Thermochimica Acta, 211 (1992) 189–197
Elsevier Science Publishers B.V., Amsterdam

Phase diagrams of the systems Li_2ZnCl_4–Na_2ZnCl_4 and Li_2ZnCl_4–Li_2MnCl_4. The spinel–olivine phase transition of Li_2ZnCl_4

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(Received 30 March 1992)

Abstract

The nature of the transformation of spinel-type to olivine-type Li_2ZnCl_4 and the phase relationships of the systems Li_2ZnCl_4–Na_2ZnCl_4 and Li_2ZnCl_4–Li_2MnCl_4 have been studied by high-temperature X-ray diffraction, high-temperature Raman spectroscopic studies, and differential scanning calorimetry (DSC). The phase transition of Li_2ZnCl_4 is martensitic in nature and can serve as an easily available model system for studying the geologically important high-pressure olivine–spinel transition of $(Mg, Fe)_2SiO_4$. The two polymorphs coexist above 50 K. The olivine-type polymorph, which is the stable form above 475 K, is metastable at ambient temperature. Olivine-type Li_2ZnCl_4 and Na_2ZnCl_4 form a complete series of solid solutions. Neither the incorporation of Na^+ in spinel-type Li_2ZnCl_4 nor the mutual solubility of Li_2ZnCl_4 and Li_2MnCl_4 (inverse spinel type) have been observed by X-ray methods. The equilibrium of the reaction $Li_2ZnCl_4 + MnCl_2 \rightleftharpoons Li_2MnCl_4 + ZnCl_2$ has been found to be fully on the right-hand-side.

INTRODUCTION

The $(Mg, Fe)_2SiO_4$ olivine to spinel transformation at high pressure is relevant for the geology of the Earth's upper mantle [1]. Therefore, the nature of this phase transition has been studied by various authors [2–4]. The mechanisms discussed are both a nucleation and growth mechanism and a martensite-type transformation [2–4]. However, investigation of this phase transition is only possible with the use of high-pressure as well as high-temperature techniques. Recently, we have established a similar phase transition for spinel-type Li_2ZnCl_4 [5–8]. Because this transformation occurs at moderately high temperatures and atmospheric pressure, the olivine- to spinel-type phase transition (and vice versa) of Li_2ZnCl_4

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has been treated as a model system for the geologically important olivine–spinel transformation discussed above [9].

Furthermore, the phase relationships of the systems Li_2ZnCl_4–Na_2ZnCl_4 and Li_2ZnCl_4–Li_2MnCl_4 have been analysed. The former system has already been studied [10], the latter, to our knowledge, is not yet known. Ternary Na_2ZnCl_4 [11] and Li_2MnCl_4 [12] crystallize in an olivine-type and an inverse spinel-type structure, respectively.

EXPERIMENTAL

Preparation and starting materials

The starting materials were LiCl and NaCl (z.A., Merck), $ZnCl_2$ (purum, Fluka), and $MnCl_2 \cdot 4H_2O$ (z.A., Riedel de Haen). The LiCl and NaCl were dried at 300°C in a vacuum. The $MnCl_2 \cdot 4H_2O$ and $ZnCl_2$ were dehydrated by heating in a stream of HCl at 300°C.

Olivine-type Li_2ZnCl_4 and Na_2ZnCl_4, as well as spinel-type Li_2MnCl_4, were prepared by fusing and annealing stoichiometric amounts of the starting materials in evacuated sealed pyrex glass ampoules [5, 11, 12]. Spinel-type Li_2ZnCl_4 was obtained by both annealing the olivine-type polymorph for some weeks at 150°C [6, 8] and by the mechano-chemical reaction of stoichiometric amounts of LiCl and $ZnCl_2$ at ambient temperature [13].

For preparation of quaternary $Li_{2-2x}Na_{2x}ZnCl_4$ and $Li_2Zn_{1-x}Mn_xCl_4$, the starting materials were fused and annealed at temperatures below and above the spinel–olivine transformation temperature, i.e. at 150 and 220°C, respectively, for up to 6 months.

