

Chemical Transport and Optical Investigation of Oxides with Complex Anions

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Chemical transport reactions are an efficient preparative method for the crystallization of a variety of inorganic phases. Especially for compounds that are characterized by high melting temperatures or complete disintegration as well as high disintegration pressures close to the melting point, chemical transport represents an alternative to crystal growth using the liquefied material.

The principles of the transport of oxides with complex anions will be illustrated by means of two examples. Both BPO_4 and rare earth vanadates (V) are of special interest for optical measurements as will be demonstrated for BPO_4 in some detail.

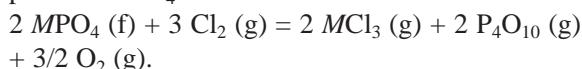
Chemical Transport of BPO_4

Investigations of the chemical transport of phosphates reveal a broad applicability of transport reactions for synthesis and, in particular, for crystallization of this class of compounds [1-3]. In addition to the use of the halogen elements chlorine, bromine and iodine, halides like NH_4X or HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) but also phosphorus-halogen mixtures P/X_2 are suitable [1-3] as a means of transport.

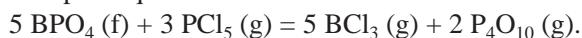
In order to investigate the transport behavior of anhydrous BPO_4 , iodine-phosphorus mixtures I_2/P and PCl_5 were used as transport media. Starting from microcrystalline BPO_4 powder the transport reactions took place in evacuated quartz glass ampoules as endothermic transport from higher to lower temperature. By means of chemical transport using PCl_5 it was possible to obtain BPO_4 in a temperature gradient of 1123 K to 1023 K as colorless, transparent crystals, which display a very strong tendency to form multiple twins. In order to improve the crystal quality of BPO_4 for use in further investigations, deposition took place on a glass carbon target.

In course of a series of investigations concerning the chemical transport of phosphates with chlorine, it was shown [2] that P_4O_{10} (g) can be regarded as the essential phosphorous-transmitting gas particle. Further thermodynamic observations [2] provided

the basis for the conclusion that phosphorous oxide chlorides POCl_3 (g) or PO_2Cl (g) [4] do not provide any crucial contribution to the transport of the phosphates, since the ratio of $p(\text{P}_4\text{O}_{10})$ to $p(\text{POCl}_3)$ is 278:1 for $p(\text{P}_4\text{O}_{10}) = p(\text{Cl}_2) = 1.013 \cdot 10^5 \text{ Pa}$ at 1273 K. Accordingly, the following general transport equation may be formulated for phosphates of the composition MPO_4 :



The chemical transport of BPO_4 with PCl_5 can be described by means of the following essential transport equation:



Due to the relatively high stability of BCl_3 (g) any notable formation of BCl_2 (g) or BCl (g) is impeded.

By means of an evaluation of the thermodynamic data of the transport reaction and of the species involved in the reaction the observed transport behavior can be described theoretically.

Based on the data of AlPO_4 and FePO_4 the following data for BPO_4 is estimated:

$$\Delta H^\circ(\text{BPO}_4, \text{f}, 1100) = -1413.765 \text{ kJ/mol}$$

$$S^\circ(\text{BPO}_4, \text{f}, 1100) = 244.997 \text{ J/mol K}$$

$$\Delta G^\circ(\text{BPO}_4, \text{f}, 1100) = -1683.253 \text{ kJ/mol}.$$

In combination with the values obtained from literature data, the parameters characteristic of a thermodynamic description of the transport reaction are obtained:

$$\Delta H_{\text{R}, 1100} = 807.136 \text{ kJ/mol}$$

$$\Delta S_{\text{R}, 1100} = 613.846 \text{ J/mol K}$$

$$\Delta G_{\text{R}, 1100} = 131.638 \text{ kJ/mol}.$$

Based on the free reaction enthalpies and according to

$$\Delta G_{\text{R}} = -R \cdot T \ln K_P$$

for the given transport equation, an equilibrium constant of $K_p = 5.4 \cdot 10^{-7}$ is obtained.

The clearly positive reaction enthalpy reflects the endothermic transport and thereby the transport direction of T_2 to T_1 as observed during the course of experiments.

