In Search for Rare-Earth Borophosphates

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In search for compounds with new crystal structures and interesting chemical and physical properties the exploration of the systems MO_x – B_2O_3 – P_2O_5 – (H_2O) (MO_x = metal oxide) has proven to be extremely successful [1]. Numerous compounds have already been synthesized with an amazing structural variety that originates from the unique arrangement of isolated tetrahedral (BO_4 and PO_4) and trigonal planar (BO_3) units and/or the condensation between them by forming complex borophosphate anions. Such anions can favorably be employed to tailor the physical properties of the resulting compounds, as is schematically shown in Figure 1. As an example M_2O_9 dimers are considered that consist of two face-sharing transition-metal centered octahedra. In perovskites the M_2O_9 units are directly interconnected to form a three-dimensional arrangement. The introduction of diphosphate groups allows for a separation of these dimeric units. This sepation can be increased further by incoporating the more complex borophosphate anions containing boron in three- and phosphorous in fourfold coordination.

So far, this general concept has been successfully developed mainly for $3d$ transition elements mainly. Our recent synthetic efforts, however, are focused on rare-earth elements, especially those with unpaired f-electrons.

A First Step: Layered Rare-Earth Borate Phosphates

A series of compounds with general formula $K_3RE[OB(OH)_2]_2[HOPO_3]_2$ (RE = Y, Yb, Lu) has been synthesized only recently [6]. The ytterbium compound as the most interesting member is chosen as a representative example for the following discussion. A single-crystal structure determination on a hexagonal prismatic crystal revealed the layered nature of the structure (Fig. 2, left). Phosphate tetrahedra are connected to isolated YbO_6 octahedra resulting in the formation of extended layers (Fig. 2, middle). This kind of linkage pattern is also present in the compounds $A_3RE(XO_4)_2$ (A = Na, K, RE = rare-earth element, X = P, V, As), which can be regarded as structural derivatives of the mineral Glaserite (Aphthitalite) [7, 8], $K_3Na(SO_4)_2$. Boron is situated in a trigonal planar coordination by oxygen. The borate units are protonated and are arranged to form layers (Fig. 2, right) above and below the Glaserite-type slabs. A detailed crystal structure analysis revealed the formation of hydrogen bonds are formed between the terminal oxygen atoms of the Glaserite-type slabs and the borate layers.

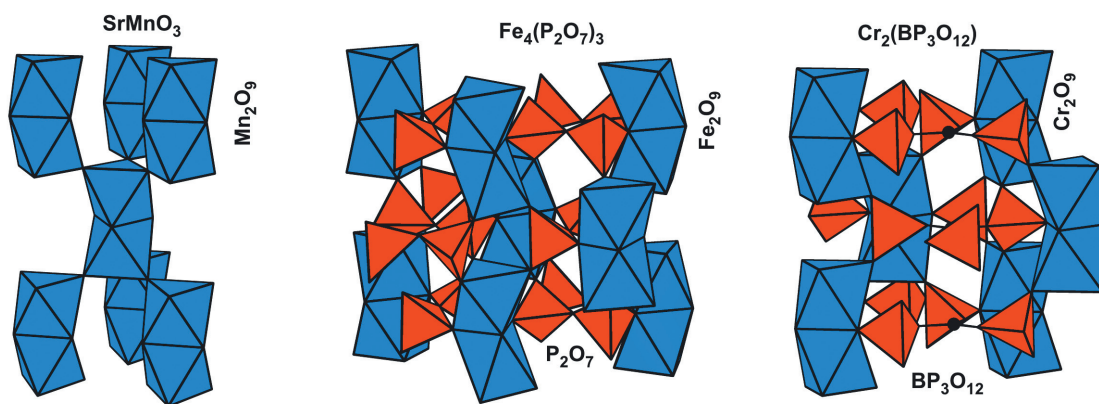### M_2O_9 Dimer Separation in Oxides, Phosphates, and Borophosphates