Apparatus and techniques

The samples were characterized by X-ray and high-temperature X-ray Guinier powder techniques. Details are reported elsewhere [5]. The unit cell dimensions were computed by a least-squares method (LSUCR). DSC (differential scanning calorimetry) measurements were carried out on a Perkin-Elmer DSC 7 calorimeter using gold crucibles as sample holders. Transition temperatures and energies were determined using indium, tin and zinc as references [9, 14]. Raman spectra, with samples taken in glass capillaries, were measured on a Dilor OMARS 89 multichannel spectrograph with the usual right-angle geometry (resolution $<4\,cm^{-1}$). For excitation, the 514.5 nm line of an Ar^+ ion laser was employed. The integration times were 1–2 s and the number of accumulations was 200 (signal averaging). Low-temperature spectra were recorded using a Coderg model CRN2 variable temperature cell. High-temperature Raman measurements were performed using a special high-temperature cell [15] with the Eurotherm PID controller 818b, and the Eurotherm thyristor controlling unit 425.

The rate of conversion of olivine-type Li_2ZnCl_4 to the spinel-type polymorph at temperatures below 185°C was determined calorimetrically in such a manner that the transition energy of samples annealed to achieve partial transformation was measured by DSC experiments and compared with that of monophase spinel-type Li_2ZnCl_4.

RESULTS

Phase diagrams of the systems Li_2ZnCl_4–Na_2ZnCl_4 and Li_2ZnCl_4–Li_2MnCl_4

As shown from samples annealed at 220°C and subsequently quenched to ambient temperature, olivine-type Li_2ZnCl_4 and Na_2ZnCl_4 form a

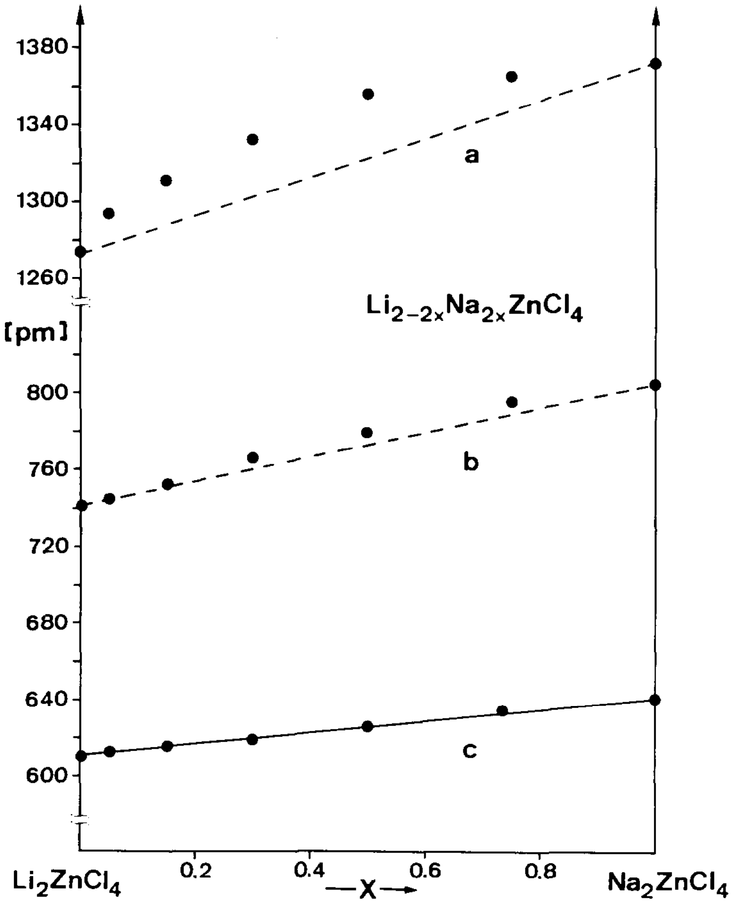

Fig. 1. Unit-cell dimensions of olivine-type *oP*28 $Li_{2-x}Na_{2x}ZnCl_4$ solid solutions (samples annealed at 220°C and subsequently quenched to ambient temperature).

