

SiC single crystals, no magnetic signal was detected. We demonstrated that the intentionally created defects are responsible for the observed magnetism and deduced that carriers play an important role in defect-induced magnetism. Our results confirm the existence of defect-induced magnetism further and point out the necessary of tuning carrier to control the magnetism, providing some clues for tuning the magnetism of WBG semiconductors by defect engineering.

[1] J.Y. Kim, J.H. Park, B.G. Park, H.J. Noh, S.J. Oh, J.S. Yang, D.H. Kim, S.D. Bu, T.W. Noh, H.J. Lin, H.H. Hsieh, C.H. Chen, *Phys. Rev. Lett.* **2003**, *90*, 017401. [2] D.C. Kundaliya, S.B. Ogale, S.E. Lofland, S. Dhar, C.J. Metting, S.R. Shinde, Z. Ma, B. Varughese, K.V. Ramanujachary, L. Salamanca-Riba, T. Venkatesan, *Nat. Mater.* **2004**, *3*, 709-714. [3] P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.H. Han, T. Butz, *Phys. Rev. Lett.* **2003**, *91*, 227201. [4] H.H. Xia, W.F. Li, Y. Song, X.M. Yang, X.D. Liu, M.W. Zhao, Y.Y. Xia, C. Song, T.W. Wang, D.Z. Zhu, J.L. Gong, Z.Y. Zhu, *Adv. Mater.* **2008**, *20*, 4679-4683. [5] X.M. Yang, H.H. Xia, X.B. Qin, W.F. Li, Y.Y. Dai, X.D. Liu, M.W. Zhao, Y.Y. Xia, S.S. Yan, B.Y. Wang, *Carbon* **2009**, *47*, 1399-1406. [6] B. Song, H.Q. Bao, H. Li, M. Lei, T.H. Peng, J.K. Jian, J. Liu, W.Y. Wang, W.J. Wang, X.L. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 1376-1377. [7] J.B. Yi, C.C. Lim, G.Z. Xing, H.M. Fan, L.H. Van, S.L. Huang, K.S. Yang, X.L. Huang, X.B. Qin, B.Y. Wang, T. Wu, L. Wang, H.T. Zhang, X.Y. Gao, T. Liu, A.T.S. Wee, Y.P. Feng, J. Ding, *Phys. Rev. Lett.* **2010**, *104*, 137201. [8] Y. Liu, G. Wang, S.C. Wang, J.H. Yang, L. Chen, X.B. Qin, B. Song, B.Y. Wang, X.L. Chen, *Phys. Rev. Lett.* **2011**, *106*, 087205.

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The first rare-earth borophosphates

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In search for new compounds with new crystal structures and properties the exploration of the systems $MO_x-B_2O_3-P_2O_5-(H_2O)$ (MO_x = metal oxide) has been shown to be extremely successful [1]. Numerous compounds have been already synthesized with an amazing structural variety originating from the unique arrangement of isolated tetrahedra (BO_4 and PO_4) and trigonal planar units (BO_3) and/or the condensation between them by the formation of complex borophosphate anions. The synthesis conditions have been mainly optimized for early main-group and 3d transition elements up to now. Our recent synthetic efforts are focused on rare-earth elements, especially those with unpaired f electrons.

In the course of experiments on rare-earth elements (RE) the first hydrated borate phosphates with the general formula $K_3RE[OB(OH)_2]_2[HOPO_3]_2$ ($RE = Y, Yb, Lu$, space group: R-3) were obtained [2]. Isolated REO_6 octahedra are interconnected by PO_4 tetrahedra resulting in layers, which can be regarded as structural derivatives of the mineral Glaserite (Aphthitalite) [3], [4], $K_3Na(SO_4)_2$. Between two of these layers potassium ions and two layers of $OB(OH)_2$ units are intercalated.

Using a reactive flux synthesis method we succeeded in the preparation of a series of isostructural rare-earth borophosphates (space group $Pa-3$, $a = 13.6508(9)$ Å (Y) – $13.5490(7)$ Å (Lu)). The centers of isolated REO_6 octahedra form rhombic dodecahedra, which fill the space by sharing common faces. In each of these rhombic dodecahedral voids potassium ions and two tetrameric BP_3O_{13} units are located.

The borophosphate units are linked by a yet not fully characterized atom group. From the point of view of charge balancing the chemical formula the missing unit – named X – has to bear one positive charge. The residual electron density distribution between two neighboring BP_3O_{13} is characterized by a corrugated circle of 12 maxima ($d = 3.6$ Å) with a toroidal arrangement in the center. By taking into account the oxygen corners of the neighboring BO_4 tetrahedra, it can be assumed that the two oligomers are interconnected either by 1) a BO^+ - group (resulting in a BO_3 unit), 2) a $B(OH)_2^+$ - group (resulting in a $O_2B(OH)_2$ - tetrahedron), and 3) a PO_2^+ - unit (resulting in a PO_4 - tetrahedron). With this in mind and supporting information of thermal analyses, NMR, and chemical analyses, the chemical composition of the RE borophosphate is best described by $K_6RE[BP_3O_{13}(X^{1+})O_{13}P_3B]$, with $X^{1+} = BO, B(OH)_2$, and/or PO_2 , at the moment.

