Thermochimica Acta, 215 (1993) 219–225
Elsevier Science Publishers B.V., Amsterdam

Rock-salt defect structures in the systems LiBr–MBr_2 (where M is Mg, Mn)

M. Schneider, P. Kuske and H.D. Lutz

Universität Siegen, Anorganische Chemie I, Postfach 101240, W-5900 Siegen (Germany)

(Received 10 June 1992)

Abstract

The phase diagrams of the systems LiBr–$MgBr_2$ and LiBr–$MnBr_2$ have been studied by high temperature X-ray powder diffraction and differential scanning calorimetry measurements. At elevated temperatures, complete series of solid solutions between NaCl-type LiBr and $CdCl_2$-type MBr_2 are formed. On cooling to ambient temperature, these solid solutions decompose to LiBr, CdI_2-type MBr_2, and the ternary compounds Li_6MBr_8 (Suzuki type) and Li_2MBr_4 ($SnMn_2S_4$ type). The structures of the ternary bromides can be characterized by different ordering schemes of the metal ions and vacancies on the octahedral sites of the cubic close-packed bromide ions. The symmetry relations to the aristotype NaCl structure and the Coulomb parts of the cohesive energies are given.

INTRODUCTION

The fast lithium ion conductors established in the systems LiCl–MCl_2 (where M is Mg, Ti, V, Cr, Mn, Fe, Co, Zn, Cd) (see refs. 1–6, and references cited therein) have been the subject of numerous investigations. This is not the case for the corresponding bromides. Stable ternary lithium bromides such as $Li_2M^{II}Br_4$ and $Li_6M^{II}Br_8$ have only been found in the systems LiBr–$MgBr_2$ and LiBr–$MnBr_2$ [7–16]. The phase diagram of the LiBr–$MnBr_2$ system has been studied by Seifert and Dau [7]. They reported that there are solid solutions in the whole range of composition and that on addition of even small amounts of LiBr to $MnBr_2$ the hexagonal close-packed arrangement of the Br^- ions (CdI_2 type) transforms to the cubic close-packed arrangement ($CdCl_2$ type). The ternary compounds Li_2MnBr_4 [8–16] and Li_6MnBr_8 [12, 13] established later on crystallize at ambient temperature in ordered rock-salt defect structures of $SnMn_2S_4$ type (oC14) [17] and Suzuki type (cF56) [18], respectively. Both compounds are polymorphic at elevated temperatures. The structures and

---

Correspondence to: H.D. Lutz, Universität Siegen, Anorganische Chemie I, Postfach 101240, W-5900 Siegen, Germany.

phase transitions have been reported in refs. 11, 15, 16 and 19. Polymorphism of binary $MnBr_2$ (without any lithium content) from CdI_2 type (hP3) to $CdCl_2$ type (hR9) was also observed [19, 20]. Because of the special metric of $MnBr_2$ hR9 at high temperatures the structure was first assumed to be cubic [13]. Similar results have been obtained in the system LiBr–$MgBr_2$ [11, 19].

In this paper, we present the phase diagrams of the systems LiBr–MBr_2 (where M is Mg, Mn) established by X-ray phase analyses and differential scanning calorimetry (DSC) measurements. Special emphasis is given to the relationships between the crystal structures of the compounds present.

EXPERIMENTAL

LiBr was dried in a vacuo at 300°C for several hours. $MgBr_2 \cdot 6H_2O$ and $MnBr_2 \cdot 4H_2O$ were slowly heated to 350°C in a dry stream of HBr. After cooling, the binary bromides were sublimated at 550–600°C in vacuo. The

