

## Low-Activation Solid-State Syntheses by Reducing Transport Lengths to Atomic Scales As Demonstrated by Case Studies on AgNO<sub>3</sub> and AgO

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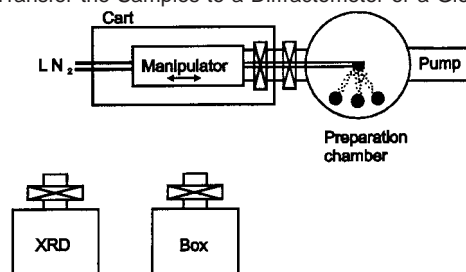
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Preparative solid-state chemistry is basically explorative in nature, and suffers from a peculiar lack of predictability.<sup>1–3</sup> This constitutes a marked contrast to most fields of molecular chemistry, in particular organic synthesis, where nowadays complicated and large molecules are accessible in directed syntheses.<sup>4,5</sup> The fundamental difference between solid-state and molecular syntheses is basically related to one particular complex issue, the transport of the reacting species. Conventional solid-state synthesis is based on reacting solid educt phases that, even after intense milling, are dispersed on a macroscopic scale compared to atomic distances, and thus reactions of solids are characterized by transport lengths of 1 to 10 μm. This is even more crucial when one recalls that the diffusion coefficients in the solid state typically range from 10<sup>–16</sup> to 10<sup>–12</sup> cm<sup>2</sup>/s.<sup>6</sup> These values are lower, or higher, respectively, by many orders of magnitude for reactions between molecules which, as a rule, are performed in homogeneous liquid or gaseous solutions. As a consequence, solid-state reactions require a high thermal activation, favoring thermodynamic control and thus formation of thermodynamically stable products, representing the global minimum of free enthalpy of the system under investigation at the given variables of state. Furthermore, due to the key role of transport properties a solid's reactivity depends not only on its chemical identity but quite crucially on the number and size of the lattice defects present, and thus on its pretreatment. These facts, though having always been taken into account during conventional solid-state syntheses, e.g. by employing specially activated educts, significantly hamper reproducibility and predictability in solid-state chemistry.

One option for straightforwardly overcoming those complications is to reduce the transport distances to atomic dimensions. This can be achieved by dispersing the components of the desired product on an atomic level and in an appropriate ratio. Such randomly “frozen” mixtures of atoms could serve as an ideal starting point for solid-state syntheses from atoms. Such a concept corresponds to simulate experimentally the approach of computational “simulated annealing”, which we have employed for predicting inorganic solids, capable of existence, and their crystal structures.<sup>2,3</sup> Here again the starting configuration is a random distribution of the constituting elements on an atomic scale. The respective energy landscape is then explored by global optimization and subsequently the minimum structures found are refined locally.<sup>7,8</sup> Comparing the results as obtained computationally and experimentally for the same system is expected to offer the opportunity to validate our long-term approach directed toward developing a tool for rationally planning and performing solid-state syntheses.

The experimental realization of the concept as outlined is based on an evaporation system consisting of an ultrahigh vacuum chamber that is equipped with five independent sources allowing for the generation of atomic gas-phase species via effusion cells,

**Scheme 1.** Stainless Steel Preparation Chamber Equipped with Different Sources (three effusion cells, an electron beam gun, a microwave plasma source), an UHV-Cryopump System, a Substrate Holder (cooled with LN<sub>2</sub>), and a Transfer System on Cart to Transfer the Samples to a Diffractometer or a Glovebox



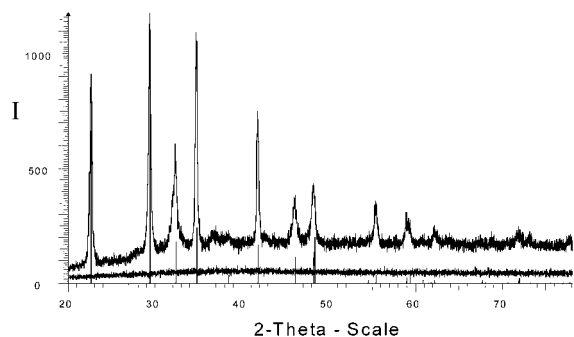
an electron beam gun, and a microwave plasma source (gas cracker), respectively. The gaseous species are simultaneously deposited onto a substrate that can be kept at temperatures ranging from 77 to 600 K. During the evaporation process, the flows from all sources are independently controlled, and residual gas species are monitored by mass spectrometry. The substrate bearing the samples can be transferred from the preparation chamber to a diffractometer or a glovebox (see Scheme 1), while maintaining vacuum and cooling, via a cart-top transfer system.

The Ag/O/N and Ag/O system were selected for testing the feasibility of our approach. In a typical run, silver and a mixture of O<sub>2</sub>/N<sub>2</sub> were co-deposited onto a sapphire substrate at 77 K. The X-ray diffraction pattern of a sample deposited at 77 K and measured directly at the same temperature does not show any Bragg reflections, see Figure 1. However, the powder pattern recorded after heating the sample to room temperature shows remarkably well-resolved reflections, and matches that of the high-temperature polymorph of silver nitrate (AgNO<sub>3</sub>, *hR30*<sup>9</sup>). The lattice constants were refined to *a* = 516.6(1) pm and *c* = 1663.9(3) pm (literature data:<sup>9</sup> *a* = 516(2) pm, *c* = 1658(2) pm).