[1] B. Ewald, Y.-X. Huang, R. Kniep, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1517-1540. [2] Y. Zhou et al., *J. Solid State Chem.* 2011, accepted. [3] B. Gossner, *Neues Jb. Geologie Palaeontologie Beilage* **1928**, 89. [4] K. Okada, J. Ossaka, *Acta Crystallogr. Sect. B.: Struct. Sci.* **1980**, *36*, 919.

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An eu coordination polymer consolidated by 2,2'-biquinoline-4,4'-dicarboxylate

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Eu(III) chloride was allowed to reaction to sodium 2,2'-biquinoline-4,4'-dicarboxylate ($bqdc^{2-}$) lead to an Eu coordination polymer (**1**). X-ray analysis reveal that **1** crystallizes in triclinic, P-1 space group, $a = 11.122(1)$, $b = 11.938(1)$, $c = 14.184(2)$ Å, $\alpha = 74.869(2)$, $\beta = 76.480(2)$, $\gamma = 73.859(2)^\circ$, $V = 1719.8(4)$ Å³. **1** consists of an asymmetric unit of $\{[Eu_2(bqdc)_3(H_2O)_2(DMF)_2] \cdot 0.5DMF \cdot H_2O\}$, in which two of Eu atoms are equivalence, each is nine-coordinated with seven O atoms from five caboxy groups of bridging $bqdc^{2-}$ anions, and two O atoms from a DMF and a water molecules (Fig 1. a), forming a distorted monocapped square antiprism polyhedron, the distance between two neighboring Eu atoms is 4.108 Å. The metal ion is bridged by two types of $bqdc^{2-}$ anions to form a layer. The hydrogen bonds between the $bqdc^{2-}$ ligands and the lattice H_2O molecules connect the neighboring layers together into a 3D network (Fig 1. b). The stack of the layers results in channels along the c axis between neighboring layers.

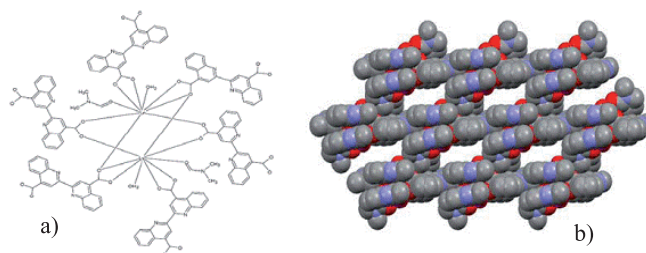


Figure 1. a). The coordination environment of Eu atom; b). Packing diagram of **1** viewed along the c axis showing channels. H atoms and the terminal and lattice DMF and H_2O molecules are omitted for clarity. Color scheme: Eu atoms, pink; C atoms, grey; O atoms, red; N atoms, blue.

1 has high sensitivity to the toxic metal ions of Hg^{2+} , Pb^{2+} , Cd^{2+} as well as Ag^+ ion. After the addition of Hg^{2+} , Pb^{2+} , Cd^{2+} , or Ag^+ alone at 0.01 M or the mixture of Hg^{2+} , Pb^{2+} , and Cd^{2+} with the total concentration of 0.01 M to the DMF emulsion of **1**, the luminescence of **1** quenched completely (Fig 2).

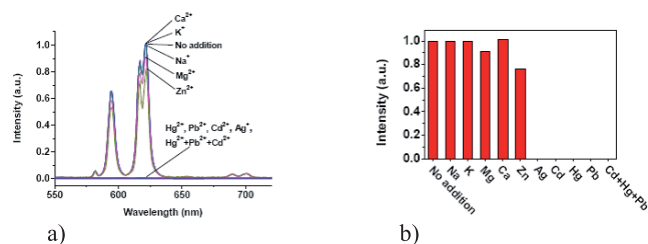


Figure 2 a) Emission spectra of **1** in DMF emulsion in the presence of various metal ions in 0.01 M $\text{M}(\text{NO}_3)_x$; b). Normalized luminescence intensities of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of **1** in DMF emulsions at 621 nm upon the addition of various metal ions in 0.01 M $\text{M}(\text{NO}_3)_x$.

[1] K.L. Wong, Y.Y. Yang, W.T. Wong *et al. Adv. Mater.* **2006**, *18*, 1051. [2] B. L. Chen, G.D. Qian *et al. Angew. Chem. Int. Ed.* **2009**, *48*(3), 500. [3] J.R. Long, O.M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213; [4] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, *et al. Chem. Soc. Rev.* **2009**, *38*(5), 1330; [5] K. Binnemans, *Chem. Rev.* **2009**, *109*(9), 4283.