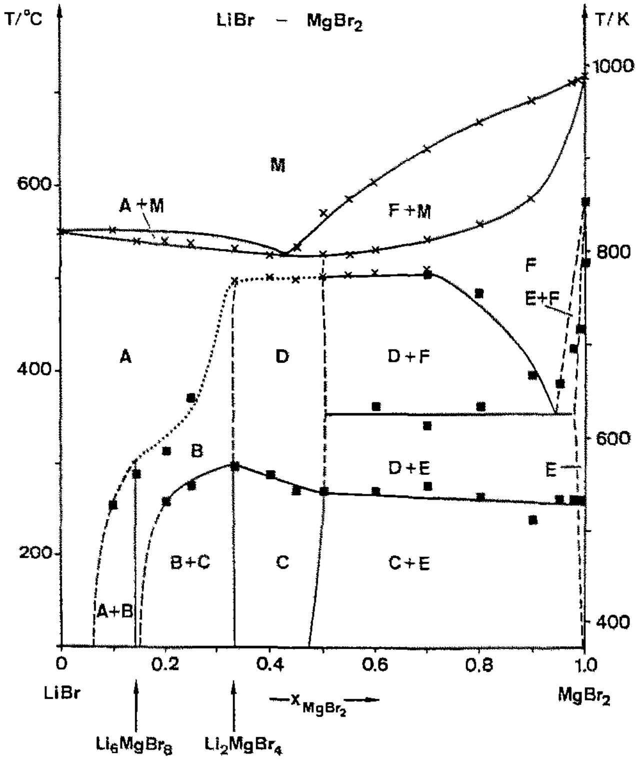

Fig. 1. Phase diagram of the system LiBr–$MgBr_2$: A, NaCl type; B, Suzuki type; C, $SnMn_2S_4$ type; D, Li_2MnBr_4 HTM I type (cF56); E, CdI_2 type; F, $CdCl_2$ type; M, melt; ■, high temperature X-ray diffraction; ×, DSC measurements; —— and – – –, observed and estimated phase boundaries; · · ·, order–disorder transitions.

ternary bromides were prepared by fusing stoichiometric amounts of the binary compounds in evacuated sealed quartz ampoules and subsequent cooling to room temperature at 10 K h^{-1}.

The samples obtained were characterized by high-temperature X-ray powder diffraction (Enraf–Nonius Guinier–Simon–FR 553 system) using Cu Kα_1 radiation. Evacuated and sealed quartz capillaries (0.3 mm in diameter) were used as sample holders. The heating and cooling rates were 1–20 K h^{-1}.

DSC measurements were performed with a Perkin-Elmer DSC7 calorimeter using gold crucibles as sample holders. For more details see ref. 21. The sample weights were 10–20 mg, the heating and cooling rates 10–20 K min^{-1}. Indium, tin and zinc were used for temperature calibration.

RESULTS

The phase diagrams of the systems LiBr–MgBr$_2$ and LiBr–MnBr$_2$ determined by high-temperature X-ray diffraction and DSC measurements are shown in Figs. 1 and 2. They are very similar with respect to both phase regions and compounds present.

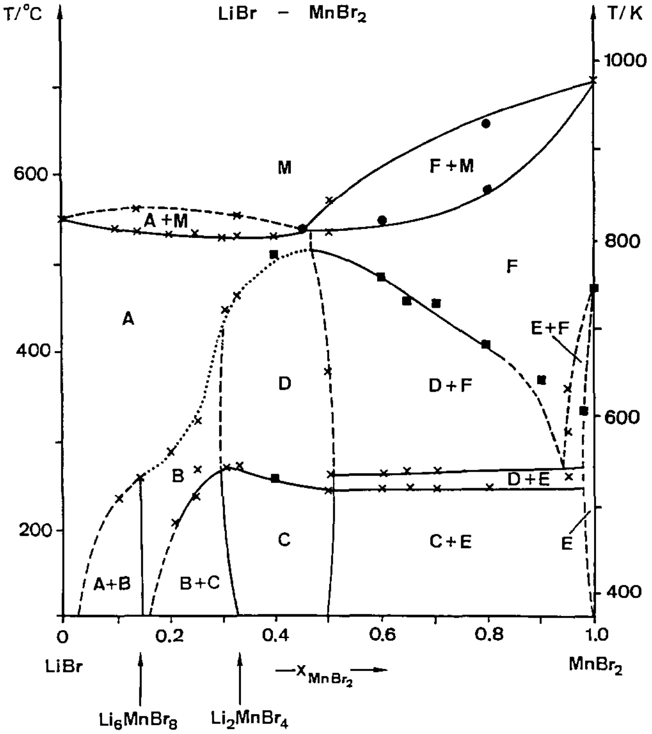

Fig. 2. Phase diagram of the system LiBr–MnBr$_2$: ●, DTA measurements [7] (for further explanations see caption to Fig. 1).

At elevated temperatures (i.e. at about 800 K) NaCl-type LiBr and $CdCl_2$-type MBr_2 (where M is Mg, Mn) form complete series of solid solutions. The unit cell dimensions slowly decrease with increase in MBr_2 content. The phase boundaries between the NaCl- and $CdCl_2$-type structures are not defined exactly. The ternary compounds Li_6MBr_8 (Suzuki type) (B) and Li_2MBr_4 ($SnMn_2S_4$ type) (C) undergo order–disorder phase transitions at elevated temperatures. (Because the X-ray photographs of Li_2MBr_4 HTM I and Li_6MBr_8 are very similar, the accurate phase boundaries between these compounds could not be definitely established.) At ambient temperature, the mutual solubilities of the com pounds present (especially those of Li_6MBr_8 and MBr_2) are only small.

