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Order–disorder phenomena in oxides with rock salt structures: the system Li_2TiO_3–MgO

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Li_2TiO_3, which belongs to the family of rock salt superstructure phases, undergoes an order–disorder phase transition at 1213° C. It forms solid solutions with MgO and the temperature of the order–disorder change falls increasingly rapidly with increasing MgO content; the ordered solid solutions could not be prepared beyond ~40 mol % MgO. Up to ~20% MgO, the transition may be observed as a DTA heat effect and is probably first order. At $\gtrsim$ 25% MgO the transition is second order; no DTA heat effect occurs and, by X-ray diffraction, the order–disorder change occurs, reversibly and continuously, over a range of several hundred ° C. For 25% MgO, the disorder, δ, is given by $\delta = \exp\,[-m(T_c - T)]$ where T_c is the critical temperature, above which only short range order exists, and m is a constant. The order, δ, is determined from the relative intensity of the (0 0 2) superstructure reflection. The mechanisms of the order–disorder processes are discussed and a method of studying the kinetics is indicated. It is likely that many other oxide phases which have rock salt superstructures will exhibit order–disorder phenomena at high temperatures.

1. Introduction

The preparation of two polymorphs of Li_2TiO_3 is well-established in the literature [1–5]. The ordered polymorph with a rock salt superstructure is the stable form, and a metastable disordered form can be prepared under certain conditions. Heat content measurements [6] have shown that Li_2TiO_3 undergoes a phase change at 1213° C and melts at 1547° C. Lang has prepared many other oxides belonging to the rock salt family and some of these can be made in both ordered and disordered forms [2, 3]. In the system Li_2TiO_3–MgO, a complete range of solid solutions with a disordered rock salt structure has been reported [1]. The crystal structure of ordered Li_2TiO_3 was proposed by Lang [2] with a subsequent amendment [3]; the correctness of the second model was confirmed independently [5]. The present work is part of a general study of rock salt oxide phases and had the initial objective of clarifying the thermodynamic status of disordered Li_2TiO_3.

2. Experimental

Reagent grade Li_2CO_3, TiO_2 and MgO were used. MgO was dried at ~600° C immediately prior to weighing; Li_2CO_3 and TiO_2 were used straight from the bottle.

Bulk (~20 g) preparations of Li_2TiO_3 were made by first mixing the ingredients into a paste with acetone and mixing continued until all the acetone had evaporated. The mixtures were fired in a Pt crucible in electric muffle furnaces, initially at 600° C for a few hours to drive off CO_2 and finally at 900 to 1100° C for a few days to complete the reaction. Mixtures of Li_2TiO_3 and MgO were mixed under acetone in the same way and heated at 1000 to 1200° C for at least 3 days. Each day, the mixtures were cooled and reground for 5 to 10 min. It was found that the higher the

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MgO content, the higher the temperature and the longer the times that were needed to complete reaction.

Crystalline phase analysis was carried out with a Philips PW 1390 X-ray powder diffractometer, Ni filtered Cu$K\alpha$ radiation. When reproducible intensities were desired, an "infinitely thick" sample was prepared by pressing a pellet, ~2 mm thick, in the window of an Al holder. The samples generally stayed in place and no additional supports such as a glass base or coverslip were used. Optical microscopy was of little use because at no stage did melting occur and the crystals produced by solid state reaction were not bigger than a few microns in size. DTA experiments used a Du Pont 990 model, 1600° C cell, with a heating rate of 5 to 20° C min^{-1}.

3. Results

Ordered Li_2TiO_3 was readily prepared by reaction at 1000° C. Its powder pattern is very similar to that reported previously [2]; powder data indexed on the correct unit cell are given in Table I. To help in the indexing, use was made of the listing of observed structure factors for single crystal Li_2TiO_3 [5].

Li_2TiO_3 undergoes an order–disorder phase change at 1213° C. This is seen on the heating cycle of DTA as a rather broad endotherm with peak temperatures of 1213 and 1220° C at heating rates of 7 and 20° C min^{-1}. These temperatures agree well with the value of 1213° C obtained by calorimetry [6]. Considerable hysteresis occurs on cooling with an exothermic peak temperature of 1153° C (estimated rate of cooling 40° C min^{-1} in the range of 1100 to 1200° C).