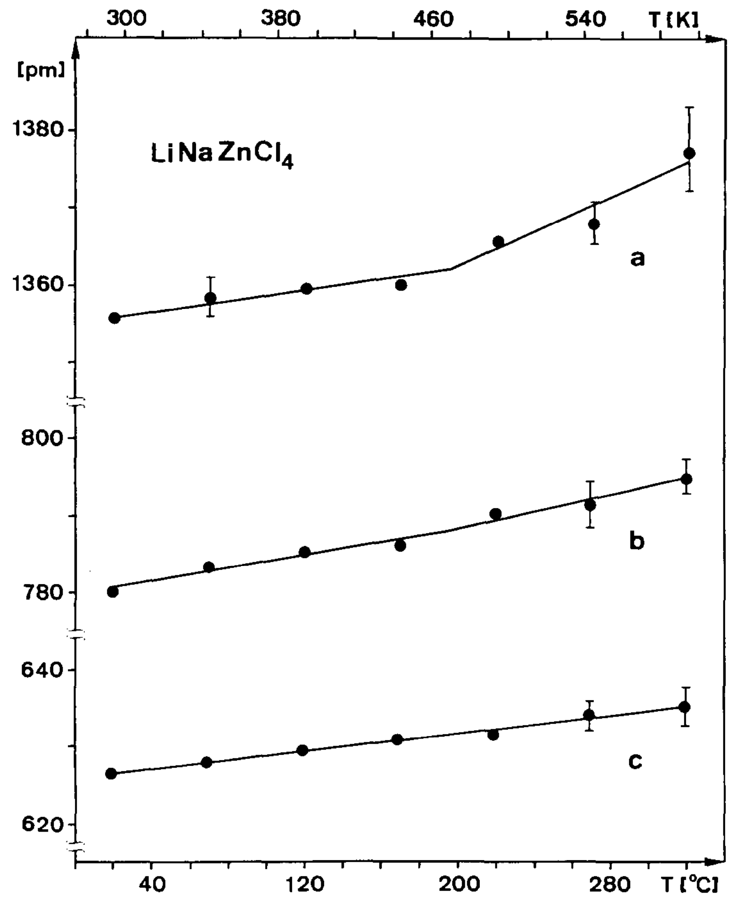

Fig. 2. Temperature evolution of the lattice constants of olivine-type $LiNaZnCl_4$.

complete series of solid solutions. The unit-cell dimensions do not fully obey Vegard's law (Fig. 1). The temperature evolution of the lattice constants of olivine-type $LiNaZnCl_4$ is shown in Fig. 2. Incorporation of Na^+ into spinel-type Li_2ZnCl_4, i.e. substitution of Li^+ by Na^+, has not been observed by X-ray methods. The Raman spectra of olivine-type $M^I_2ZnCl_4$ ($M^I = Li$, Na) are very similar [5] and, hence, the same is true for those of the respective solid solutions. Raman spectra, therefore, are not suitable for analysing the composition of these mixed crystals.

Obviously, because of the different site preferences of the Zn^{2+} and Mn^{2+} ions, mutual solubilities of Li_2ZnCl_4, both spinel type (normal spinel) and olivine type, and Li_2MnCl_4 (inverse spinel type) are negligible. Mixed crystals like $(Zn_{1-x}Li_x)^t[Li_{2-x}Mn_x]^oCl_4$ with altering positive charges on the tetrahedral and octahedral sites of the close-packed arrangement of the Cl^- ions, tend to ordering and, hence, to decomposition to the ternary chlorides. Thermodynamically, Li_2MnCl_4 is more stable than Li_2ZnCl_4

each relating to the binary chlorides. This is shown from the Madelung parts of the cohesive energies (MAPLE), namely 200 versus 168 kJ mol^{-1} for the formation from the binary chlorides. The sums of the cohesive energies of Li_2MnCl_4 and $ZnCl_2$, and Li_2ZnCl_4 and $MnCl_2$ are 7050 and 6960 kJ mol^{-1}, respectively [9]. These calculations are confirmed by the equilibrium of the reaction $Li_2ZnCl_4 + MnCl_2 \rightleftharpoons Li_2MnCl_4 + ZnCl_2$, which is found to be fully on the right-hand side [9].

