Intercalation of 1,2-alkanediols into Vanadyl and Niobyl Phosphate

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Abstract. Intercalation compounds of $VOPO_4$ and $NbOPO_4$ with 1,2-alkanediols (from C3 to C16) have been prepared. The diol molecules are placed between host layers in a bimolecular way with their aliphatic chains tilted at an angle of $70°$. It was found that the intercalates contain 1.5 molecules of diol per formula unit. Three ways of bonding of the diol molecules to the host layers are proposed. Two molecules of diol are coordinated to the metal atoms by their first and second oxygen, respectively. The third diol molecule is anchored in the interlayer space by H-bonds.

Key words: vanadyl phosphate, niobyl phosphate, intercalation, alkanediols.

1. Introduction

Vanadyl phosphate forms a number of intercalation compounds with molecular guests having Lewis base character (for example aliphatic and aromatic amines [1–5], heterocycles [5–8], carboxylic acids and their derivatives [9, 10]). Aliphatic alcohols are also examples of such guests.

The interactions of alcohols with this host were first studied by Ladwig [11] and in more detail by Beneš *et al.* [12]. Intercalates with the composition $VOPO_4 \cdot 2C_nH_{2n+1}OH$ were prepared by the reaction of the anhydrous host with an excess of liquid alcohol. No alcohols longer than butanol can be intercalated by this method. Longer alkanols (up to C_{18}) can be intercalated by the reaction of $VOPO_4 \cdot 2H_2O$ with liquid or molten solid alkanols in a microwave field [13]. The structure of all these polycrystalline complexes retains the original layers of $(VOPO_4)_\infty$. The molecules of alcohols are placed between the host layers in a bimolecular arrangement, being anchored to them by donor-acceptor bonds between the oxygen atom of the OH group and the vanadium atom as well as by a hydrogen bond. The aliphatic chains of the alcohol molecules possess an *all-trans* configuration and their axes are perpendicular to the host layers.

The direct reaction of $VOPO_4 \cdot 2H_2O$ with liquid or molten 1,ω-alkanediols (C_2-C_{10}) in a microwave field leads to layered complexes with composition $VOPO_4 \cdot C_nH_{2n}(OH)_2$ [13]. The diol molecules form bonds similar to those of the

alcohol molecules and are arranged as monomolecular bridges linking the adjacent layers of the host.

Recently, similar complexes of niobyl phosphate and arsenate with 1-alkanols and 1,ω-alkanediols have been studied [14]. In this case, the aliphatic chains of both guest types are tilted to the host layers.

This present report gives results of studies of intercalation of 1,2-alkanediols into the vanadyl and niobyl phosphates.

2. Experimental

Vanadyl phosphate dihydrate and niobyl phosphate trihydrate were synthesized as previously described [15, 16]. Intercalates of both hosts with all diols were prepared by a reintercalation reaction. The solid propanol intercalated hosts [13, 14] were prepared in advance and used as a starting material for the reactions with diols. Intercalates of $VOPO_4$ were obtained by a long-lasting contact of $VOPO_4 \cdot 2C_3H_7OH$ with an acetonitrile solution of the corresponding diol. The intercalates of $NbOPO_4$ were prepared by suspending microcrystalline $NbOPO_4 \cdot 2C_3H_7OH$ in dry liquid or melted diol. This reaction mixture was exposed to a microwave field for about 10 min. The solid product formed was filtered off. All samples for X-ray diffraction analyses were left with a small residue of the respective diol. The samples for TG-DTA and elemental analyses were washed with dry acetonitrile or diethylether and dried at room temperature.

The microwave apparatus used for preparing the complexes was especially constructed by Radan Ltd. Pardubice, Czech Republic. It operates at a frequency of 2450 ± 30 MHz with a total generator output of 800 W out of which 30 to 50 W is absorbed by the reaction mixture. The metal waveguide with a square cavity (5.2 $\times$ 5.2 cm) is equipped by an opening of 2 cm diameter which serves for locating the reaction vessel into the waveguide axis.

The powder data of the intercalates with a minor surplus of the guest diol were obtained with an X-ray diffractometer (HZG-4, Germany) using $CuK\alpha1$ radiation ($\lambda = 1.54051$ Å) with discrimination of the $CuK\beta$ by a Ni-filter. The $CuK\alpha2$ intensities were removed from the original data. Silicon ($a = 5.43055$ Å) was used as internal standard. Diffraction angles were measured from 1.5 ° to 50 ° (2Θ). The obtained data were refined by the least squares program minimizing $(2\Theta_{exp} - 2\Theta_{calc})^2$. Temperature measurements (from 22 to 240 °C) were carried out on a heated corundum plate with a thermocouple [17]. Each diffractogram was measured at constant temperature and a cycle of heating and measuring lasted about 20 min.