Fig. 1: Separation of face-sharing transition-metal dimers. In the $4H$ perovskite $SrMnO_3$ [2] (left) the dimers share common apical oxygen atoms and form a three-dimensional arrangement. Separation of the dimeric units is realized in the diphosphate $Fe_4(P_2O_7)_3$ [3] (middle) and more pronounced in the borophosphate $Cr_2(BP_3O_{12})$ [4,5] (right).
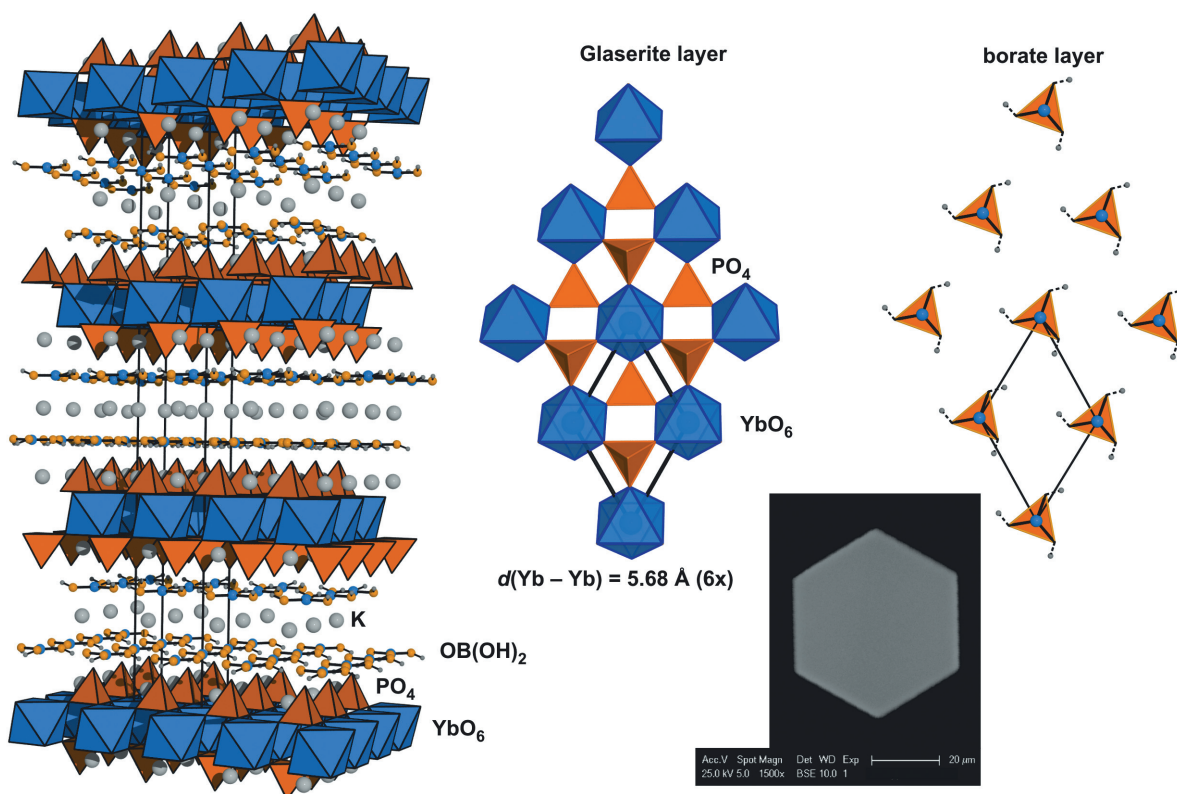
Fig. 2: Crystal structure of $K_3Yb[OB(OH)_2]_2[HOPO_3]_2$. Single crystal: hexagonal platelet (SEM image, bottom right); left: overall crystal structure; middle: Glaserite-type slab; right: borate layer.

