solution phase as a function of composition.

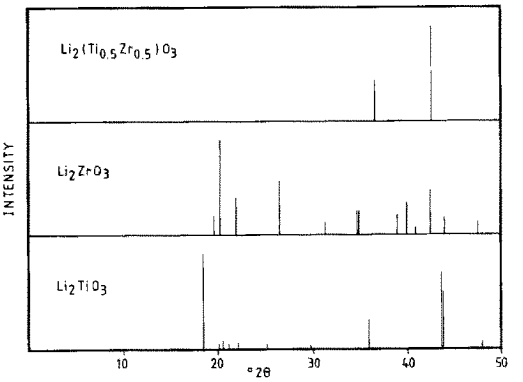

FIG. 3. X-ray line diagrams for cubic α solid–solution, $x = 0.50$, at room temperature, Li_2ZrO_3 and Li_2TiO_3 (low form).

Li_2TiO_3-rich compositions; it is estimated to be stable at temperatures ≥1500°C. The lattice parameters for the α solid solutions as a function of composition are shown in Fig. 2. A linear variation is seen for the range of compositions over which the α phase could be quenched to room temperature.

The low temperature monoclinic polymorph (*3*) of Li_2ZrO_3 forms an extensive range of solid–solutions containing up to ~30% Li_2TiO_3. Corresponding solid–solution in the low form of Li_2TiO_3 is small, <5%. X-ray line diagrams for the low forms of Li_2TiO_3, Li_2ZrO_3, and an α solid–solution are shown in Fig. 3.

Conclusions

Evidence is presented for a new, high temperature polymorph of Li_2ZrO_3 with complete cation disorder and the cubic, rock salt structure.

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