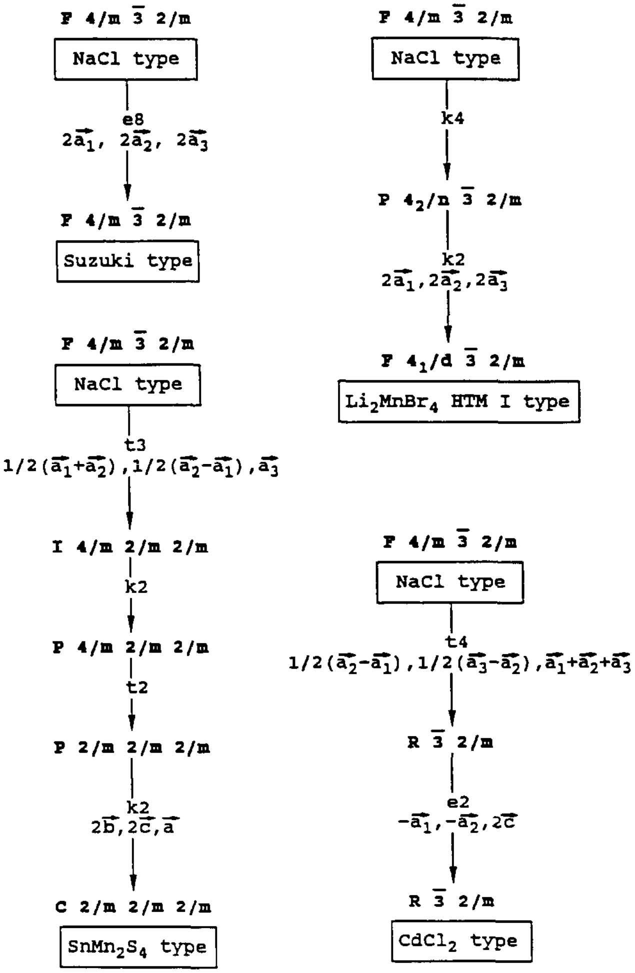

Fig. 3. Symmetry relations of the observed structure types in the systems LiBr–MBr_2 (where M is Mg, Mn) to the aristotype NaCl structure: t, k and e, translationengleiche, klassengleiche and equivalente subgroups, respectively [24].

DISCUSSION

With the exception of CdI_2-type MBr_2 (E), all phases present possess more or less ordered rock-salt defect structures. They are characterized by a special cation ordering scheme on the octahedral sites of the eutactically cubic close-packed arrangement of the bromide ions. The symmetry relations [22, 23] of the various structure types observed with respect to the NaCl structure are given in Fig. 3. The various ordering schemes of the metal layers arranged perpendicularly to the space diagonal of the cubic cells or to the *c* axes in the case of a hexagonal metric are shown in Fig. 4.

Ordering of vacancies and M^{2+} ions in a rocksalt type structure is possible in different manners, producing deficient NaCl superstructures. Considering the $M^{II}Br_6$ and $\square Br_6$ ($\square$ vacancy) units formed by incorporation of bivalent metal ions in LiBr as point defects, the most trivial superstructure imaginable is an NaCl-like structure for arrangement of these units. This ordering occurs only in the Suzuki-type structures of $Li_6M^{II}Br_8$ (where M^{II} is Mg, Mn). With increase in M^{II} content, the octahedral units mentioned above are edge-shared and hence a structure

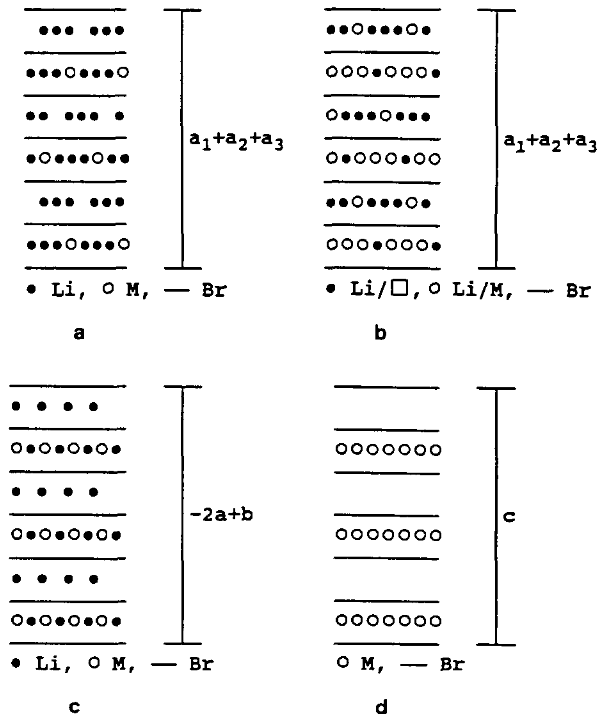

Fig. 4. Cation ordering of the NaCl defect structures observed in the systems LiBr–MBr_2 (where M is Mg, Mn): $\square$, vacancy; a, Suzuki type; b, Li_2MnBr_4 HTM I type; c, $SnMn_2S_4$ type; d, $CdCl_2$ type.

with a one-dimensional dislocation-like clustering of the point defects defined above is that of the $SnMn_2S_4$ type, which is also observed in the systems under study. Further increase of M^{II} and □ leads to a two-dimensional layer-like clustering of the defects, as in the $CdCl_2$- and CdI_2-type structures of $MgBr_2$ and $MnBr_2$, respectively.

