High Pressure Synthesis and Structures of Scandium-Zinc Intermetallic Compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$ and $\text{Sc}_{13}\text{Zn}_{58}$

Xiaoyang Liu, Regina Ehrl and Klaus-Jürgen Range
Institute of Inorganic Chemistry, Regensburg University
Universitystreet 31, D-93053 Regensburg, Germany

Three kinds of scandium-zinc intermetallic compounds, ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$ and $\text{Sc}_{13}\text{Zn}_{58}$ have been prepared from the elements under high pressure and high temperature. ScZn_2 crystallizes in the hexagonal system with lattice constants $a=5.2509\text{\AA}$, $c=8.4774\text{\AA}$, $c/a=1.6147$, and unit cell volume $202.42\text{\AA}^3$. $\text{Sc}_3\text{Zn}_{17}$ crystallizes in the cubic system with lattice constant $a=13.8406\text{\AA}$ and unit cell volume $2661.35\text{\AA}^3$. $\text{Sc}_{13}\text{Zn}_{58}$ crystallizes in the hexagonal system with lattice constant $a=13.744\text{\AA}$, $c=13.632\text{\AA}$, $c/a=0.9919$, and unit cell volume $2230.06\text{\AA}^3$. The usefulness of high pressure methods for the synthesis of intermetallic phases with highly volatile components could again be demonstrated here. [high pressure synthesis, scandium-zinc intermetallic compounds, alloy, X-ray diffraction]

1. Introduction

In recent years a number of reports on the alloying behaviour of the rare earths with zinc have been published. Full structure data on the MZn and MZn_2 compounds are available. For Zn-rich alloy, crystal structures have been found corresponding to the formulae M_2Zn_{17} , MZn_{11} , MZn_{12} , and MZn_{13} . The alloy phase diagrams of Zn with Y, La, Ce, Pr, Nd, Sm, and Yb are known and are generally characterized by a large number of intermetallic phases[1], but no phase diagram is available for the Sc-Zn system. Recently we have succeeded in the preparation of a new compound with 1:2 stoichiometry, ScZn_2 , hitherto unknown in the Sc-Zn system [2]. In the present paper, we report the latest developments in Sc-Zn system, which are about the high pressure synthesis and structures of scandium-zinc intermetallic compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$ and $\text{Sc}_{13}\text{Zn}_{58}$.

2. Experimental details

High pressure experiments were carried out in a modified Belt-type apparatus using crucibles made of h-BN for the synthesis of scandium-zinc intermetallic compounds, and starting with stoichiometric mixtures of scandium (99.999%; Alfa) and zinc (99.999%; Alfa) for ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$, respectively. The crystals of ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$ were found after the following treatment:

ScZn_2 Heating to 1900°C at 3.5GPa (heating rate $190^\circ\text{C}/\text{min}$), keeping the temperature at 1900°C for 20 min, cooling down (cooling rate $35^\circ\text{C}/\text{min}$) to 1200°C . The samples were annealed at this value for another 60min. After cooling down to the room temperature (cooling rate $25^\circ\text{C}/\text{min}$), the pressure was released.

$\text{Sc}_3\text{Zn}_{17}$ Heating to 1900°C at 3.5GPa (heating rate $190^\circ\text{C}/\text{min}$), keeping the temperature at 1900°C for 30 min, cooling down (cooling rate $10^\circ\text{C}/\text{min}$) to 1600°C , keeping the temperature at this value for another 100min. The sample was quenched to the room temperature before the pressure was released.

$\text{Sc}_{13}\text{Zn}_{58}$ Heating the starting materials to 1900°C at 4.0GPa (heating rate $190^\circ\text{C}/\text{min}$), keeping the temperature at 1900°C for 100 min, cooling down (cooling rate $8^\circ\text{C}/\text{min}$) to 1200°C . The samples were annealed at this value for another 150min. After cooling down to the room temperature (cooling rate $12^\circ\text{C}/\text{min}$), the pressure was released.

The brittle reaction products which were in a grey matrix were not very sensitive to moist air.

After high pressure and high temperature experiments, crystal fragments suitable for a single crystal X-ray study could be selected from the reaction products. The crystals were checked by oscillation and Weissenberg photograph and subsequently used for data collection on an Enraf-Nonius CAD-4 diffractometer or STOE imaging plate diffraction system.

X-ray powder diffraction studies were performed using STOE X-ray powder diffraction system.

EDX measurement (Zeiss DSM 950) confirmed the existence of scandium zinc intermetallic compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$.

