The Perovskite Carbides A₃MC (A = Sc, Y, La - Nd, Sm, Gd - Lu; M = Al, Ga, In, Tl, Sn, Pb)

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Crystal Structure, Perovskite Carbides

Twentyfive new perovskite carbides have been obtained either by arc-melting cold-pressed pellets of the elemental components with subsequent annealing at 900 °C or by heating stoichiometric quantities of the elements in a high-frequency furnace. Also, thirtyseven compounds of this structure type are confirmed and their lattice constants are reported. The crystal structures of Sc₃MC (M = Al, Ga, In, Tl) were refined from X-ray powder data, and in all cases only the octahedral voids formed by scandium atoms were found to be fully occupied. The hydrolysis of the carbides Sc₃GaC, Y₃SnC, Y₃PbC and Ho₃PbC with diluted hydrochloric acid resulted in about 84 - 97 (wt-)% methane and 3 - 16 % saturated and unsaturated higher hydrocarbons. The cell volumes of the ternary carbides A₃MC and the corresponding binary Cu₃Au type compounds A₃M are compared and several inconsistencies are pointed out.

Introduction

Ternary carbides A₃MC with a structure corresponding to that of the mineral perovskite CaTiO₃ were first investigated almost 40 years ago [1, 2]. In these cubic compounds the A (mostly rare earth and transition elements) and M atoms (metallic and semimetallic main group elements) form a cubic close-packed Cu₃Au type lattice (Fig. 1). The carbon atoms have always been assumed to occupy those octahedral voids of the A₃M lattice formed only by the A atoms, i.e. they take the positions of the titanium atoms of CaTiO₃, and this was actually proven for Ti₃AlC [3]. However, the carbon positions are not always fully occupied, e.g. in Ni₃ZnC₁₋ₓ and Co₃SnC₁₋ₓ the carbon content is only about 10 % (x ~ 0.5), and some of these ternary carbides have large homogeneity ranges, which include the binary Cu₃Au type phases [1, 2]. In other cases Cu₃Au type phases were reported, but more careful investigations suggested that these compounds are stabilized by interstitial impurities [4]. Frequently it is difficult to prepare single-phase samples and thermodynamic equilibrium is not always reached for ternary samples with components differing greatly in their melting points. For that reason the composition of the binary Cu₃Au and the ternary perovskite phases is best established by structure refinements, where the occupancy factors of the interstitial positions are allowed to vary. In the present paper we report such refinements for the ternary perovskite phases with the main group elements M = Al, Ga, In, Tl. We also report new ternary perovskite phases with the main group elements M = Al, Ga, In, Tl, Sn and Pb, and compare their lattice constants with the literature data of compounds with similar composition. A preliminary account of this work has been presented at a conference [5].

Sample Preparation and Lattice Constants

Starting materials for the preparation of the perovskite carbides were filings of aluminum,
Table I. Lattice constants [pm] of the cubic perovskite carbides $A_3MC$ ($A =$ rare earth elements, $M =$ Al, Ga, In, Tl, Sn, Pb). The lattice constants of the 25 compounds reported for the first time are listed with bold type figures. The presently determined lattice constants (with their standard deviations) of previously reported compounds are listed in normal type. The corresponding literature data are shown in italics (without standard deviations) together with the literature citation. Standard deviations listed in parentheses are only given for the presently reported compounds.