The ternary lithium bromides under investigation are stable with respect to decomposition to the respective binary bromides. In the case of the magnesium compounds (for Li_6MnBr_8 the structure parameters are still lacking) this is also revealed from the Coulomb parts of the cohesive energies (MAPLE [25]). The data obtained are (in kJ mol^{-1}): LiBr, −882.4; $MgBr_2$, −2236; Li_2MgBr_4, −4088; Li_6MgBr_8, −7644 (for crystal structures of Li_6MgBr_8 and Li_2MgBr_4 see ref. 19). Hence the energies of decomposition are (in kJ): $Li_6MgBr_8 \rightarrow 4LiBr + Li_2MgBr_4$, +26.4; $Li_6MgBr_8 \rightarrow 6LiBr + MgBr_2$, +113.6; $3Li_2MgBr_4 \rightarrow Li_6MgBr_8 + 2MgBr_2$, +148; $Li_2MgBr_4 \rightarrow 2LiBr + MgBr_2$, +87.2. In the systems $LiBr–M^{II}Br_2$ (where M^{II} is V, Cr, Fe, Co, Ni), ternary compounds obviously do not exist. The reason is not yet known.

ACKNOWLEDGMENTS

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

REFERENCES

1 H.D. Lutz, W. Schmidt and H. Haeuseler, Z. Anorg. Allg. Chem., 453 (1979) 121.
2 Ch. Cros, L. Hanebali, L. Latié, G. Villeneuve and Wang Gang, Solid State Ionics, 9/10 (1983) 139.
3 H.D. Lutz, P. Kuske and K. Wussow, Naturwissenschaften, 73 (1986) 623.
4 R. Kanno, Y. Takeda, A. Takahashi, O. Yamamoto, R. Suyama and M. Koizumi, J. Solid State Chem., 71 (1987) 189.
5 H.D. Lutz, P. Kuske and K. Wussow, Solid State Ionics, 28–30 (1988) 1282.
6 A.R. West, Ber. Bunsenges. Phys. Chem., 93 (1989) 1235.
7 H.-J. Seifert and E. Dau, Z. Anorg. Allg. Chem., 391 (1972) 302.
8 H.D. Lutz, W. Schmidt and H. Haeuseler, Naturwissenschaften, 68 (1981) 328.
9 W. Schmidt and H.D. Lutz, Ber. Bunsenges. Phys. Chem., 88 (1984) 720.
10 H.D. Lutz, W. Schmidt and H. Haeuseler, J. Solid State Chem., 56 (1985) 21.
11 R. Kanno, Y. Takeda, O. Yamamoto, Ch. Cros, Wang Gang and P. Hagenmuller, J. Electrochem. Soc., 133 (1986) 1052.
12 P. Kuske, Doctoral Thesis, University of Siegen, 1988.
13 P. Kuske and H.D. Lutz, Z. Kristallogr., 186 (1989) 178, 323.
14 K. Wussow, H. Haeuseler, P. Kuske, W. Schmidt and H.D. Lutz, J. Solid State Chem., 78 (1989) 117.
15 H.D. Lutz, J.K. Cockcroft, P. Kuske and M. Schneider, Mater. Res. Bull., 25 (1990) 451.
16 H.D. Lutz, M. Schneider, P. Kuske and H.-J. Steiner, Z. Anorg. Allg. Chem., 592 (1991) 106.
17 M. Wintenberger and J.C. Jumas, Acta Crystallogr., Sect. B, 36 (1980) 1993.

18 K. Suzuki, J. Phys. Soc. Jpn., 16 (1961) 67.

19 M. Schneider, Doctoral Thesis, University of Siegen, 1991.

20 M. Schneider, P. Kuske and H.D. Lutz, Acta Crystallogr., in press.

21 H.D. Lutz, W. Schmidt and H.-J. Steiner, Z. Anorg. Allg. Chem., 604 (1991) 39.

22 Th. Hahn (Ed.), International Tables for Crystallography, Vol. A, 2nd edn., Reidel, Dordrecht, 1987.

23 H.T. Stokes and D.M. Hatch, Isotropy Subgroups of the 230 Crystallographic Space Groups, World Scientific, Singapore, 1988.

24 H. Bärnighausen, Commun. Math. Chem., 9 (1980) 139; Chem. Abstr., 94 (1980) 56381h.

25 R. Hoppe, Z. Kristallogr., 150 (1979) 23.