3. Discussion

The basic crystal data for scandium-zinc intermetallic compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$ are listed in Table 1. X-ray powder diffraction data of scandium zinc intermetallic compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$ are listed in Table 2,

Fig.1. Unit cell structure of scandium-zinc intermetallic compound ScZn_2

Table 3 and Table 4, respectively, which are average value derived from a least squares fitting of X-ray powder diffraction data.

Table 1 Crystal Data for scandium-zinc intermetallic compounds ScZn_2 , $\text{Sc}_3\text{Zn}_{17}$, and $\text{Sc}_{13}\text{Zn}_{58}$

Compounds	Crystal System	Cell Constants(Å)	Cell Volume(Å ³)	Structural Types	Space Group
ScZn_2	Hexagonal	$a = 5.2509(8)$ $c = 8.4774(14)$ $c/a = 1.6147$	202.42	MgZn_2	$P6_3/mmc$ (No.194)
$\text{Sc}_3\text{Zn}_{17}$	Cubic	$a = 13.8406(6)$	2661.35	$\text{Ru}_3\text{Be}_{17}$	$I\bar{m}\bar{3}$ (No.204)
$\text{Sc}_{13}\text{Zn}_{58}$	Hexagonal	$a = 13.744(1)$ $c = 13.632(1)$ $c/a = 0.9919$	2230.06	$\text{Gd}_{13}\text{Zn}_{58}$	$P6_3mc$ (No.186)

Table 2. X-ray Powder Diffraction Data of Scandium Zinc Intermetallic Compounds ScZn_2

2θ	I/I_0	$h\ k\ l$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$
10.439	9.4	0 0 1	8.4673	8.4672
19.495	22.6	1 0 0	4.5495	4.5470
20.940	18.0	0 0 2	4.2389	4.2381
22.162	16.7	1 0 1	4.0078	4.0068
34.119	21.4	1 1 0	2.6257	2.6252
37.445	52.0	1 0 3	2.3997	2.3998
39.611	19.2	2 0 0	2.2733	2.2735
40.378	100.0	1 1 2	2.2319	2.2317
41.060	86.3	2 0 1	2.1964	2.1959
42.642	26.9	0 0 4	2.1185	2.1190
45.228	28.7	2 0 2	2.0032	2.0034
47.291	16.5	1 0 4	1.9205	1.9207
51.555	11.7	2 0 3	1.7713	1.7713
53.280	5.5	2 1 0	1.7179	1.7186
63.295	17.8	2 1 3	1.4681	1.4683
65.328	16.9	3 0 2	1.4272	1.4271
66.064	6.1	0 0 6	1.4131	1.4127
69.073	22.0	2 0 5	1.3587	1.3590
70.497	9.2	2 1 4	1.3347	1.3348
71.859	20.9	2 2 0	1.3127	1.3126
83.960	7.8	3 1 3	1.1516	1.1516
86.247	9.4	4 0 1	1.1268	1.1267
87.308	15.9	2 2 4	1.1159	1.1159
90.613	5.2	3 1 4	1.0836	1.0837

ScZn_2 From the X-ray diffractometer data a hexagonal unit cell with lattice constant $a = 5.2509(8)\text{\AA}$, $c = 8.4774(14)\text{\AA}$, $c/a=1.6147$ and unit cell volume $202.42\text{\AA}^3$ was found. The observed reflection conditions ($l=2n$ for $hh\text{-}2hl$) pointed to the possible space group $P6_3mc$ and $P6_3/mmc$. From statistical analysis of the normalized structure amplitudes an inversion centre was found, arriving at the centric space group $P6_3/mmc$. The result of the structure refinement confirmed this space group choice[2]. The unit cell structure of scandium-zinc intermetallic compound ScZn_2 is shown in figure 1. It crystallizes with a C14 (MgZn_2) type structure.

$\text{Sc}_3\text{Zn}_{17}$: A cubic unit cell with lattice constant $a=13.8406(6)\text{\AA}$ and unit cell volume $2661.35\text{\AA}^3$ was found from the X-ray diffractometer data. The observed reflection conditions ($h+k+l=2n$ for hkl) pointed to the space group $I\bar{m}\bar{3}$.

$\text{Sc}_{13}\text{Zn}_{58}$: From the X-ray diffractometer data a hexagonal unit cell with lattice constants $a=13.744\text{\AA}$, $c=13.632\text{\AA}$, $c/a=0.9919$, and unit cell volume $2230.06\text{\AA}^3$ was found. The observed

reflection conditions ($l=2n$ for $hh\text{-}2hl$) pointed to the space group $P6_3mc$.