<table>
<thead>
<tr>
<th>$A$</th>
<th>M = Al</th>
<th>Ga</th>
<th>In</th>
<th>Tl</th>
<th>Sn</th>
<th>Pb</th>
</tr>
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<tbody>
<tr>
<td>Sc</td>
<td>449.8(1)</td>
<td>446.8(1)</td>
<td>453.7(1)</td>
<td>451.6[21]</td>
<td>452.8[21]</td>
<td></td>
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<tr>
<td>Y</td>
<td>487.8(1)</td>
<td>481.8[10]</td>
<td>485.9(1)</td>
<td>487.8(1)</td>
<td>486.6(1)</td>
<td>488.2(1)</td>
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<tr>
<td>Pr</td>
<td>505.4(2)</td>
<td>500.7[1[2]</td>
<td>505.6(2)</td>
<td>493.5[16]</td>
<td>493.0[16]</td>
<td>494.8[34]</td>
</tr>
<tr>
<td>Nd</td>
<td>502.5(2)</td>
<td>496.5[16]</td>
<td>505.4[16]</td>
<td>503.2(1)</td>
<td>493.4[15]</td>
<td>494.9[33]</td>
</tr>
<tr>
<td>Sm</td>
<td>496.8(4)</td>
<td>490.1[11]</td>
<td>498.9(1)</td>
<td>498.6[28]</td>
<td>498.9(1)</td>
<td>498.6[28]</td>
</tr>
<tr>
<td>Gd</td>
<td>493.5(2)</td>
<td>490.9(2)</td>
<td>495.3(2)</td>
<td>493.1(1)</td>
<td>493.0[17]</td>
<td>494.8[17]</td>
</tr>
<tr>
<td>Tb</td>
<td>489.4(1)</td>
<td>479.4[8]</td>
<td>486.8(2)</td>
<td>491.6(1)</td>
<td>494.5[17]</td>
<td>494.8[17]</td>
</tr>
<tr>
<td>Dy</td>
<td>486.0(1)</td>
<td>483.1(1)</td>
<td>488.8(1)</td>
<td>487.7(1)</td>
<td>485.3(1)</td>
<td>486.8(1)</td>
</tr>
<tr>
<td>Ho</td>
<td>482.6(1)</td>
<td>483.4(2)</td>
<td>484.8(1)</td>
<td>482.9[17]</td>
<td>484.7(1)</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>480.42(2)</td>
<td>478.0(1)</td>
<td>481.3(1)</td>
<td>482.4(1)</td>
<td>480.6[17]</td>
<td>481.7[17]</td>
</tr>
<tr>
<td>Tm</td>
<td>478.1(2)</td>
<td>475.2(3)</td>
<td>480.1(1)</td>
<td>479.3(1)</td>
<td>477.2[17]</td>
<td>479.1(1)</td>
</tr>
<tr>
<td>Yb</td>
<td>475.7(1)</td>
<td>472.2(2)</td>
<td>478.2(2)</td>
<td>484.4[17]</td>
<td>484.3[17]</td>
<td>483.4(1)</td>
</tr>
<tr>
<td>Lu</td>
<td>473.4(1)</td>
<td>472.0(2)</td>
<td>476.2(1)</td>
<td>475.2(1)</td>
<td>473.3(1)</td>
<td>475.7(1)</td>
</tr>
</tbody>
</table>

Scandium, yttrium, and the rare earth elements (all $> 99.9 \%$), and small pieces of gallium, indium, thallium, tin, and lead ($> 99.9 \%$). Most of the compounds were prepared by arc-melting cold-pressed pellets ($\sim 300$ mg) of the ideal composition in an atmosphere of argon (99.996 \%). In the case of the tin and lead samples an excess of these elements (starting ratio $3 : 1.1 : 1$) was used to compensate the loss by evaporation of these elements during the melting process. The argon was purified by repeatedly melting a titanium button before the reactions. For the annealing processes (21 days at 900 °C) the samples were wrapped in steel or tantalum foil and enclosed in evacuated silica tubes. Using these
Fig. 2. Cell volumes of the perovskite carbides $A_3MC$ (filled circles) and the corresponding $Cu_3Au$ type binaries $A_3M$ (open circles). Note that the scale for the gallium compounds is not the same as the scale for the other compounds.

preparation conditions, the synthesis of the ytterbium compounds was unsuccessful because of the low melting point of this element. The ytterbium carbides were prepared by heating stoichiometric mixtures of the elements at about 1500 °C in evacuated tantalum tubes in a high-frequency furnace for fifteen minutes.

The cubic lattice constants (Table I) were obtained by least-squares fits of the Guinier powder data. CuKα1 radiation was used with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To prevent hydrolysis, the powder samples were investigated under a protective film of dry paraffin oil. A plot of the cell volumes is shown in Fig. 2.

Hydrolysis Results

Powder samples of the perovskite carbides are black and react readily with the humidity of the air. The complete decomposition of the arc-melted buttons in air takes up to one week, depending on the reactivity of the rare earth component.

The hydrolysis products of several samples were investigated by mass spectroscopy. For this purpose the coarsely ground samples were placed in an evacuated glass vessel and reacted with diluted (2N) hydrochloric acid. The gaseous reaction products were analysed in a Varian MAT (CH5) mass spectrometer (20 °C, 70 eV). They consisted mainly of methane with various higher hydrocarbons as byproducts. The following amounts of methane (in weight-%) were obtained: $Y_3SnC$ - 94, $Y_3PbC$ - 93, $Ho_3PbC$ - 84, and $Sc_3GaC$ - 97. The remainder was in all cases saturated and unsaturated $C_2-C_6$ hydrocarbons. Much larger amounts of higher hydrocarbons are usually observed, when the hydrolysed ternary rare earth carbide contains a transition metal as the third component [35].