The TGAs of the intercalates were performed with a Derivatograph MOM (Hungary), the measurements being carried out in the temperature interval of 30–600 °C in air at a heating rate of 5 °C/min. The weight of the samples was 100 mg. In some cases, particularly for complexes of solid diols, the composition was determined by elemental analysis (C, H).

Table I. Lattice parameters of intercalates of VOPO$_4$ and NbOPO$_4$ with 1,2-alkanediols

Guest	VOPO$_4$		NbOPO$_4$	
	a [Å]	c [Å]	a [Å]	c [Å]
1,2-propanediol	6.21	12.98	6.47	13.19
1,2-butanediol	6.21	15.43	6.45	15.28
1,2-pentanediol	6.20	17.52	6.45	18.16
1,2-hexanediol	6.21	20.78	6.46	20.59
1,2-octanediol	6.20	24.80	6.46	24.92
1,2-decanediol	6.21	29.89	6.46	29.31
1,2-dodecanediol	6.20	34.10	6.47	34.47
1,2-tetradecanediol	6.21	39.91	6.46	39.88
1,2-hexadecanediol	–	–	6.45	44.20

Infrared spectra were recorded on a Bio-Rad FTS spectrometer with a spectral range of 4000–500 cm^{-1} using dry KBr powder containing 10% of the intercalate. The resultant reflectance spectra were converted into Kubelka–Munk format.

3. Results and Discussion

In contrast to 1,ω-alkanediols [13] pure intercalates of VOPO$_4$ with 1,2-alkanediols cannot be directly prepared by replacing water molecules in VOPO$_4 \cdot$2H$_2$O in a microwave field. Therefore the previously described reintercalation of VOPO$_4 \cdot$2C$_3$H$_7$OH with an excess of liquid or molten diols was chosen as a method of preparation. The intercalates prepared are yellow, well crystalline products. Their diffractograms show the set of (00l) reflections which determine the lattice parameter c very precisely. The lattice parameter a of the tetragonal cell is determined by a very weak (200) reflection. Other diffraction lines, i.e., (hk0) and (hkl) were usually not observed.

The intercalates of 1,2-alkanediols with isostructural NbOPO$_4$ were similarly prepared by substituting propanol molecules in NbOPO$_4 \cdot$2C$_3$H$_7$OH for diol molecules. The intercalates are well crystalline white powders. Besides the set of the (001) lines, their diffractograms usually contain the (110) and (200) reflections and only exceptionally the (hkl) reflections. The presence of the (hk0) and the absence of the (hkl) reflections in the intercalates is characteristic of a turbostratic structure. In this structure, the original tetragonal layers of the hosts are retained but shifted in the directions of the x and/or y axes. The lattice parameters are given in Table I. The examples of the diffractograms of the intercalates studied are shown in Figure 1.
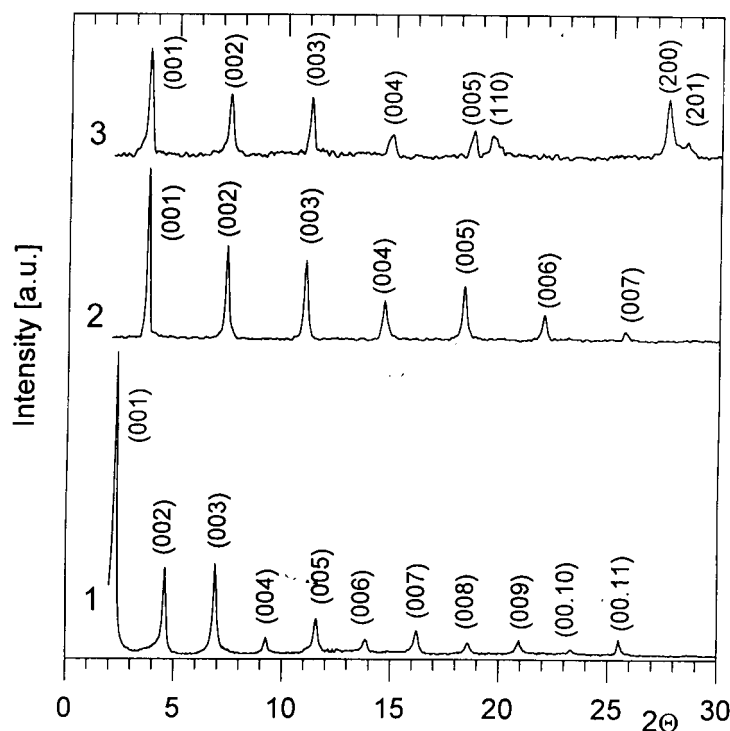
Figure 1. Diffractograms of VOPO$_4$ intercalated with 1,2-tetradecanediol (1), 1,2-octanediol (2) and NbOPO$_4$ intercalated with 1,2-octanediol (3).