During the preparation of zinc-rich alloys, problems often arise due to the relative high volatility of zinc. Consequently,

Table 3. X-ray Powder Diffraction Data of Intermetallic Compounds $\text{Sc}_3\text{Zn}_{17}$

2θ	I/I_0	$h\ k\ l$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$
9.014	2.2	1 1 0	9.8023	9.7867
12.784	5.4	2 0 0	6.9186	6.9191
20.272	6.9	3 1 0	4.3769	4.3768
24.037	5.0	3 2 1	3.6991	3.6992
27.300	4.2	3 3 0	3.2640	3.2623
28.821	13.5	4 2 0	3.0951	3.0949
31.642	4.8	4 2 2	2.8254	2.8253
32.992	4.1	4 3 1	2.7127	2.7144
35.488	6.8	5 2 1	2.5275	2.5270
37.870	73.2	4 3 3	2.3738	2.3737
39.008	29.3	4 4 2	2.3071	2.3068
40.129	100.0	5 3 2	2.2452	2.2453
41.214	9.6	6 2 0	2.1886	2.1884
42.278	5.3	5 4 1	2.1359	2.1357
44.351	39.7	6 3 1	2.0408	2.0407
46.348	28.5	5 4 3	1.9574	1.9574
47.321	20.6	6 4 0	1.9194	1.9194
48.280	5.2	5 5 2	1.8835	1.8835
49.221	8.6	6 4 2	1.8496	1.8496
57.209	3.5	7 4 3	1.6089	1.6090
65.311	4.8	7 6 3	1.4275	1.4276
66.089	3.6	8 4 4	1.4126	1.4126
66.868	14.3	7 7 0	1.3980	1.3981
67.636	4.1	8 6 0	1.3840	1.3841
69.912	2.9	9 4 3	1.3444	1.3444
70.669	2.9	6 6 6	1.3319	1.3318
71.420	19.2	7 6 5	1.3197	1.3197
72.921	5.5	7 7 4	1.2962	1.2963
73.645	2.8	8 6 4	1.2852	1.2851
74.395	6.5	9 6 1	1.2741	1.2742
75.872	2.7	8 7 3	1.2529	1.2531
84.505	3.7	9 7 4	1.1456	1.1455
86.644	6.5	10 6 4	1.1227	1.1226
87.357	2.7	9 8 3	1.1154	1.1153
88.785	2.4	10 7 3	1.1011	1.1011
90.197	4.8	8 7 7	1.0875	1.0874
90.914	2.6	8 8 6	1.0808	1.0808
91.623	2.4	9 7 6	1.0742	1.0742
93.049	2.4	9 8 5	1.0615	1.0615
94.464	1.9	10 7 5	1.0493	1.0492

Table 4. X-ray Powder Diffraction Data of Intermetallic Compounds $\text{Sc}_{13}\text{Zn}_{58}$