In the case of $Sc_3GaC$ we also checked for nitrogen, which might been present as an impurity. Therefore some solid sodium hydroxide was added to the hydrochloric suspension in a second reaction step after the removal of the hydrocarbons, however, no ammonia was thus found.

Powder Diffractometry

The structures of $Sc_3AlC$, $Sc_3GaC$, $Sc_3InC$ and $Sc_3TIC$ were refined from X-ray powder diffractometer data collected with a STOE (STADI P) diffractometer using a focussing germanium (111) monochromator, CuKα1 radiation, a step width of 0.05°, a channel width of 0.02° and a constant measuring time of 100 s/step. The least-squares refinements were carried out with a Microsoft-Windows version [36] of the Rietveld analysis program Rietan [37]. A total of 13 general parameters were refined for each data set: the zero point of the counter, six background parameters, the scale factor and five profile parameters. In addition, the lattice constant of the cubic phase and the occupancy parameter of the carbon position were refined.

The refinements were carried out in the space group Pm3m with the scandium atoms at the position 0, 0, 0, and the carbon atoms at 1/2, 1/2, 1/2. The thermal
The binary cubic close packed Cu3Au type parent structure contains – in addition to the one interstitial site with octahedral copper coordination – also three voids formed by four copper and two gold atoms. Thus, if all octahedral voids were filled, the carbon content of such a carbide might be as high as 50 at.-%, corresponding to the ideal composition A3MC4. However, such a high carbon content has never been reported before for a "filled" Cu3Au type structure. The occupancy of such “mixed” octahedral sites was especially considered for the “inverse” perovskite carbide ThRu3C. A careful single-crystal structure refinement had shown, however, that the carbon atoms in this compound occupy only those sites, which are formed by six ruthenium atoms [39].

In Fig. 2 we have plotted the cell volumes of the ternary carbides A3MC together with the volumes of the corresponding "unfilled" binary Cu3Al type compounds. It can be seen that, in general, the cell volumes of the ternary compounds are larger than those of the corresponding binary ones. The difference usually is close to 10 %. However, there are some notable exceptions. Two of these concern the carbides La3SnC and La3TlC with their corresponding “binaries” “La3Sn” and “La3Tl”. The cell volumes of the ternary compounds fit well with the volumes of the other Ln3SnC and Ln3TlC carbides. The corresponding binary compounds, however, have practically the same cell volumes as the ternaries, and this indicates, that the binary compounds are stabilized by interstitial impurities, like carbon, nitrogen, and/or oxygen.

Similarly, the cell volumes of the binaries Ln3Al (Ln = Y, La, Ce, Pr) are only slightly smaller than those of the corresponding ternaries. Again, this can

<table>
<thead>
<tr>
<th>( \text{Sc}_3 \text{AlC} )</th>
<th>( \text{Sc}_3 \text{GaC} )</th>
<th>( \text{Sc}_3 \text{InC} )</th>
<th>( \text{Sc}_3 \text{TlC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Formula mass} )</td>
<td>173.86</td>
<td>216.60</td>
<td>261.70</td>
</tr>
<tr>
<td>( a \ [\text{pm}] ) (powder diffractometer)</td>
<td>449.81(1)</td>
<td>446.83(1)</td>
<td>453.68(1)</td>
</tr>
<tr>
<td>( V \ [\text{nm}^3] )</td>
<td>0.091010</td>
<td>0.089213</td>
<td>0.093379</td>
</tr>
<tr>
<td>( \text{Formal units/cell} )</td>
<td>3.17</td>
<td>4.03</td>
<td>4.65</td>
</tr>
<tr>
<td>( \text{Scanner range} \ [^\circ] )</td>
<td>30&lt;2θ&lt;100</td>
<td>15&lt;2θ&lt;85</td>
<td>15&lt;2θ&lt;90</td>
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<td>( \text{Number of data points} )</td>
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<td>3501</td>
<td>3751</td>
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<tr>
<td>( \text{Variable parameters} )</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>( \text{Residual (profile)} )</td>
<td>( R_p = 0.026 )</td>
<td>( R_p = 0.055 )</td>
<td>( R_p = 0.055 )</td>
</tr>
<tr>
<td>( \text{Weighted residual (profile)} )</td>
<td>( R_{wp} = 0.034 )</td>
<td>( R_{wp} = 0.043 )</td>
<td>( R_{wp} = 0.041 )</td>
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<tr>
<td>( \text{Residual (intensities)} )</td>
<td>( R_i = 0.022 )</td>
<td>( R_i = 0.009 )</td>
<td>( R_i = 0.022 )</td>
</tr>
<tr>
<td>( \text{Residual (structure factors)} )</td>
<td>( R_F = 0.012 )</td>
<td>( R_F = 0.007 )</td>
<td>( R_F = 0.013 )</td>
</tr>
</tbody>
</table>

