After More than 60 Years, a New NaTl Type Zintl Phase: KTl at High Pressure

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Received July 27, 1999

According to Zintl's classical work in the early 1930s, $A^{I}B^{III}$ Zintl phases LiAl,[1] LiGa,[2] LiIn,[2] NaIn,[3] and NaTl [4] crystallize in the NaTl type structure. In these five Zintl phases B^- ions with four valence electrons build up a three-dimensional four-connected (3D4C) diamond net. All B−B bonds are of equal length and form the ideal tetrahedral angle of 109.5°. The A^+ counterions fill the cavities of the 3D4C net and do not play a significant role in covalent bonding. Calculation of the density of states, e.g., for NaIn[5] support Zintl's ionic formulation A^+B^-. Detailed band calculations on NaTl type Zintl phases have been given elsewhere.[6,7]

More than 60 years after Zintl's work it has not been possible to prepare even one new $A^{I}B^{III}$ phase with the NaTl type structure. Evidently the NaTl type structure is stable only with small alkali counterions Li^+ and Na^+. It seems that the cavities in the 3D4C B net are too small for a larger alkali counterion, e.g., K^+. For the compound NaTl one calculates a ratio of covalent radii[8] (coordination number 8) $r_{Na}/r_{Tl} = 1.843/1.588 = 1.16$, but for KTl a ratio $r_K/r_{Tl} = 2.296/1.588 = 1.45$ is obtained, which is 20% higher than the value for NaTl. Since potassium is more compressible than thallium,[9] it seems possible to decrease the ratio of radii by application of high pressure (HP). Also charge transfer, formally to K^+Tl^-, must reduce this ratio. Therefore KTl is a promising candidate to stabilize the NaTl type structure at HP.

However, at normal pressure (NP) KTl crystallizes in the KTl type structure.[10] In this structure isolated distorted Tl_6^{6-} octahedra are built up by four-connected Tl atoms. To transform these octahedra into the 3D4C net of the NaTl type structure HP experiments on KTl were started. Since the melting temperature T_m of KTl at NP is relative low ($T_m = 541$ K),[10] it seemed difficult to quench such a HP phase in a belt apparatus to ambient pressure, because recrystallization starts[11] even at $2/3T_m \approx 90$ °C. Therefore in situ HP experiments on KTl were performed with a diamond anvil cell.

The NP phase of KTl was prepared in a water-cooled copper boat by inductive heating of an equiatomic mixture of the constituent elements under argon.[12] Starting materials were high-purity potassium (Koch-Light, nominal purity: 99.97%) and high-purity thallium (Johnson-Matthey, 99.997%). All manipulations were performed in a glovebox with high-purity argon. After each melting experiment the regulus was cooled to room temperature, turned, and then melted several times again. X-ray Guinier diffractograms (Mo $K\alpha_1$ radiation, quartz monochromator) were analyzed by the Rietveld method[13,14] with the structural data of KTl-NP.[10] By this procedure it was shown that a phase-pure sample was synthesized.

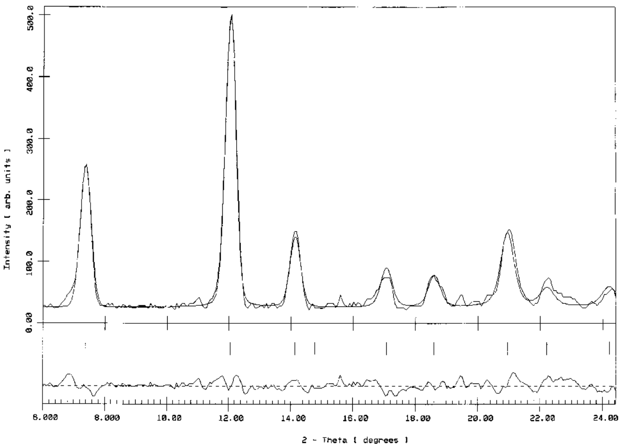

Figure 1. Rietveld plot for KTl with the NaTl type structure at 45 kbar (diamond cell diffractometer, Ag Kα radiation, lattice parameter $a = 7.56(2)$ Å).