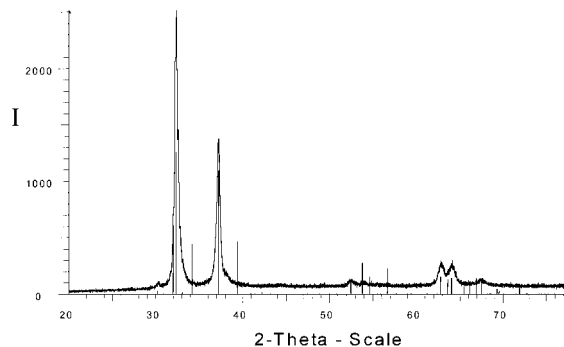
In another series of experiments silver has been co-deposited with oxygen onto a sapphire substrate at 298 K. The as-obtained dark-colored samples are shown to consist of silver(I,III) oxide (AgO, *mP8*<sup>10</sup>) by X-ray powder diffraction, see Figure 2. However, in contrast to the above study on HT-AgNO<sub>3</sub>, the pattern exhibits strong texture-dependent intensity deviations, indicating a pronounced preference of orientation of the (111) layer parallel to the substrate.

Upon assessing the results, the straightness of the approach appears to be a particularly noticeable feature. This becomes obvious when comparing this route to the cascade of steps needed to conventionally synthesize AgNO<sub>3</sub>, which includes production of ammonia from nitrogen (air separation) and hydrogen (decomposition of water) and its transformation to nitric acid along the lines of the industrial Ostwald process. Furthermore, the ease with which

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**Figure 1.** X-ray powder diffraction pattern of a Ag/O/N deposit; bottom, measured directly after deposition at 77 K; top, measured after heating to 298 K. Line pattern of silver nitrate (HT-polymorph).<sup>9</sup>



**Figure 2.** X-ray powder diffraction pattern of a Ag/O deposit measured at 298 K. Line pattern of silver(I,III) oxide.<sup>10</sup>

nitrogen is oxidized to the pentavalent state, which otherwise cannot be directly achieved, is amazing.

However, the most striking detail among the observations is the unprecedented low thermal activation needed to transform the solid educt mixtures into well crystalline product phases. The mild conditions allow for the synthesis of, e.g., a compound as labile as AgO in an all-solid state reaction, which so far had only been accessible through precipitation<sup>11,12</sup> or electrocrystallization<sup>10,13</sup> from cooled aqueous solutions. Thus, we feel that by the two studies presented it has been convincingly demonstrated that, by employing the setup presented, all-solid state reactions can be performed at temperatures as low as those usually applied in solution chemistry.

The main reason behind the remarkable readiness by which the reactions proceed appears to be the extremely finely dispersed educt mixtures used. By this, the transport lengths have been reduced to atomic dimensions, which has indeed been the underlying concept of our study. This is also the only way to understand the difference from the results of Johnson and co-workers<sup>14,15</sup> who, in a similar approach, have deposited the educt materials layer by layer. However, judging by the thicknesses applied (some nanometers), the boarder to macroscopic dimensions seems to have been reached, and rather high temperatures (450–800 K) have been required to achieve the reactions as desired.

In addition to the kinetic arguments mentioned, there is a thermodynamic aspect that contributes to the enhanced reactivity of the co-deposits used in our experiments. Since we do not start from the elements in their states at standard conditions the heat of reaction is increased by the energies of atomization, which are physically provided prior to the chemical reaction. This generally raises the driving force and, in particular, facilitates the access to metastable compounds.<sup>16</sup>

It appears to be a paradox that through a low-temperature synthesis the high-temperature polymorph of AgNO<sub>3</sub> has been obtained.

This raises the question of the selection mechanisms that determine which modification is actually formed. By employing differently orientated substrates we have ruled out any kind of epitaxial induction from the substrate surface to be presented. Most probably the selection occurs in the first step of the crystallization process, i.e., nucleation. According to Ostwald's, or Volmer's, rule,<sup>17</sup> the nuclei of lower density polymorphs reach their critical sizes the quickest at supersaturated conditions. Nucleation-controlled solid-state reactions have been studied in detail by Johnson et al.<sup>18,19</sup> To summarize, by dispersing educts for a solid-state reaction at an atomic level the transport distances can be reduced drastically. By using such starting mixtures solid-state reactions can be run at temperatures as amazingly low as room temperature, or even lower. This opens the door for the synthesis of thermally labile or metastable solids, and can be regarded as the experimental counterpart to computational approaches to rational design of solid-state synthesis.

**Experimental Section.** (i) Formation of silver nitrate: Ag (99,99% Heraeus, Hanau) was evaporated from a molybdenum crucible by using an electron beam gun at a deposition rate of 0.3 nm/min. The oxygen and nitrogen (purity 5.0; Westfalen, Münster) mass flows were controlled to 1.0 sccm O<sub>2</sub> and 0.3 sccm N<sub>2</sub> (ratio: 3.3:1). The gas mixture was streamed into the preparation chamber through a microwave plasma source (tectra, Frankfurt, 2.45 GHz, 50 mA). A sapphire substrate (random, both sides optical polished; TBL-Kelpin, Neuhausen) was cooled to liquid nitrogen temperature. The deposition process was run with a process pressure of  $4 \times 10^{-5}$  mbar for 5.5 h, and resulted in a layer thickness of ca. 100 nm. (ii) Formation of silver(I,III) oxide: Ag (0.45 nm/min) and oxygen (1.3 sccm) were deposited onto a sapphire substrate (details see above) at 298 K for 3 h. The obtained dark-colored samples have a layer thickness of ca. 100 nm. (iii) All X-ray powder diffraction patterns were measured on a  $\theta/\theta$  D8-advance powder diffractometer (Bruker AXS, Karlsruhe) with a parallel beam (Göbel mirror, Cu K $\alpha$ ) under vacuum ( $5 \times 10^{-7}$  mbar, incidence angle 2 to 10°, step 0.01°). The program Topas (Bruker AXS) was used for refinement of lattice constants.

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