In addition to the reversibility of the reactions and the existence of a potential gradient, an essential precondition for transport reactions is a bal-

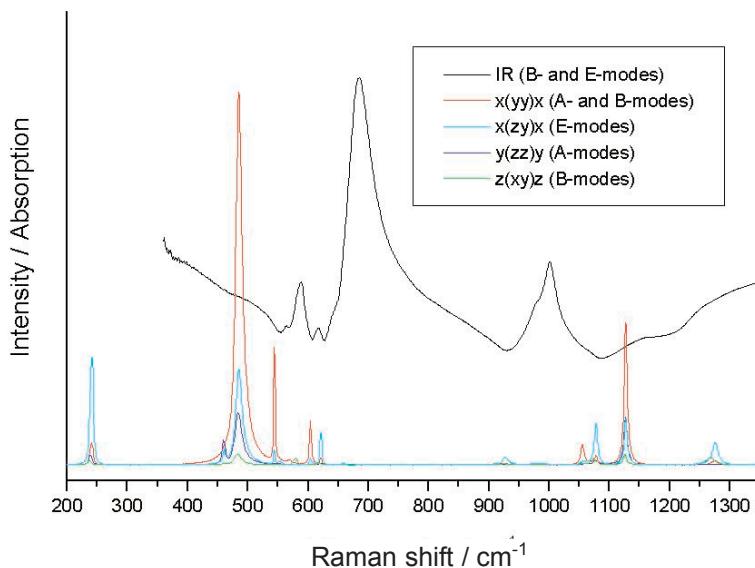


Fig. 2: Powder infrared- and polarized Raman-spectra of an oriented BPO_4 single crystal

possible modes were detected and the mode symmetry could be determined. Theoretical *ab initio* calculations of the vibrational modes are in progress to confirm the symmetry of those modes with weak intensities.

Crystal growth of rare-earth vanadates(V)

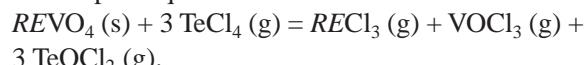
As an example for the chemical transport of rare earth containing compounds, crystal growth via the gaseous phase of rare-earth vanadates(V), which are of particular interest due to their optical properties, will be discussed.

In 1981, Matsumoto et al. [6] described the crystallization of YVO_4 at temperatures around 1273 K using telluric chloride. Although a detailed thermochemical investigation of the transport behavior

was not performed, the information given in their study is of some fundamental use.

Starting with polycrystalline powders, a series of rare earth vanadates of the general composition REVO_4 ($\text{RE} = \text{Pr, Nd, Sm, Tb, Dy, Ho}$) can be obtained in the form of well developed crystals by chemical transport at $T_2 = 1373$ K and $T_1 = 1223$ K using telluric chloride as a means of transport (Fig. 3).

Based on the experimental results and using preliminary thermodynamic considerations, the endothermic transport behavior observed in rare earth vanadates may be attributed to the following general transport equation:



It is assumed, that the rare earth component is transported as the corresponding trichloride and the vanadium component, in analogy to V_2O_5 , via $\text{VOCl}_3(\text{g})$ [7]. By using telluric chloride instead of chlorine as a means of transport, the formation of $\text{TeOCl}_2(\text{g})$ is enabled resulting in a decrease of the oxygen partial pressure in comparison to transport with pure chlorine. As a secondary effect, the formation of rare earth oxide halides is prevented.

General transport behavior of rare-earth vanadates(V) can be described thermodynamically for TbVO_4 since variation of the rare earth element merely influences the thermodynamic data of the respective solid vanadate and the corresponding gaseous rare-earth trichloride whereas all other species and their thermodynamic data remain



Fig. 3: NdVO_4 crystal (length 4 mm) obtain by chemical transport.

range of -100 kJ/mol to 100 kJ/mol this requirement is fulfilled for transport reactions which are characterized by an independent reaction equation. In contrast, the value of the free reaction enthalpies for the investigated reaction seems to be relatively high. However, if the correlation between equilibrium constants and partial pressures of the individual species

$$K_p = p^5(\text{BCl}_3) \times p^2(\text{P}_4\text{O}_{10}) / p^3(\text{PCl}_5)$$

is considered and if a pressure of the transporting agent of

$$p(\text{PCl}_5) = 1.013 \times 10^5 \text{ Pa}$$

is assumed, then transport-effective partial pressures which are distinctly above 1 Pa are produced for both BCl_3 (g) and P_4O_{10} (g). Hence, the chemical transport of BPO_4 with PCl_5 is obvious and can be described relatively well by the given essential transport equation.