As inferred from the thermogravimetric and elemental analyses, the intercalates have a general formula MOPO$_4$·xG (M = V, Nb; G = 1,2-alkanediol) with the coefficient x equal to 1.53 ± 0.15 for both hosts. For comparison, the value of this coefficient is $x = 1$ and $x = 2$ when the guest molecules G are 1,ω-alkanediols and 1-alkanols [13, 14], respectively. As both starting propanol intercalates, VOPO$_4$·2C$_3$H$_7$OH and NbOPO$_4$·2C$_3$H$_7$OH, do not contain water [12, 14], the presence of water molecules in the interlayer space of the products can be excluded.

In contrast to 1,ω-alkanediols, which are stable in air for several hours to days, 1,2-alkanediols undergo decomposition (reintercalation of water to the corresponding hydrate) in tens of minutes. Generally, the VOPO$_4$ intercalates are more stable than the NbOPO$_4$ intercalates.

The results of thermogravimetric analysis and the thermal dependence of the basal spacing of the NbOPO$_4$·1.5C$_4$H$_{10}$O$_2$ intercalate are given in Figure 2. As can be seen from the TG analysis, 1,2-butanediol is released in two steps. The total weight loss corresponds to the presumed stoichiometric coefficient. The decrease of the basal spacing is observed at a considerably lower temperature than that corresponding to the weight loss. The basal spacing is almost constant up to 80 °C. At 100–125 °C, diol is released from the interlayer space as evident from the steep
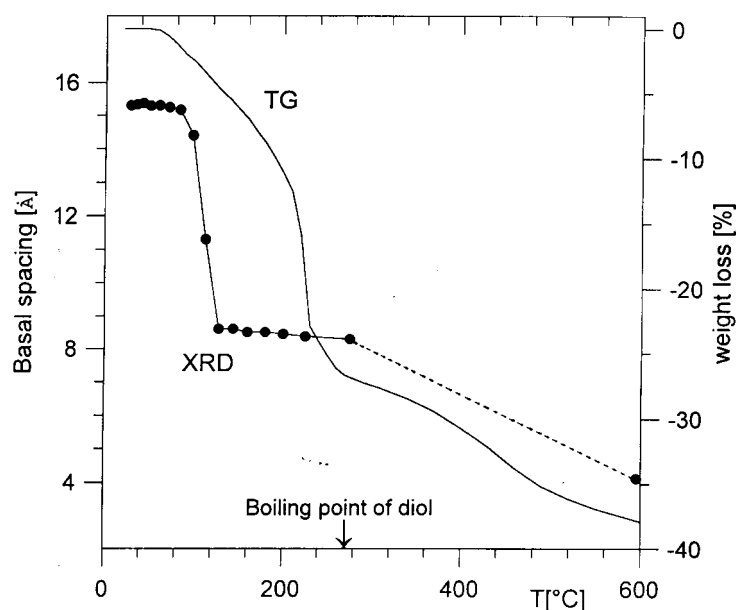
Figure 2. Thermal decomposition of 1,2-butanediol intercalated $NbOPO_4$ followed by XRD and thermogravimetry.

decrease of the basal spacing. This phenomenon is accompanied by a broadening of the (00l) diffraction lines, which is caused by a disorder of the regular stacking of the layers. The corresponding weight loss in the TGA curve occurs at a higher temperature close to the boiling point of 1,2-butanediol (235 °C). This weight loss corresponds exactly to the release of one diol molecule from the intercalate. The product contains a half molecule of diol per formula unit and has a basal spacing of 8.5 Å which is practically constant up to 240 °C. On further heating, the sample turns gray to black due to the pyrolysis of the remaining diol. White anhydrous niobyl phosphate (c = 4.12 Å) is formed by calcination at 600 °C in air. The slow decrease of weight in the region 240–600 °C corresponds to this process.