Spinel-type to olivine-type phase transition of Li_2ZnCl_4

The spinel- to olivine-structure transformation of Li_2ZnCl_4 has been established by DTA and DSC experiments, high-temperature X-ray

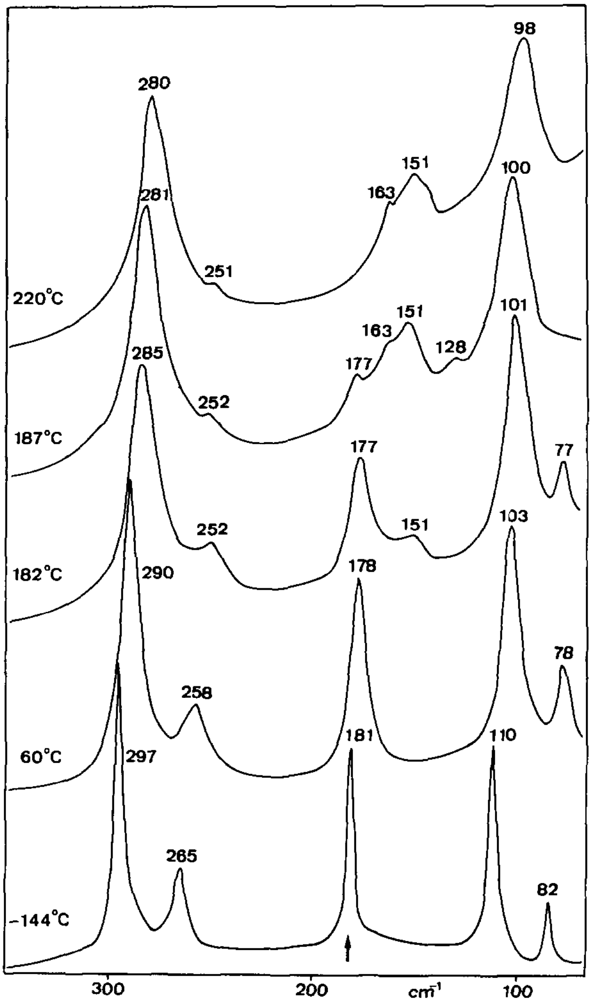

Fig. 3. Raman spectra of Li_2ZnCl_4 at various temperatures revealing the spinel–olivine structure transformation.

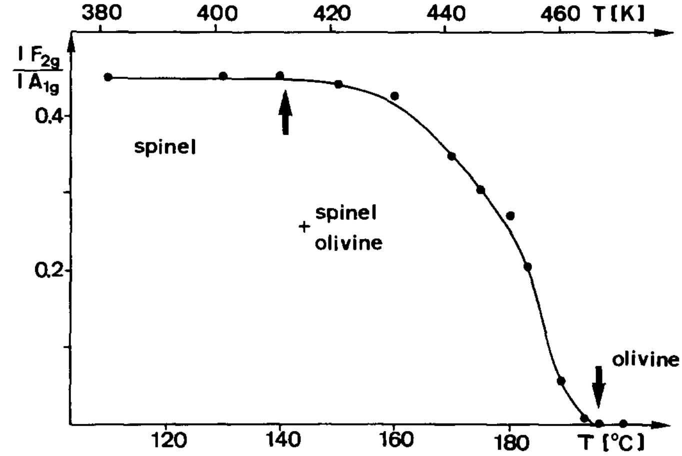

Fig. 4. Temperature evolution of the relative intensity of the band at 179 cm^{-1} of spinel-type Li_2ZnCl_4 (species F_{2g}) in relation to that of the $ZnCl_4^{2-}$ breathing mode (species A_{1g} and A_g, respectively) $I_{F_{2g}}/I_{A_{1g}}$.

diffraction patterns, temperature evolution of the electric (ionic) conductivity [6] and high-temperature Raman spectra (see Fig. 3). Raman spectra of the two Li_2ZnCl_4 polymorphs have already been presented in refs. 5 and 16.