These investigations concerning the chemical transport of BPO_4 represent the starting point for further transport experiments as a result of which it was possible to obtain substantially more complex borophosphates such as $\text{Cr}_2\text{BP}_3\text{O}_{12}$. The transport took place with iodine as an endothermic process at $T_2 = 1373 \text{ K}$ to $T_1 = 1273 \text{ K}$. Thus, it was possible to obtain $\text{Cr}_2\text{BP}_3\text{O}_{12}$ as well-developed dark-green crystals at a very small transport rate (approx. 1 mg/day).

Crystal structure and optical spectroscopy of BPO_4

The crystal structure of BPO_4 was refined by means of single crystal X-ray diffraction data. BPO_4 crystallizes in the non-centrosymmetric space group $I\bar{4}$. The unit cell ($a = 434.04(1) \text{ pm}$; $c = 665.02(2) \text{ pm}$) contains two formula units. The B atoms occupy the $2d$, the P atoms the $2a$ position. The O atoms are located at $8g$ ($0.8595(2)$, $0.7421(2)$, $0.8729(1)$). Each B and P atom is tetrahedrally coordinated by four O atoms. The tetrahedra are condensed via common vertices to form a three-dimensional network. Within this framework $\text{BO}_{4/2}$ tetrahedra are exclusively linked to $\text{PO}_{4/2}$ building units and vice versa (Fig. 1).

Infrared and Raman measurements of BPO_4 have been reported earlier but a full assignment of the mode symmetry has not been performed. Here, polarized Raman measurements on a BPO_4 single crystal as well as infrared measurements on powder samples are presented.

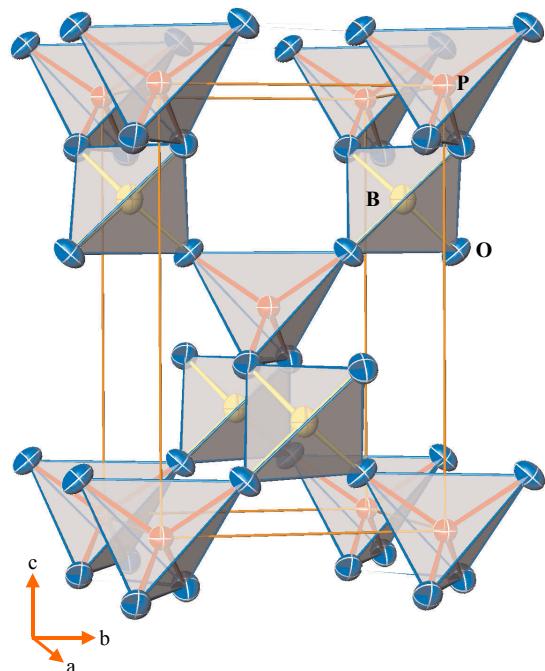


Fig. 1: Polyhedra representation of BPO_4 showing the three-dimensionally linked tetrahedral building units.

According to a group theoretical analysis BPO_4 shows 13 modes [5]. The modes and the atoms involved in the vibrations are listed below. Out of these one B and one E mode are acoustic ones and hence, they can not be observed in our measurements.

Atoms	Modes
B	$B \oplus E$
P	$B \oplus E$
O	$3A \oplus 3B \oplus 3E$
total	$3A \oplus 5B \oplus 5E = 13 \text{ modes}$

The frequency of optical vibrations is dependent on the mass of the involved atoms as well as on the force constants. Due to the natural abundance of ^{10}B and ^{11}B (1:4), such modes where displacements of boron atoms are involved will show at two frequencies. Thus, two additional modes ($B \oplus E$) are expected leading to a total of $3A \oplus 5B \oplus 5E$ modes. However, since the space group does not contain an inversion center as a symmetry element, the LO/TO-splitting of the B - and E -modes is visible in the Raman spectra. This gives a total of $3A \oplus 5B_{LO} \oplus 5B_{TO} \oplus 5E_{LO} \oplus 5E_{TO} = 23$ modes.