The infrared spectrum of the intercalate (Figure 4) shows bands characteristic of alcohol intercalates. In the region 3000 to 3500 cm^{-1}, a typical set of broad bands corresponding to OH group vibrations is observed. The widths and positions of the bands are influenced by the mutual interactions of the guest molecules and by the interactions of the OH groups with the lattice of the host. All the intercalates show C-H stretching bands in the 2850 to 2960 cm^{-1} region. The spectra of the $VOPO_4$ intercalates contain the ν(V=O) band in the region 1000–1020 cm^{-1}, overlapping the intense bands of the PO_4 tetrahedron. This indicates the presence of a donor-acceptor bond between an oxygen atom of the diol and the vanadium atom. In the case of $NbOPO_4$ compounds, the ν(Nb=O) band is completely overlapped by the bands of the PO_4 group.
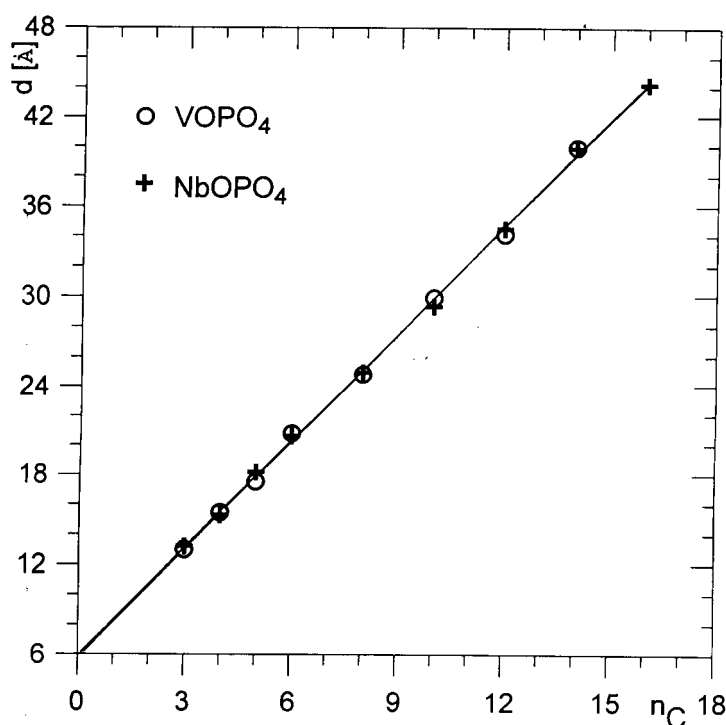
Figure 3. Basal spacing of the intercalates prepared as a function of the number of carbon atoms in the aliphatic chain of 1,2-alkanediols.

The observed basal spacings of the intercalates of both hosts with 1,2-alkanediols as a function of the length of the alkyl chains of the diols are given in Figure 3. Both dependencies are strictly linear with the slopes of the lines corresponding to the increments of the basal spacing $\Delta c/\Delta n$ caused by an elongation of the alkyl chain of the guest by one carbon. This increment is 2.40 Å and 2.41 Å for the intercalates of 1,2-alkanediols into $VOPO_4$ and $NbOPO_4$, respectively. From $\Delta c/\Delta n$, the inclination α of the carbon chain to the host layer can be calculated according to Equation 1 [18, 13]