HP experiments were performed in a diamond cell of Mao-Bell type[15] (culet, 300 μm; starting gasket thickness, 80 μm; gasket hole, 130 μm). More experimental details are given elsewhere.[16] A mixture of KTl-NP, silver powder, and a drop of dried oil was treated in the glovebox with a micromanipulator under a video-microscope and filled into the gasket hole. Before leaving the glovebox sufficient pressure was applied in order to seal the very sensitive sample KTl-NP within the metal gasket against air and moisture. Pressure was calibrated with silver powder for which specific volumes are tabulated up to 900 kbar.[17]

HP diffractograms were recorded with Ag Kα radiation (filtered with Pd) in the range $\theta = 3-12.5°$ (increment, 0.03°; counting time per increment, 500 s). Structural data were obtained by the Rietveld method with both diffractometer zero point and asymmetry parameter fixed. The first diffractogram with increasing pressure, recorded at 20 kbar, showed that KTl-NP was completely transformed into a new phase. From comparison with the Guinier diffractogram of NaTl, taken at NP, it was evident that KTl-HP crystallizes also in the NaTl type structure. In Figure 1, a Rietveld plot of KTl-HP (without silver powder, 45 kbar, Ag Kα radiation, lattice parameter $a = 7.56(2)$ Å) is presented. Experimental

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10.1021/ic990894s CCC: $19.00

Table 1. Number of Neighbors and Distances (Å) for Dimorphic KTl

KTl-NP at 1 bar		KTl-HP at 2 kbar[a]
	Tl Neighbors	
Tl(1)−4Tl	Tl(2)−4Tl	Tl−4Tl
3.055, 3.081 3.341, 3.466	3.055 2×, 3.081 2×	3.47
Tl(1)−6K	Tl(2)−5K	Tl−10K
3.612, 3.621 3.671, 3.680 3.768, 3.969	3.612 2×, 3.733 4.032, 4.040	3.47 4×, 4.01 6×
	K Neighbors	
K(1)−4Tl	K(2)−6Tl	K−10Tl
3.680 2×, 3.768 2×	3.612 2×, 3.621 2× 3.969 2×	3.47 4×, 4.01 6×
K(3)−7Tl		
3.612 2×, 3.671 2× 3.733, 4.032, 4.040		

[a] Calculated for lattice parameter $a = 8.01(1)$ Å.

evidence for a pressure-induced transformation[15] into a β-brass type structure was not found up to 45 kbar. With decreasing pressure the metal gasket and the diamonds were sealed additionally with two-component glue from outside in order to avoid decomposition of the KTl sample by air and moisture when pressure is released near to ambient pressure. By this procedure a diffractogram of KTl-HP near 2 kbar was recorded, but it was impossible to quench the HP phase to 1 bar.

In Table 1 the number of neighbors and the distances (Å) are compared for KTl-NP (1 bar) and KTl-HP (2 kbar, $a = 8.01(1)$ Å). Although the Tl atoms remain four-connected in both phases, the high-symmetric 3D4C diamond net in the HP phase allows better space filling with higher coordination numbers than the less symmetric NP phase. As a result, density is raised by 18% from 5.163 g/cm^3 for the NP phase (at 1 bar) to 6.29 g/cm^3 for the HP phase (at 2 kbar). Therefore, the K:Tl coordination must increase during the HP transformation. In Table 1 it is shown that in the HP phase each potassium atom has (up to 4.1 Å) 10 Tl neighbors and each thallium atom has also 10 K neighbors. In KTl-NP the situation is more complicated, since here different crystallographic positions are occupied.[10] Tl(1) atoms in position 16g have six K neighbors, but Tl(2) atoms in position 8f have five K neighbors. Thus Tl:K coordination is $6(2/3) + 5(1/3) = 5.67$. On the other hand, K(1), K(2), and K(3) atoms are in positions 8e, 8d, and 8f with four, six, and seven Tl neighbors, respectively. Therefore K:Tl coordination is $(4 + 6 + 7)(1/3) = 5.67$. During the HP transformation the K:Tl coordination is increased from 5.67:5.67 to 10:10.

Up to now, there exists at NP no phase with composition NaAl and NaGa although LiAl[1] and LiGa[2] are stable Zintl phases with NaTl type structure. Nevertheless, the ratios of covalent radii[8] ($r_{Na}/r_{Al} = 1.843/1.376 = 1.34$ and $r_{Na}/r_{Ga} = 1.843/1.394 = 1.32$) show that these values are only 8% lower than that for KTl with $r_K/r_{Tl} = 1.45$. At first sight it seems easy to stabilize also here the NaTl type structure at HP. But contrary to KTl, now one must perform in situ HP syntheses at about 500 °C from the constituent elements instead of a phase HP transformation at room temperature.

Acknowledgment. Support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic details and Rietveld plots of several diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990894S