EPR Spectroscopy and Magnetic Susceptibility

Only a limited number of reports on Yb^{3+} microwave absorption spectra is available due to its fast relaxation. Consequently, information on fundamental parameters, e.g., the g value for different crystal field symmetries is missing. In the new borate phosphate the crystal field of Yb^{3+} exhibits the rare point symmetry C_{3i}. Therefore, continuous-wave X-band (9.4 GHz) and L-band (1.1 GHz) electron paramagnetic resonance (EPR) spectra of powdered $K_3Y_{1-x}Yb_x[OB(OH)_2]_2[HOPO_3]_2$ ($x = 0.01$) were investigated (Fig. 3). Well-defined microwave absorption spectra were observed. The figure presents the main ^{170}Yb resonance line (natural abundance 69.6%) along with its full hyperfine structure, resulting from the isotopes ^{171}Yb ($I = 1/2$) and ^{173}Yb ($I = 5/2$). The main line was analyzed by fitting to a Lorentzian-type lineshape, from which a T-independent g-value of 3.16(1) was obtained. This g-value indicates a significant diviation of the local Yb coordination from a regular octahedron, for which a g-value of 2.6667 [9] was expected. The evolution of the EPR linewidth

(ΔB) with T is presented in the inset of Figure 3 for both X- and L-band measurements. The following features are noteworthy: i.) the T-dependency of ΔB is characteristic of an Orbach relaxation process [9] (green line, Fig. 3 inset) where the localized spins relax due to an interaction with excited crystal field levels. From the Orbach-analysis the crystal field splitting of the first excited levelwas extracted:
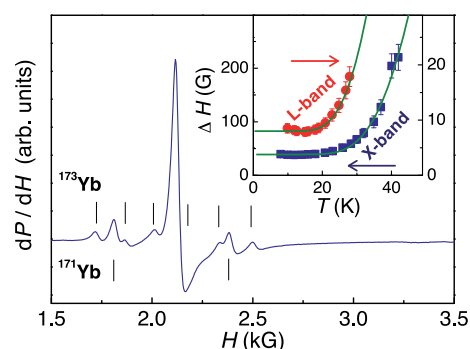

Fig. 3: EPR X-band spectrum of powdered $K_3Y_{1-x}Yb_x[OB(OH)_2]_2[HOPO_3]_2$ ($x = 0.01$) at 10 K. The inset shows the temperature dependence of the linewidth for X-band and L-band resonances. The solid line (green) corresponds to an Orbach-like relaxation.

of $\Delta = 211(30)$ K and $\Delta = 163(20)$ K for X- and L-band, respectively. ii.) ΔB is strongly field-dependent indicating an inhomogeneous resonance, with this inhomogeneity resulting from the presence of inequivalent Yb sites and/or a distribution of crystal field parameters. In general, our EPR data are consistent with a distorted octahedral coordination of Yb^{3+}. The asymmetry of the lineshape is most likely due to an admixture of the main resonance with parts of the hyperfine structure.

For $K_3Y_{1-x}Yb_x[OB(OH)_2]_2[HOPO_3]_2$ ($x = 1$) a modified Curie-Weiss fit ($\chi = C/(T-\theta) + \chi_0$) yielded an effective magnetic moment of $\mu_{eff} = 4.7\,\mu_B$ close to the expected free-ion moment of Yb^{3+}. The Weiss temperature of $\theta = -65(1)$ K points to a crystal electric-field interaction. There is no indication-for magnetic ordering. The magnetization isotherm at 1.8 K shows a saturation of the paramagnetic magnetization at $\approx 1.9\,\mu_B$ for fields above 40 kOe.

The First Rare-Earth Borophosphates

Using a two-step reactiveflux route we succeeded in the preparation of a series of isostructural (space group $Pa\bar{3}$) rare-earth borophosphates [10]. High-quality X-ray diffraction data (Ag Kα–radiation [11]) of the Y-compound enabled us to establish a reasonable structure model (Fig. 4), which was further supported by synchrotron and neutron diffraction data, chemical analyses, and EDXS.