$$\Delta c/\Delta n = m(\Delta h/\Delta n)\sin\alpha,$$

where m is the number of the guest layers in the interlayer space and $\Delta h/\Delta n$ = 1.28 Å is the increment of the basal spacing calculated for the aliphatic carbon chain in an *all-trans* conformation perpendicular to the host layer. According to the value of $\Delta c/\Delta n$, the arrangement of the guest molecules can be divided into the following groups: (i) $\Delta c < 1.28$ Å when the carbon chains of the guest molecules are tilted at an angle α to the host layers and the guest molecules form a monomolecular layer, as observed in 1,ω-alkanediols intercalated $NbOPO_4$ and $NbOAsO_4$ [14]. (ii) $\Delta c/\Delta n = 1.28$ Å when the layers are interconnected by monomolecular layers of perpendicularly arranged diol molecules.
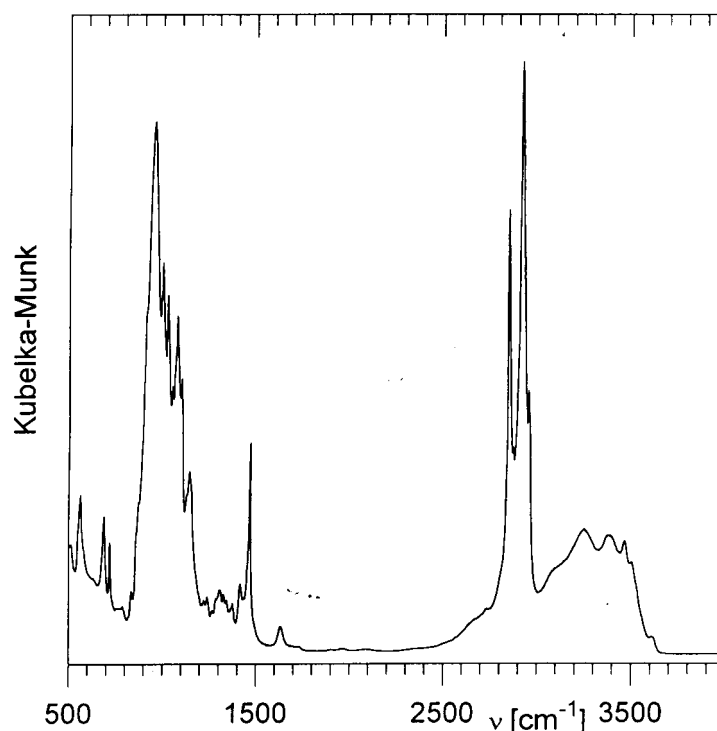
Figure 4. IR spectrum of $VOPO_4$ intercalated with 1,2-butanediol.

This is the case for 1,ω-alkanediols intercalated $VOPO_4$. (iii) $\Delta c/\Delta n = 2.56$ Å is typical of a bimolecular arrangement with the guest molecules perpendicular to the host layer, e.g., 1-alkanol intercalated $VOPO_4$ [13]. (iv) $\Delta c/\Delta n > 1.28$ Å indicates a bimolecular arrangement of the guest in the interlayer space with the chains tilted at an angle α to the host layers. This arrangement was observed in 1-alkanol intercalated $NbOPO_4$ and $NbOAsO_4$ [14]. As inferred from the use of Equation 1 for the prepared intercalates the 1,2-alkanediol molecules are placed in the interlayer space of $MOPO_4$ in a bimolecular way with the alkyl chain oriented at $\alpha = 70°$ to the host layers.

The bilayer arrangement indicates that the 1,2-alkanediol molecules are placed in a way somewhat similar to that found for the alcohol intercalates, i.e., with functional hydrophilic OH groups close to the $VOPO_4$ layers and with the alkyl group extending into the interlayer space. The intercalates contain 1.5 molecules of the diol per formula unit. The host/guest molar ratio (2/3) suggests that the arrangement of the diol molecules in the interlayer space is more complicated in comparison with 1,ω-alkanediols and 1-alkanols. Similar to the alcohol intercalates, we can presume that a part of the guest molecules is coordinated by its oxygen to vanadium atoms of the $VOPO_4$ layer. 1,2-Alkanediols can be coordinated to the vanadium atoms either by the first (O1) or by the second (O2) oxygen of the hy-
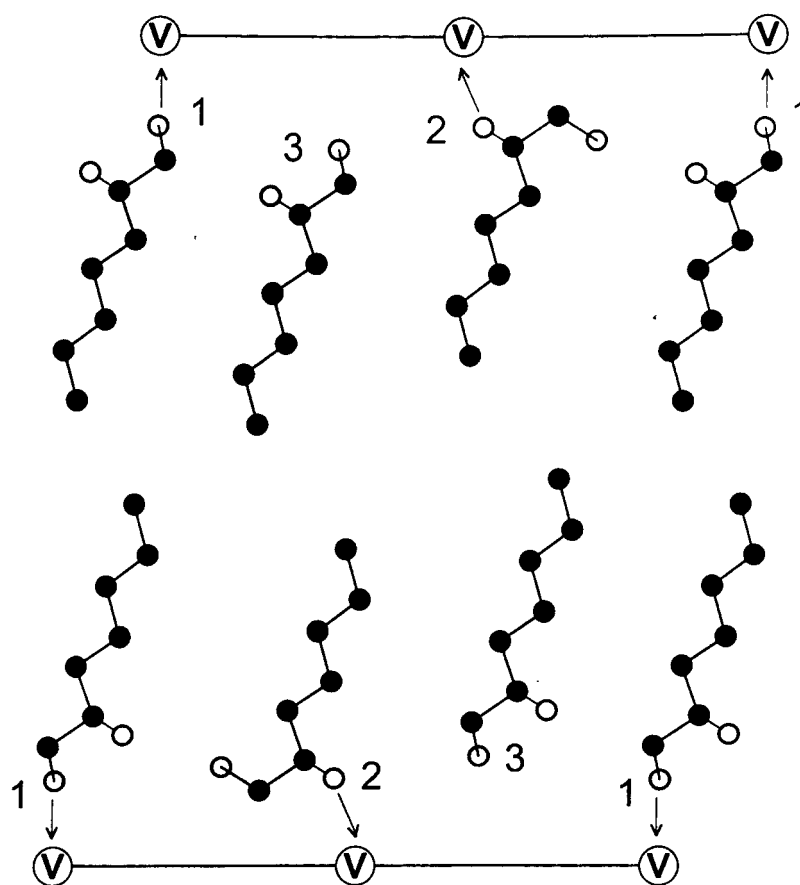
Figure 5. Coordination of the 1,2-alkanediol molecules to the $VOPO_4$ layer. Open circles – oxygen, full circles – carbon atoms. Hydrogen atoms are omitted. (1) diol molecules coordinated to vanadium by O1; (2) diol molecules coordinated to V by O2; (3) diol molecules anchored by weak H-bonds.