In the infrared experiment, only the B - and E -modes are active while in the Raman experiment all modes are active. Polarized Raman spectra and the powder infrared spectrum are shown in Fig. 2. All

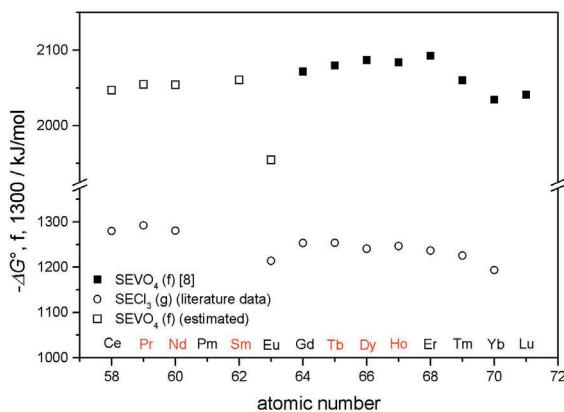


Fig. 4: Comparison of the free enthalpies of the solid rare-earth vanadates and of the gaseous rare-earth trichlorides.

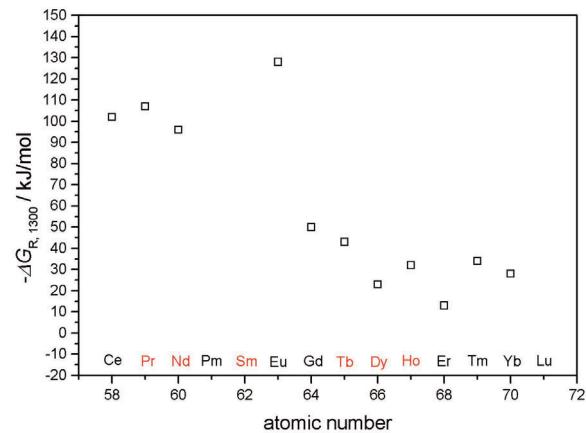
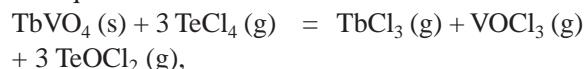


Fig. 5: Free reaction enthalpy for general transport equation:
 $\text{REVO}_4(\text{s}) + 3\text{TeCl}_4(\text{g}) = \text{RECl}_3(\text{g}) + \text{VOCl}_3(\text{g}) + 3\text{TeOCl}_2(\text{g})$.

unchanged. Comparison of the free enthalpies of the solid rare earth vanadates and of the gaseous rare earth trichlorides (Fig. 4) shows a relatively small variance of the data for the various rare-earth compounds; the difference of the free enthalpies of the solid rare earth vanadates and of the gaseous rare earth trichlorides of an element increases with increasing nuclear charge. The resulting decrease of the free reaction enthalpy for the given general transport equation (Fig. 5) is well in accordance with experimentally observed strong decline of transport rates of the terbium, dysprosium or holmium vanadates in comparison to the praseodymium or neodymium vanadates.

For the chemical transport of TbVO_4 we obtain for the equilibrium



by using the provided thermodynamic data (Table 1) a clearly positive reaction enthalpy of $\Delta H_{R, 1300 \text{ K}} = 394.1 \text{ kJ/mol}$, correlating with the recorded endothermic transport behavior.

Reaction entropy and free reaction enthalpy results in $\Delta S_{R, 1300 \text{ K}} = 363.3 \text{ J/mol K}$ or $\Delta G_{R, 1300 \text{ K}} = -43.1 \text{ kJ/mol}$, respectively.

	$\text{TbVO}_4(\text{s})$	$\text{TeCl}_4(\text{g})$	$\text{TbCl}_3(\text{g})$	$\text{VOCl}_3(\text{g})$	$\text{TeOCl}_2(\text{g})$
$\Delta H^\circ_{1300 \text{ K}}$ [kJ/mol]	-1592.7	-111.5	-606.4	-597.4	-109.8
$S^\circ_{1300 \text{ K}}$ [J/mol K]	347.6	535.9	498.2	488.6	443.9
$\Delta G^\circ_{1300 \text{ K}}$ [kJ/mol]	-2079.7	-808.1	-1254.1	-1232.6	-686.8

Table 1: Thermodynamik data for the chemical transport reaction of TbVO_4 with TeCl_4 .

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