The nature of the change in Li_2TiO_3 at 1213° C was proven by studies in the system Li_2TiO_3–MgO, whose partial subsolidus phase diagram is shown in Fig. 1. With increasing MgO content, the transition occurs at increasingly lower temperatures and the DTA peak becomes more spread out. With $\gtrsim 20$ mol%* MgO, no heat effect is observed on DTA, using the highest sensitivity of the instrument (0.1° C in.$^{-1}$). At the same time, for solid solutions with $\gtrsim 20\%$ MgO it is possible to preserve the high temperature, disordered solutions to room temperature by rapid cooling. At slower cooling rates or on annealing these latter solid solutions at ~500 to 900° C (depending on composition) for several hours, the low tem-

TABLE I X-ray powder diffraction data Li_2TiO_3 refined cell $a = 5.069 \pm 0.002$ Å, $b = 8.799 \pm 0.007$ Å, $c = 9.759 \pm 0.009$ Å, $\beta = 100.2 \pm 0.1°$

d_{obs}*	d_{calc}	I_{obs}†	hkl‡
4.8053	4.8024	100	0 0 2
4.4001	3.3995	5	0 2 0
4.3451	4.3399	8	1 1 0
4.2090	4.2054	4	$\bar{1}$ 1 1
4.0048	3.9999	6	0 2 1
3.7456	3.7444	1	1 1 1
3.4988	3.4992	2	$\bar{1}$ 1 2
3.2431	3.2440	1	0 2 2
2.9978	2.9983	2	1 1 2
2.7932	2.7899	<1	$\bar{1}$ 1 3
2.5894	2.5887	1	0 2 3
2.5017§	2.5010 2.4958	30	$\bar{1}$ 3 1 2 0 0
2.4043§	2.4054 2.4012 2.3938 2.3928	1	1 1 3 0 0 4 $\bar{2}$ 0 2 1 3 1
2.2541	2.2532	<1	$\bar{1}$ 1 4
2.1910	2.1904	<1	$\bar{2}$ 2 1
2.0754	2.0770	80	$\bar{1}$ 3 3
2.0687	2.0688	~50	2 0 2
2.0456	2.0498	1	2 2 1
1.9030§	1.9076 1.9029	7	$\bar{2}$ 0 4 1 3 3
1.8734	1.8722	<1	2 2 2
1.8128	1.8130	<1	0 4 3
1.6588	1.6596 1.6593 1.6588	1	1 5 0 $\bar{3}$ 1 1 $\bar{2}$ 4 1
1.6502	1.6518 1.6499	<1	$\bar{1}$ 5 1 2 4 0
1.6337	1.6362 1.6340	<1	$\bar{3}$ 1 2 3 1 0
1.6192	1.6220 1.6197 1.6194	<1	0 4 4 $\bar{2}$ 4 2 1 5 1
1.5998§	1.6008 1.6003 1.5979 1.5952 1.5946	9	0 0 6 $\bar{1}$ 3 5 $\bar{1}$ 5 2 2 4 1 2 0 4
1.5411	1.5420 1.5408	1	$\bar{2}$ 4 3 1 5 2
1.4698§ 1.4641§	1.4709 1.4708 1.4675 1.4665 1.4641	20	3 1 2 $\bar{2}$ 0 6 1 3 5 0 6 0 $\bar{3}$ 3 1
1.4005§	1.4026 1.4018 1.4013 1.3991	9	0 6 2 $\bar{3}$ 3 3 2 4 3 3 3 1

* KCl, $a = 6.2931$ Å, added as an internal standard.

‡ Space group $C2/c$ with systematic absences hkl: $h + k = 2n + 1$ and $h0l$: $l = 2n + 1$.

† Peak heights measured by diffractometry.

§ Broadened or doubled peak.

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*All percentages are in mol%.

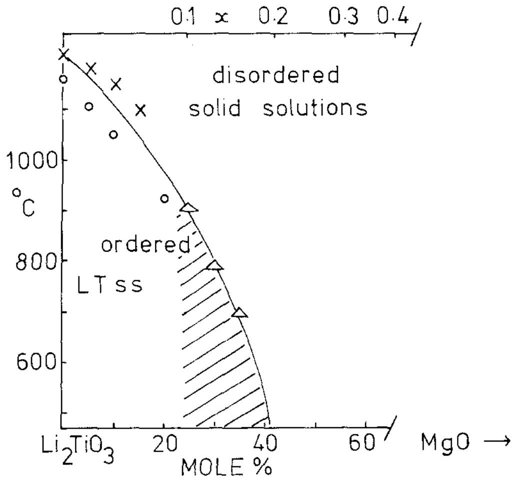

Figure 1 Partial subsolidus phase diagram for the join Li_2TiO_3–MgO. X and ○ are DTA peak temperatures observed on heating and cooling. Δ are X-ray powder diffraction results. In the shaded region, the intensity of the (0 0 2) diffraction peak of the ordered solid solutions changes with temperature. Solid solution compositions may also be written as $Li_{2/3(1-x)}Ti_{1/3(1-x)}Mg_xO$.