droxy groups. We assume that pairs of the intercalated guest molecules are formed with one of them being bonded by its O1 to one vanadium atom and the second by its O2 to a neighboring vanadium (Figure 5). The space between these two guest molecules in the pair is filled by their free OH groups which mutually interacts by H-bonds. Such an arrangement generates a space between these pairs so that another molecule of the diol can be bonded by its OH group to the oxygens of the $VOPO_4$ layers. The motif formed is composed of three guest molecules per two vanadium atoms of the host layer. The orientation of these chains can vary so that a turbostratic structure is formed. Due to the similarity in the stoichiometry and the basal spacing between vanadyl and niobyl phosphate intercalates, the same structure is presumed for the niobyl phosphate intercalates.

Acknowledgement

References

1. K. Beneke and G. Lagaly: *Inorg. Chem.* **22**, 1503 (1983).
2. L. Beneš, R. Hyklová, J. Kalousová, and J. Votinský: *Inorg. Chim. Acta* **177**, 71 (1990).
3. H. Nakajima and G. Matsubayashi: *Chem. Lett.* **423** (1993).
4. N. Kinomura, T. Toyama, and N. Kumada: *Solid State Ionics* **78**, 281 (1995).
5. A. De Stefanis, S. Foglia, and A. A. G. Tomlinson: *J. Mater. Chem.* **5**, 475 (1995).
6. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich: *Inorg. Chem.* **21**, 3820 (1982).
7. A. De Stefanis, and A. A. G. Tomlinson: *J. Mater. Chem.* **5**, 319 (1994).
8. T. Yatabe and G. Matsubayashi: *J. Mater. Chem.* **6**, 1849 (1996).
9. L. Beneš, J. Votinský, J. Kalousová, and K. Handlíř: *Inorg. Chim. Acta* **176**, 255 (1990).
10. M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, S. Bruque-Gamez, and A. Rodriguez-Garcia: *Mat. Res. Bull.* **21**, 13 (1986).
11. G. Ladwig: *Z. Anorg. Allg. Chem.* **338**, 266 (1965).
12. L. Beneš, J. Votinský, J. Kalousová, and J. Klikorka: *Inorg. Chim. Acta* **114**, 47 (1986).
13. L. Beneš, K. Melánová, V. Zima, J. Kalousová, and J. Votinský: *Inorg. Chem.* **36**, 2850 (1997).
14. L. Beneš, K. Melánová, V. Zima, and J. Votinský: *J. Solid State Chem.* **141**, 64 (1998).
15. G. Ladwig: *Z. Chem.* **19**, 368 (1979).
16. S. Bruque, M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, B. Casal, and E. Ruiz-Hitzky: *Inorg. Chem.* **26**, 847 (1987).
17. L. Beneš: *Sci. Pap. Univ. Pardubice Ser. A* **2**, 151 (1996); *Chem. Abstr.* **126**, 310616v (1997).
18. G. Lagaly: *Angew. Chem., Int. Ed. Engl.* **15**, 575 (1976).