2θ	I/I_0	$h\ k\ l$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$
7.426	4.4	1 0 0	11.8945	11.8985
9.849	2.3	1 0 1	8.9731	8.9638
12.880	2.3	1 1 0	6.8674	6.8696
18.310	2.2	1 1 2	4.8412	4.8383
19.489	2.6	0 0 3	4.5511	4.5436
20.925	4.1	1 0 3	4.2417	4.2447
23.336	6.6	3 0 1	3.8088	3.8082
23.686	4.1	2 1 2	3.7532	3.7537
24.634	3.5	2 0 3	3.6109	3.6110
25.919	4.6	2 2 0	3.4348	3.4348
27.194	2.3	1 0 4	3.2765	3.2760
27.884	2.1	2 1 3	3.1969	3.1963
29.244	2.9	1 1 4	3.0513	3.0528
30.213	2.7	2 0 4	2.9556	2.9570
30.749	2.0	4 0 1	2.9053	2.9062
35.160	3.1	4 1 1	2.5503	2.5506
36.055	4.5	4 0 3	2.4890	2.4887
37.138	3.1	2 2 4	2.4189	2.4191
37.771	6.6	5 0 0	2.3798	2.3797
38.440	50.5	3 2 3	2.3399	2.3399
39.318	40.0	3 3 0	2.2896	2.2899
39.634	5.8	0 0 6	2.2721	2.2718
40.106	100.0	5 0 2	2.2464	2.2467
40.371	14.1	1 0 6	2.2323	2.2315
41.854	2.3	1 1 6	2.1566	2.1569
42.270	4.9	5 1 0	2.1363	2.1370
42.853	7.1	5 0 3	2.1086	2.1081
43.801	2.6	4 1 4	2.0651	2.0653
44.393	4.3	5 1 2	2.0390	2.0391
44.947	5.2	4 2 3	2.0151	2.0153
46.009	17.6	3 0 6	1.9710	1.9713
46.228	9.9	6 0 1	1.9622	1.9624
46.945	9.3	5 1 3	1.9339	1.9338
47.274	3.9	1 0 7	1.9212	1.9217
47.819	9.3	3 3 4	1.9005	1.9006
48.380	7.0	4 3 2	1.8798	1.8802
49.650	2.2	5 2 2	1.8347	1.8349
50.368	3.1	5 1 4	1.8102	1.8105
53.314	3.6	4 4 0	1.7169	1.7174
57.417	2.4	6 2 2	1.6036	1.6037
60.853	2.9	5 3 4	1.5210	1.5211
62.631	1.8	4 3 6	1.4820	1.4823
64.575	2.5	5 3 5	1.4420	1.4424
66.037	5.0	8 0 3	1.4136	1.4135
67.571	3.1	2 2 9	1.3852	1.3858
68.192	2.4	5 5 0	1.3741	1.3739
68.767	2.5	8 1 2	1.3640	1.3644
70.668	6.0	7 3 1	1.3319	1.3323
71.803	6.9	7 3 2	1.3136	1.3136
73.185	3.6	8 2 1	1.2922	1.2924
73.402	3.4	8 1 4	1.2889	1.2891
74.389	3.5	5 5 4	1.2742	1.2742
79.611	1.9	6 0 9	1.2032	1.2037
82.206	2.1	6 5 4	1.1717	1.1713
86.582	2.8	10 0 4	1.1233	1.1233
91.658	1.7	5 4 9	1.0739	1.0741

the desired stoichiometry is difficult to adjust because of vaporization losses inevitably found in normal pressure experiments. This problem can be overcome, however, by synthesis in a closed high pressure system. The intermetallic compound studied in the present work is almost certainly not a real high pressure phase. The function of the applied pressure, however, is merely to keep the reactants together and to allow in this way for the application of rather high temperature which are needed for crystal growth.

Although higher temperature is beneficial to the mixing of starting materials under high pressure, it is found that it is not advantageous to the formation of perfect single crystals in the process of synthesis of zinc-rich intermetallic compounds. It is found that within the temperature range of formation of a certain crystal, the lower the temperature, the more perfect the crystal. It can be explained as follows. The atoms in a crystal are in the state of thermal vibration. The kinetic energy of vibration of particles with a mass m is equal to $p^2/2m$, where p is the momentum. If this energy exceeds $U(r)$, which is the potential energy of interaction between atoms, the bonding forces will be overcome. Thus the condition for the existence of a condensed system, a crystal in particular, can be written as

$$p^2/2m < U(r)$$

Above condition also holds for a liquid. But in the transition from a crystal to a liquid the nature of the order of the atoms changes sharply, because with increasing momenta the average interatomic distances also increase, and the atoms are found more and more often far from the minimum of the $U(r)$. In a liquid, some preferred mutual configurations of atoms are formed statistically, but they are destroyed all the time by thermal motion; ordering is lower the higher is the temperature. At 0K when only zero vibrations of the atoms exist, all the phase are crystalline, with the exception of helium, a most quantum liquid. It is obvious that in a solid the amplitude of vibrations of the atoms is less than the interatomic distance, otherwise they would dominate over the processes of free redistribution - atom migration - which are characteristic of the liquid state, but which may also exist in crystals as fluctuations.

The route for the synthesis of intermetallic compounds mentioned above have several advantages over other methods. Firstly, it is more easy to obtain the expected products. Secondly, the synthesis of Sc-Zn intermetallic compounds can be carried out in a shorter time. It would last at least 24 hours under normal conditions[3]. In the presence of an external pressure, phase states shift towards condensation and crystallization, and substances whose atomic interaction is described by $U(r)$ without a minimum may crystallize. The effect of the pressure is similar to an increase in attraction forces and opposite to the temperature effect.

References

- [1] G. Bruzzone, M.L.Forasini & F.Morlo, *J. Less-Common Metals*, **22**, 253(1970).
- [2] X.Liu, J. Breu, F. Rau, K. -J. Range, *J. Alloys Comp.*, **243**, L5(1996).
- [3] T.Siegrist & Y.LePage, *J. Less-Common Metals*, **127**, 189(1987).