On the description of structural trends of \( \text{A}_{2}\text{MX}_{4} \) compounds by means of the Biltz' concept

Rune Sjövall

SAFT AB, Tech. Dept., P.O. Box 709, S-572 28 Oskarshamn, Sweden

Received 27 November 1997

The ideas of Biltz [Raumchemie der festen stoffe (Leopold Voss, Leipzig), 1934] provide a useful tool to predict the status of a given crystal structure in terms of compression and expansion relative to an optimal degree of space-filling. The same concept has been used to explain structural trends for homologous series of alkali metal-transition metal-halides with composition \( \text{A}_{2}\text{MX}_{4} \).

In the 1930s, Biltz investigated the relation between the molar volumes of solid state compounds. On the basis of such relations he developed a useful concept, which allows a global comparison between different structures of compounds with the same composition and even between compounds of different compositions.

Compounds with the composition \( \text{A}_{2}\text{MX}_{4} \) (A = Li → Cs; M = Cr, Mn, Fe, Co, Ni, Zn, Cd, Hg; X = F → I) are legion and of course this group comprises several structure types. In this note Biltz' concept will be applied to three series of selected compounds: \( \text{Rb}_{2}\text{CoX}_{4} \), \( \text{A}_{2}\text{ZnCl}_{4} \), \( \text{A}_{2}\text{ZnBr}_{4} \), \( \text{Cs}_{2}\text{MBr}_{4} \), M = Mn, Co, Cu, Zn, Cd, Hg. The aim is to show general structural trends when one of the three atoms is exchanged with the higher homologues.

The Biltz' concept

It is well known that the molar volume of a compound will, in most cases, not simply be derived by the summation of the volumes of the atoms. This is due to the volume contraction which is the result of chemical bonding and of interactions between the atoms in a crystal lattice. In order to develop a model in which this contraction is taken into consideration, Biltz introduced the concept of volume increments for different elements. The basis of the concept is that the atoms in a crystal are supposed to completely fill space. This in turn gives each element a specific volume value (increment, \( V_{i} \)) depending on the kind of bonding in the crystal. Biltz found that inorganic compounds can be divided into three groups: ionic salt-like compounds, intermetallic compounds, and compounds formed by a metal and a metametal, usually classified as Zintlphases. Within such a group the volume increment of a particular element is almost constant in different compounds, but depends strongly on the character of the chemical bonding.

A complete list of increments for different elements in their different bonding situations has been tabulated by Biltz. To achieve these values, the unit cell volume is divided into atomic increments, whose magnitudes, \( V_{m} \) are determined from successive difference calculations of unit cell contents for a large series of isomorphous compounds having the same kind of bonding. It should be emphasized that this method is independent of any structural knowledge such as space group, bond distances, etc. The only required data are either the unit cell dimensions and number of formula units per cell, or the density of the crystal. Since the elemental volume increments of Biltz are related to 0 K, the \( V_{m} \) values have been corrected by a factor 0.98 (due to room temperature), in accordance with a study of Klemm and von Schnering.

Biltz' concept states that chemical compounds realize structures so that the molar volume \( V_{m} \) matches the sum of the elemental increments \( V_{\text{opt}} = \sum V_{i} \) as closely as possible. It is observed that deviations up to 10% are tolerable. Exceeding this value means that the compounds probably will crystallize in another, more favourably, structural modification. In order to facilitate the interpretation of the results the ratio \( V_{m} / V_{\text{opt}} \) has been used.

Results and discussion

The results from the calculations for the \( \text{Rb}_{2}\text{CoX}_{4} \) series are shown in Fig. 1. There is a distinct kink in
Table I — Ratio of the observed molar volume \( V_m \) to the volume according to Biltz \( V_{opt} \) for \( Cs_2MBr_4 \) compounds (\( \beta-K_2SO_4 \) type). A ratio value exceeding 1.10 indicates that the compound is expanded with impact of that particular structure type.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{V_m}{V_{opt}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Cs_2MnBr_4 )</td>
<td>1.01</td>
</tr>
<tr>
<td>( Cs_2CoBr_4 )</td>
<td>1.01</td>
</tr>
<tr>
<td>( Cs_2CuBr_4 )</td>
<td>0.99</td>
</tr>
<tr>
<td>( Cs_2ZnBr_4 )</td>
<td>1.02</td>
</tr>
<tr>
<td>( Cs_2CdBr_4 )</td>
<td>1.06</td>
</tr>
<tr>
<td>( Cs_2HgBr_4 )</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The graph in Fig. 2 illustrates the effect of different alkali metal atoms in the compounds \( A_2ZnCl_4 \). It is obvious that the room temperature modification of \( Li_2ZnCl_4 \) is more compressed than the corresponding high temperature phase which is close to \( V_{opt} \). The structure of \( Na_2ZnCl_4 \) is on the other hand rather expanded since the obtained value exceeds \( V_{opt} \) by 8%. Therefore, \( K_2ZnCl_4 \) will crystallize in another structure type \( \beta-K_2SO_4 \), which allows a more favourable arrangement of the atoms in the lattice. The remaining two modifications, \( Rb_2ZnCl_4 \) and \( Cs_2ZnCl_4 \) are also of the orthorhombic \( \beta-K_2SO_4 \) type.

The compounds in the \( A_2ZnCl_4 \) series exhibit various, but extensively related, structural modifications. At room temperature \( Li_2ZnCl_4 \) crystallizes in the cubic inverse spinel type \( (Fd\overline{3}m) \), while there is a phase transition to the orthorhombic olivine type \( (Pnma) \) at temperatures above 488 K (HT). These phases can be described as consisting of close packed (fcc) chlorine ions in the cubic phase, or nearly close packed (hcp) in the orthorhombic phase. The Zn and Li ions are tetrahedrally and octahedrally coordinated by Cl ions. The structure of \( Na_2ZnCl_4 \) is of the chrysoberyl type \( (rK3) \), which is a very slightly distorted modification of the olivine type structure. The re-
maining compounds, K$_2$ZnCl$_4$, Rb$_2$ZnCl$_4$ and Cs$_2$ZnCl$_4$, in this series crystallize in orthorhombic $\beta$-K$_2$SO$_4$ type structures. For the potassium and rubidium compounds there also exists a number of modulated phases which, however, will not be discussed further here.

In the series including the compounds Cs$_2$MnBr$_4$, Cs$_2$CoBr$_4$, Cs$_2$CuBr$_4$, Cs$_2$ZnBr$_4$, Cs$_2$CdBr$_4$ and Cs$_2$HgBr$_4$,

the role of the transition metal in isostructural compounds of the $\beta$-K$_2$SO$_4$ type is exemplified. As is shown in Table 1 there are just small deviations within the same row of the periodic table, but the cadmium and mercury compounds tend to be a little more expanded than the remaining structures. Since the obtained ratio values lie close to 1.00, an optimum adaption of compound and structure is met.

In conclusion, the Biltz' concept has proved to be a useful tool showing the structural trends for the selected A$_2$MX$_4$ compounds on going towards higher homologues.

Acknowledgement

Dr. Ulrich Häussermann is gratefully acknowledged for valuable discussions.

References