The "clear" part of the crystal structure (Fig. 4) contains the K and RE positions as well as the tetrameric borophosphate units BP_3O_{13} with B and P in tetrahedral coordination. The RE sites (in octahedral coordination owing to the oxygen corners of neighboring PO_4-groups) are arranged in form of rhombic dodecahedra which fill the space by sharing common faces. These rhombic dodecahedra are filled with potassium and two tetrameric borophosphate groups. The blue triangle between the two BP_3O_{13} groups (Fig. 4a) corresponds to an atomic arrangement, which has so far eluded clear-cut identification. Yet, it can be assumed that this unidentified group interconnects the two BP_3O_{13} units and completes a borophosphate oligomer. From the point of view of charge balancing the missing unit (named X) has to bear one positive charge. The residual electron density distribution between the two neighboring BP_3O_{13} groups is characterized by 12 maxima surrounding a toroidal

arrangement in the center (Fig. 4b and 4c). By taking into account the "free" oxygen corners of the neighboring BO_4 tetrahedra, it can be assumed that the two oligomers become interconnected by i.) a BO^+-group (resulting in a BO_3-unit), ii.) a $B(OH)_2^+$-group (resulting in a $O_2B(OH)_2$-tetrahedron), and iii.) a PO_2^+-unit (resulting in a PO_4-tetrahedron). Bearing this in mind, the chemical composition of the RE borophosphate is best described by $K_6RE_3[BP_3O_{13}(X^{1+})O_{13}P_3B]$, with $X = BO$, $B(OH)_2$ and/or PO_2, at the moment.

a)

b)

c)

3.6 Å

RE	a(Å)	V(Å³)	material
Y	13.6508(9)	2543.7(3)	powder, single crystal
Er	13.5808(1)	2504.4(1)	powder, single crystal
Yb	13.5707(8)	2499.2(2)	powder
Lu	13.5490(7)	2487.3(2)	powder
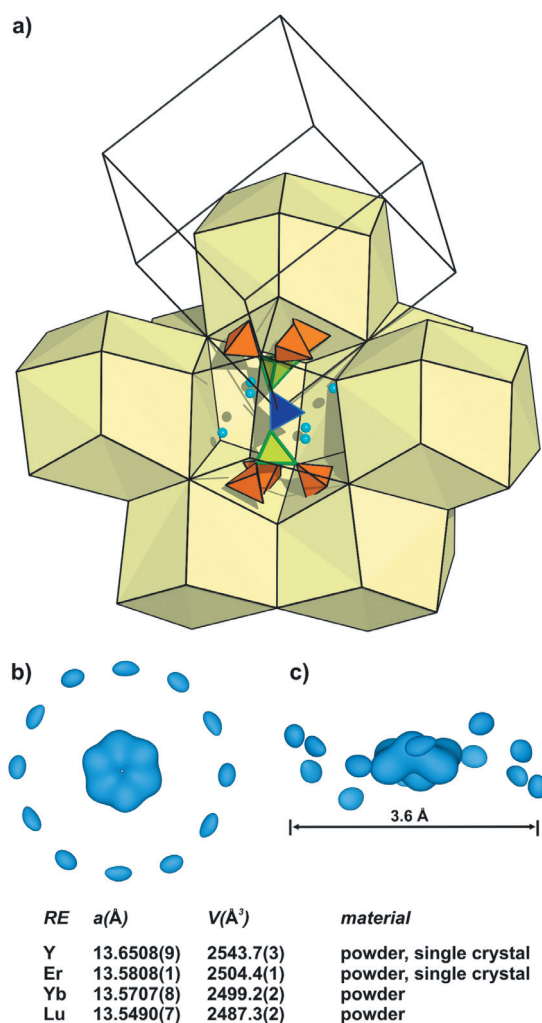
Fig. 4: Crystal structure of $K_6RE_3[BP_3O_{13}(X^{1+})O_{13}P_3B]$. The RE ions form an arrangement of condensed rhombic dodecahedra (yellow), which are filled with K^+ (light blue) and borophosphate groups (orange: PO_4, green BO_4, blue: X^{1+}, see text). Residual electron density in the voids viewed along [111] is shown in (b) and perpendicular to [111] in (c).

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