Distinction between the two polymorphs is possible on the basis of the Raman band at 179 cm^{-1} of the spinel-type modification (species F_{2g}). Figure 4 shows the intensity of this band in relation to that of the band at 292 cm^{-1}, which is assigned to the breathing mode (species A_{1g} and A_g,

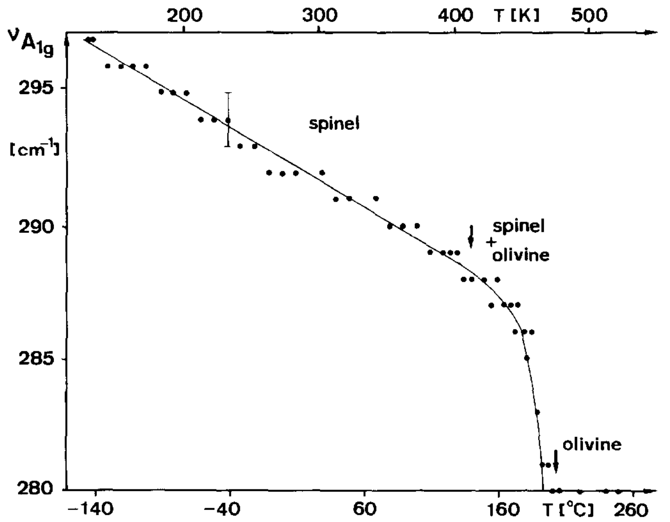

Fig. 5. Frequency decrease of the $ZnCl_4^{2-}$ breathing mode (species A_{1g} and A_g, respectively) of Li_2ZnCl_4 with increase in temperature.

respectively) of the tetrahedral $ZnCl_4^{2-}$ units. The frequency of this mode decreases with increase in temperature, as shown in Fig. 5. This frequency decrease is related to the thermal expansion of the lattice in the monophase regions, but it is predominantly governed by the transformation to the olivine-type form in the two-phase region (see below) because the A_{1g} mode frequency of the latter compound is somewhat smaller (namely 283 cm^{-1} at ambient temperature [5]) than that of the spinel-type polymorph given above.

The rate of transformation of Li_2ZnCl_4 from olivine to spinel structure at various temperatures, established by DSC measurements as described above, is shown in Fig. 6. At temperatures above 405 K, the phase transition remains incomplete even for reaction times greater than 300 h. Samples annealed above 460 K (temperature uncertainty ±5 K) remain unconverted. This means that the two polymorphs coexist in a temperature range of at least 50 K in an equilibrium, as shown in Fig. 7. High-temperature X-ray diffraction patterns reveal a two-phase region above 425 K. (The DSC signal due to the phase transition under study is at 460 K (departure), 475 K (onset) and 485 K (peak), respectively. These temperatures are slightly increased for samples annealed at temperatures near the transition temperature [9].) At temperatures below 370 K, the transformation is likewise incomplete within the reaction times chosen because of the low reaction rates at these temperatures.

The energy of the spinel- to olivine-type transition of Li_2ZnCl_4 (monophase samples) is 4.7(1) kJ mol^{-1}, the entropy of transformation is 9.7(5) J mol^{-1} K^{-1}, and the increase in molar volume is 3.68 cm^3 (4.41%).