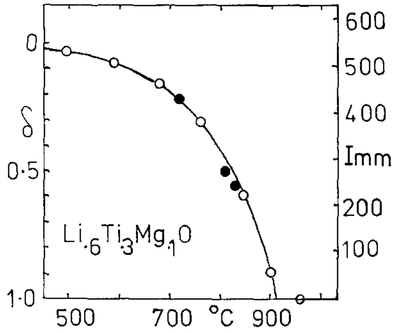

Figure 2 Height (mm) of (0 0 2) supercell peak (I mm) against temperature for composition 75% Li_2TiO_3 25% MgO ($\equiv Li_{0.6}Ti_{0.3}Mg_{0.1}O$). ○ and ● are results determined on stepwise cooling and heating cycles. δ is the disorder, given by $\delta = I_{\max} - I/I_{\max}$.

perature ordered solid solutions may be prepared, as judged, for example, by the appearance in the powder pattern of the (0 0 2) supercell reflection at ~4.8 Å. The solid curve in Fig. 1 which gives the upper temperature limit (T_c) of existence of the ordered solid solutions, was obtained from a combination of these X-ray experiments (for 20 to 35% MgO) and DTA (0 to 20% MgO). The two sets of data match well and prove that the transition in Li_2TiO_3 at 1213° C is of the type order–disorder.

Conclusive evidence was obtained to show that, at least for the solid solutions containing $\gtrsim 20\%$ MgO, the order–disorder transition takes place continuously and over a range of several hundred degrees. Composition 25% MgO was the most studied. A sample was subjected to annealing treatments and the height of the (0 0 2) supercell peak measured using a scan speed of $\frac{1}{8}^\circ$ 2θ min^{-1}. The same sample was used each time to ensure reproducibility and was prepared for mounting as an "infinitely thick" specimen using the method described earlier. Annealing treatments varied in length between 1 and 5 days. The treatment was repeated at each temperature until a constant (0 0 2) peak intensity was obtained. The series of experiments was commenced at 1000° C, which is in the disordered solid solution region, and annealing treatments carried out every 40 to 100° C, down to 500° C. Afterwards, several measurements were made in a stepwise heating cycle.

Results are shown in Fig. 2, where the height of the (0 0 2) peak is plotted against temperature. The height changes continuously over the range 910 to 500° C. The ordering reaction observed on cooling is reversible on heating, indicating that the peak heights represent equilibrium values for the sample used. Thus, it is clear that the order–disorder process takes place, under equilibrium conditions and for this composition, over a temperature range of at least 410° C. The large temperature range over which the order–disorder change occurs is represented schematically by the shaded region in Fig. 1. An attempt was made to similarly study the order–disorder transition for Li_2TiO_3 and composition 15% MgO. However, the experiments were not successful largely because it was not possible to preserve disordered or partially ordered samples to room temperature without further ordering taking place during cooling.

The order–disorder change in 25% MgO (this composition may also be written as $Li_{0.6}Ti_{0.3}Mg_{0.1}O$) is, from Fig. 2, a continuous process with no sign of a discontinuity as T_c (910° C) is approached. Attempts were made to find a simple, empirical expression which relates the degree of long range order with temperature. The degree of long range order, S, is defined from the intensity of the (0 0 2) supercell peak, relative to the intensity of the peak when this composition is fully ordered, i.e.

$$S = \frac{I}{I_{\max}}. \qquad (1)$$

I_{max} could not be measured directly because a constant value at lower temperatures had not been reached in Fig. 2 and further ordering below 500° C did not occur at measurable rates. An initial estimate of I_{max} of 550 to 600 mm was made by extrapolation of Fig. 2. Various graphs were plotted, such as log S against log $(T_c - T)$ and log S against T/T_c, but in none of these did the data fit a straight line. Graphs were then tried which had the disorder, δ, as the ordinate, where

$$\delta = 1 - S = \frac{I_{max} - I}{I_{max}}. \qquad (2)$$

The temperature dependence of the disorder, δ, was found to fit the expression

$$\delta = \exp\left[-m(T_c - T)\right] \qquad (3)$$

where m is a constant. This is shown by the graph of $\log_e \delta$ against $(T_c - T)$(Fig. 3), which is a straight line that passes through the origin. The best value of I_{max}, 545 mm, was found by trial and error. Equation 3 is very sensitive to the value of I_{max} used in Equation 2, especially at lower temperatures as shown (dotted line) in Fig. 3 for $I_{max} = 530$ mm.

