PREPARATION OF NEODYMIUM DIGERMANIDE

K. A. Lynchak, T. Ya. Kosolapova, and Yu. B. Kuz'ma

Germanides of the rare-earth elements are among the least investigated inorganic compounds. Studies of germanides of these elements have consisted essentially in examining, by x-ray diffraction, products obtained by synthesis from the elements by the arc melting process [1-7].

Of considerable interest is the possibility of reducing oxides of the rare-earth elements with germanium, resulting in the formation of germanides and the volatile germanium monoxide:

\[ \text{Me}_2\text{O}_3 + 7\text{Ge} \rightarrow 2\text{MeGe}_2 + 3\text{GeO}. \]

The atoms of the rare-earth elements are characterized by the presence of deep-lying incompletely-filled \( f \)-electron states. The \( f \)-state electrons do not participate directly in the formation of chemical bonds, but may move into the \( d \)-states. The probability of this taking place decreases from cerium to gadolinium, and increases from gadolinium to lutecium [8]. Since the rare-earth elements generally have a valence of 3, these transitions will evidently take place according to the scheme:

\[ f^{3}\rightarrow f^{n}d^{5}. \]

In oxides of the rare-earth elements, the majority of which are described by the formula \( \text{Me}_2\text{O}_3 \), \( d \) and \( s \) electrons of the metal atoms are transferred to stabilize the electronic configuration \( s^2p^4 \) of the oxygen atom, which tends to establish the stable \( s^2p^5 \) configuration. Under these conditions, the metal atom attains the stable \( d^2 \)-state [9]. At the same time, some of the electrons of the metal atoms are expended on participation in covalent \( \text{Me}^+ \text{Me}^- \) bonds. In view of this, the number of collectivized electrons is negligible, the metal and oxygen atoms in the oxide sublattice are energetically isolated, and the \( \text{Me}^+ \text{O}^- \) bond is weak.

As a result of reaction between oxides of the rare-earth metals and germanium, the \( \text{Me}^+ \text{O}^- \) bonds are severed, and at the same time the \( d \) and \( s \) electrons of the metal are expended on stabilizing the \( sp^3 \) configuration of the germanium atoms, the formation of which is probable on account of \( s-p \) transition \( (s^2p^4 \rightarrow sp^3) \), and on establishing the \( \text{Me}^+ \text{Ge}^- \) bond; this is accompanied by the disturbance of the excited \( s^2p^5 \) states of the oxygen atoms as a result of reaction with germanium, giving rise to the formation of \( \text{GeO} \).

On the basis of this hypothesis, the present investigation was undertaken with the object of studying, on the

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Weight Loss, %</th>
<th>Composition, %</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd</td>
<td>Ge</td>
<td>Nd+Ge</td>
</tr>
<tr>
<td>Calculated composition</td>
<td>49.83</td>
<td>50.17</td>
<td>100</td>
</tr>
<tr>
<td>800</td>
<td>9</td>
<td>39.8</td>
<td>50.2</td>
</tr>
<tr>
<td>1000</td>
<td>8</td>
<td>33.4</td>
<td>56.6</td>
</tr>
<tr>
<td>1200</td>
<td>14.2</td>
<td>34.1</td>
<td>51.7</td>
</tr>
<tr>
<td>1300</td>
<td>25.1</td>
<td>28.3</td>
<td>46.6</td>
</tr>
<tr>
<td>1400</td>
<td>30.2</td>
<td>25.0</td>
<td>45.0</td>
</tr>
</tbody>
</table>

* The weight loss in calculation based on the formation of \( \text{NdGe}_2 \) is 31.4%.
example of neodymium digermanide, the conditions of preparation of rare-earth metal germanides by the process of reduction of oxides with germanium. Conducting the reaction in a vacuum over the temperature range 800-1400°C ensures the removal of the germanium monoxide evolved, which vaporizes at a temperature of 710°C.

The starting materials employed were single-crystalline germanium (99.99% Ge) and "ch" ("pure") grade neodymium oxide. A study was made of the influence of temperature, pressure in the system, charge composition, and holding time at the optimum temperature on the chemical and phase composition of the reaction products, which were subjected to chemical and x-ray diffraction analyses.* Analysis for neodymium was performed by complexonometric titration with trilon B solution, using "arsenazo" indicator; the germanium content was determined volumetrically by titrating mannite-germanic acid with caustic soda solution after forming a neodymium complex with trilon B solution.

The data in Table 1 show that, up to a temperature of 1200°C, the reduction proceeds very slowly. At a temperature of 1300°C, the reaction products contain, according to x-ray diffraction analysis, not only the digermanide, but also an unknown phase "A," which could not be identified, as well as metallic germanium.

It may be assumed that phase "A" is neodymium germanate. At a temperature of 1400°C, the reaction products contained only one phase, Nd₄Ge₃, whose formation was made possible by the evaporation of metallic germanium, as the result of which the product became enriched in the metal and its composition approached that of the Nd₄Ge₃ phase (calculated composition 76.8% Nd and 23.2% Ge). Evacuation of the system apparently promotes a rapid extraction of the evaporating germanium. In this connection, additional experiments were carried out at a pressure of 6.5-7.5·10⁻² mm Hg in the system, which gave the results presented in Table 2.

As can be seen from this table, the optimum process parameters for the preparation of neodymium digermanide are: a temperature of 1400°C, a pressure of the order of 6-7.5·10⁻² mm Hg, and a holding period of 1 h. The resulting product is fused.

In view of the volatility of germanium at the reaction temperatures, a study was made of the influence of an excess of germanium. It was found, however, that a germanium excess of up to 10% exerts no significant influence on the composition of the reaction products. At a 10% excess of germanium, the reaction products are deficient in the metal and enriched in germanium.

Experiments in which the holding period was varied (0.25, 0.50, and 1 h) established that 1 h is sufficient for complete reduction.

The particle size of the neodymium digermanide obtained by germanium-thermic reduction is finer than that of the digermanide produced synthetically from the elements by arc melting. The latter differs slightly also in chemical properties: thus, for instance, it is less resistant to attack by acids (HNO₃) and atmospheric oxygen.

**LITERATURE CITED**


*X-ray diffraction analysis was performed in the Inorganic Chemistry Department of the Lvov State University.