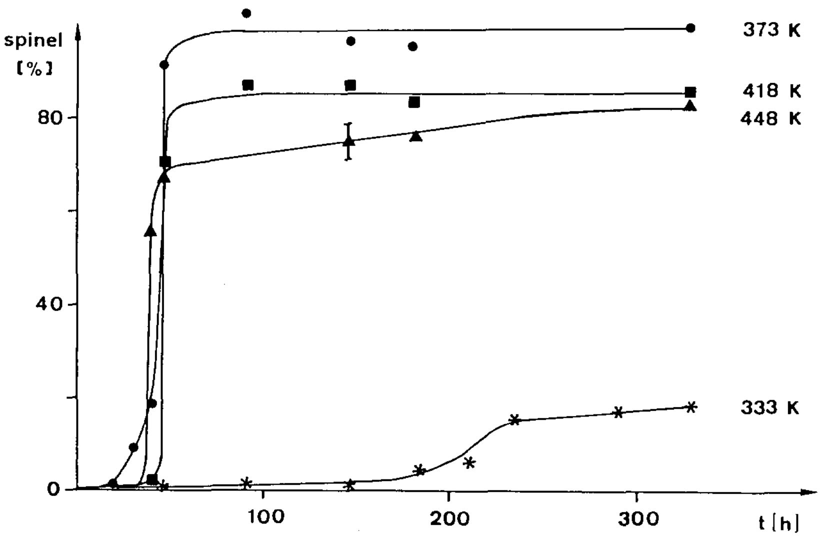

Fig. 6. Reaction rates of the olivine–spinel structure phase transition of Li_2ZnCl_4 at various temperatures established by DSC measurements as described in the text.

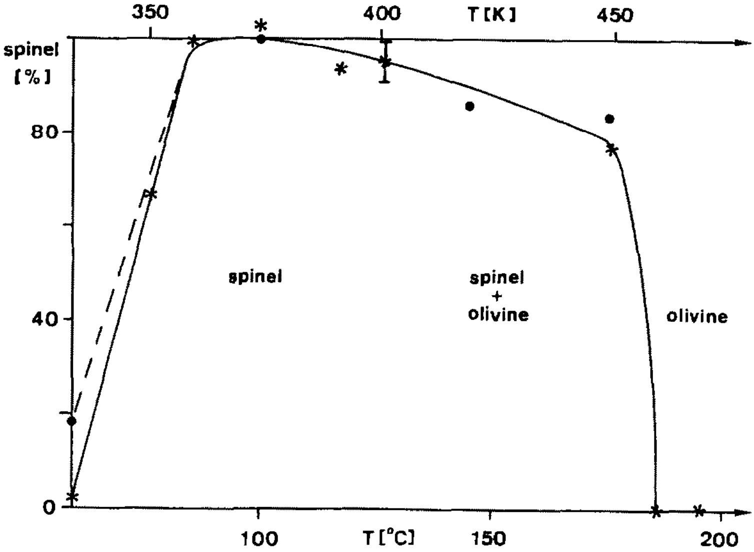

Fig. 7. Amounts of the spinel-type polymorph (%) in olivine-type Li_2ZnCl_4 samples annealed for 90 (*) and 330 h (●) at various temperatures.

The relation between transformation entropy and volume increase correlates with the corresponding data for spinel-type silicates and germanates [17].

DISCUSSION

The results obtained reveal that the phase transition of spinel-type to olivine-type Li_2ZnCl_4 (and vice versa) is thermodynamically first-order and that there is a relatively large temperature range within which the two phases coexist. In the case of a nucleation and growth mechanism, the coexistence of two polymorphs is only possible if their composition is different. This is not the case for olivine- and spinel-type Li_2ZnCl_4 (in contrast to the inverse spinel-type chlorides $Li_2M^{II}Cl_4$ (M^{II} = Mg, Mn, Cd) [14, 18]). We therefore assume that the phase transition under discussion is martensitic in nature. As mentioned above, the mechanism of this transformation can be investigated in any detail as a model system for the geologically important high-pressure olivine–spinel phase transition. Such studies can also be performed using single crystals, which are easily grown from the melt in the case of the olivine-type polymorph [9].

ACKNOWLEDGEMENTS

The authors thank Dipl.-Chem. A. Becker for experimental help, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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