The mechanism of the ordering of initially disordered solid solutions has been studied briefly. A sample of disordered 25% MgO was prepared by cooling rapidly from 1000 to 1100° C. The X-ray pattern was similar to that of MgO (with slight shifts in d-spacing) and there was no evidence of any superstructure peaks. The sample was then annealed for various lengths of time at 700° C, and after each treatment, the angular 2θ range between 17 and 19° was scanned with the diffractometer at $\frac{1}{8}°$ 2θ min^{-1} in order to look for the appearance of the (0 0 2) supercell peak. For short times the supercell peak is extremely broad and as the sample is annealed for longer times, the peak gradually narrows and increases in height. These results show that the mechanism of ordering is first to form very small, ordered regions which then grow larger with longer annealing times.

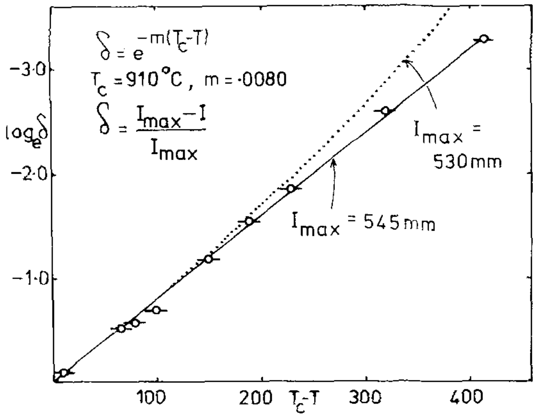

Figure 3 Disorder, δ, plotted against temperature. Results are very sensitive to the value of I_{max} that is used.

The disordering process at higher temperatures, however, is not the reverse of the ordering mechanism. Instead of the size of the ordered regions decreasing to zero, the size of the ordered regions remains large (relatively) but disordering gradually occurs throughout the crystals. This was shown by annealing a sample of ordered 25% MgO at 1000° C (i.e. above T_c) for increasing times; the intensity of the (0 0 2) peak gradually decreased to zero but without any peak broadening.

4. Discussion

The occurrence of high temperature, disordered Li_2TiO_3 as an equilibrium polymorph of Li_2TiO_3 indicates that order–disorder phenomena are probably an equilibrium feature at high temperatures of many other complex oxides that have rock salt superstructures, e.g. Li_2SnO_3, Li_3NbO_4, $LiCrO_2$ and $LiFeO_2$.

Order–disorder phenomena have been much studied in metals where it appears that they may be thermodynamically of either first or second order. In this work, a preliminary experimental study has been made of order–disorder phenomena in complex oxides. For Li_2TiO_3 and solid solutions containing up to 15 to 20% MgO, a DTA heat effect is observed and the order–disorder transition is probably of thermodynamic first order. For 25% MgO, and probably all compositions between 20 and 40% MgO, the transition is second order. There are two pieces of evidence for this. First, no heat effect is observed on DTA and, therefore, there is no change in ΔH at T_c. It could, of course, be argued that the transition does have a ΔH but it is so small that it cannot be detected by DTA. Second, the transition begins at very low temperatures and occurs continuously up to T_c; at T_c the transition terminates but without any discontinuity in the degree of long range order, S. This is shown by Figs. 2 and 3 and especially by the straight line of Fig. 3 which passes through the origin and indicates that there is no discontinuous change in entropy, ΔS, due to disordering of the cations. If the transition for 25% MgO were first order, a non-zero intercept in Fig. 3 would be expected. At the transition temperature, T_c, the free energy, ΔG, given by $\Delta G = \Delta H - T\Delta S$ is zero by definition. We have independent evidence that both ΔH and ΔS are zero at T_c and, therefore, the phase change is second order.

The thermodynamic status of the previously reported disordered Li_2TiO_3 is now clear. However, there appear to be, as yet unknown, factors which influence the kinetics of ordering in Li_2TiO_3. We could not quench the disordered form to room temperature whereas Kordes appeared to have no difficulty in doing this [1].

Preliminary results with 25% MgO suggest a method for following the kinetics of the ordering reaction. The mechanism of ordering is shown to be the growth of initially very small ordered regions. It should be possible to determine the size of these ordered regions by measuring the extra broadening of X-ray powder lines. If this can be done as a function of temperature, time and composition, we will have a simple method of studying kinetics of cation ordering.

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