Table II. X-ray crystallographic data of \( \text{Sc}_3 \text{MC} \) (\( M = \text{Al, Ga, In, Tl} \)).
be taken as an indication for considerable impurity contents of the “binaries”, since the cell volumes of these ternary carbides fit well to the general patterns of the cell volumes observed for the other ternary compounds. Buschow [40] reported La$_3$Al to crystallize with the hexagonal Mg$_3$Cd type structure. He also remarked that he was not successful in preparing a Cu$_3$Au type modification of this compound. It seems possible to grow metastable binary Cu$_3$Au type compounds once a nucleus of that structure is formed, which is stabilized by an interstitial impurity. The resulting, essentially binary crystals however, should eventually grow with the lattice constant expected for the binary phase.

The binary gallides La$_3$Ga, Ce$_3$Ga, Pr$_3$Ga, Nd$_3$Ga and Sm$_3$Ga are a special case. They are listed in Pearson's Handbook [41], but it is obvious from Fig. 2 that the cell volumes reported for these compounds are too large. This is difficult to rationalize, and indeed the compounds Ce$_3$Ga and Pr$_3$Ga could not be confirmed during the careful studies of the corresponding binary systems [42, 43]. More recently Corbett et al. [4] reported, that they could not prepare a compound La$_3$Ga with Cu$_3$Au type structure. A Cu$_3$Au type compound of the composition Nd$_3$Ga has been reported to exist in the binary system neodymium-gallium, however in that report is too small. A binary compound of this composition should have a lattice constant of about 490 pm.

The six ternary lanthanoid gallium carbides A$_3$GaC (A = Pr, Nd [15], Dy - Tm [17]) have been reported some time ago. However, the lattice constants listed in those reports are larger than those of the corresponding aluminum and indium compounds (Table I). With the present work we have confirmed these ternary gallium compounds and the lattice constants found by us are slightly smaller than those of the corresponding aluminum compounds. This is in agreement with the slightly smaller metallic radius for gallium (141 pm) as compared to that of aluminum (143 pm) [44].

A slight inconsistency is also found for the two series of ternary carbides A$_3$InC and A$_3$TIC. Generally, the ternary indium containing carbides have been reported with slightly larger lattice constants than the corresponding thallium compounds, and this is confirmed by us for most cases. Since the metallic radius of thallium is greater than that of indium, this is an indication that the two series of carbides do not have corresponding compositions. It seems possible that the carbon sites have different occupancies in the two series. Another possibility concerns the A/In and A/Tl ratios. Haschke, Nowotny and Benesovsky [17] had reported that

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**Fig. 3.** X-ray powder diagram of Sc$_3$TIC. CuKα$_1$ radiation; the difference between the observed and calculated intensities is also plotted.
they found differing lattice constants for the carbide with the ideal composition Nd$_3$InC, not only depending on the carbon content, but also depending on the initial Nd/In ratio of the sample.

The plot of the cell volumes (Fig. 2) also allows to draw some conclusions as to the valency of the rare earth components of the filled and unfilled Cu$_3$Au type phases. The cell volumes of Ce$_3$PbC, Ce$_3$SnC, Ce$_3$TlC, and Ce$_3$InC fit well between the values found for the corresponding lanthanum and praseodymium compounds, suggesting cerium to be trivalent in these carbides. In contrast, the cell volume of Ce$_3$AlC is smaller than that of Pr$_3$AlC, and this indicates a mixed +3/+4 valence for the cerium atoms. The europium compounds are all missing, obviously because europium prefers the divalent state. Ytterbium is trivalent in Yb$_3$InC, Yb$_3$GaC, and Yb$_3$AlC, whereas a mixed +2/+3 valence is indicated by the cell volumes of Yb$_3$PbC, Yb$_3$SnC, and Yb$_3$TlC.

Acknowledgements

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