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MS81.P20

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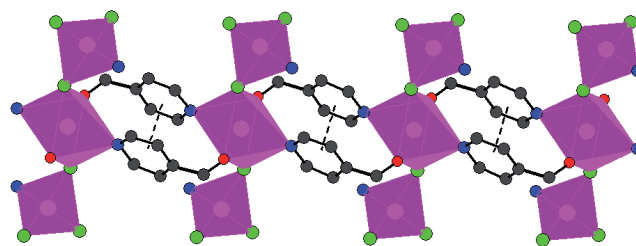
Coordination driven and/or H-bonded M(II)-N,N-dialkylisonicotinamide networks

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The search for strategies enabling assembling of transition metal complexes into multidimensional frameworks is one of the main challenges in crystal engineering. The metal embedded supramolecular networks, having specific dimensions and topologies are associated with many magnetic, electronic, zeolitic, catalytic and optical properties thus leading to the creation of “functional materials” [1], [2], [3]. Coordination polymerization or hydrogen bonding are the two strategies employed in assembling metal complexes into multidimensional networks. Recently, a combination of the two has also been used effectively to increase the dimensionality. The strength of coordinate bond along with the flexibility imparted by hydrogen bonding provide ideal environment for multi-dimensional framework expansion. Among various ligands used for construction of supramolecular networks, the pyridine based ligands such as nicotinic acid, isonicotinic acid and their amide derivatives are ideal as they have the structural adaptability for both: metal-ligand coordination [4], [5] as well as the intermolecular hydrogen bonding [6].

Our work involving the Metal(II)-N,N-dialkylisonicotinamide complexes [7] has shown that these fully substituted amide derivatives of isonicotinic acid provide the necessary rigidity and binding sites that enhance the chances of formation of coordination networks instead of isolated entities and therefore provide a fertile route to metal organic frameworks (MOF's). Furthermore, intermolecular interactions among 1D coordinated and/or H-bonded chains make feasible the formation of more complex networks (2D and 3D). Each of these levels contains remarkable features making the complexes

unique from a structural point of view. This work also reinforces the role played by counter ions present in the lattice such as perchlorates and nitrate to enable assembling of metal complexes into networks. To explore the magnetism among such systems, in depth magnetic measurements (variable temperature magnetic susceptibility, epr etc.) have also been made [7].



[1] C. Janiak, *Dalton Trans.* **2003**, 2781-2804. [2] S.L. James, *Chem. Soc. Rev.* **2003**, *32*, 276-288. [3] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629-1658. [4] J. Moncol, M. Mudra, P. Lönnecke, M. Hewitt, M. Valko, H. Morris, J. Svorec, M. Melnik, M. Mazur, M. Koman, *Inorg. Chim. Acta.* **2007**, *307*, 3213-3225. [5] B.R. Bhogala, P.K. Thallapally, A. Nangia, *Cryst. Growth Des.* **2004**, *4*, 215-218. [6] C.B. Aakeröy, A.M. Beatty, D.S. Leinen, *Angew. Chem., Int. Ed.* **1999**, *38*, 1815-1819. [7] P. Kapoor, A.P.S. Pannu, G. Hundal, R. Kapoor, M. Corbella, N. Aliaga-Alcalde, M.S. Hundal, *Dalton Trans.* **2010**, *39*, 7951-7959.

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Five new metal-organic frameworks: novel topologies and characteristics.

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Metal-organic frameworks (MOFs) are a subgroup of coordination polymers and coordination networks. We are engaged in the preparation of MOFs using a range of common metal salts and organic ligands, including multitopic aromatic carboxylates. Topological analysis is a useful tool for analysing coordination networks. It allows one to see the arrangement of molecules in a structure in a simple manner and therefore helps in the determination of why that structure was formed. This enables a more systematic design of coordination polymers¹.

Three MOFs were prepared from gadolinium(III) nitrate and 5-nitroisophthalic acid (NIA) using the same method with only the concentration of starting materials in the solvent system varying. $[\text{Gd}_2(\text{NIA})_9(\text{DMF})_4] \cdot 1.5\text{H}_2\text{O}$ (**1**), $[\text{Gd}(\text{NIA})_5(\text{DMF})_2] \cdot 3\text{H}_2\text{O}$ (**2**) and $[\text{Gd}_4(\text{NIA})_{14}(\text{DMF})_6(\text{H}_2\text{O})_3] \cdot 4\text{DMF} \cdot x\text{H}_2\text{O}$ (**3**) have a distinctive paddle-wheel motif with four NIA molecules coordinated to a pair of gadolinium metal centres.

Network analysis revealed the six connected $(4^{12}.8^3)$ -**pcu** net for **1**. **1** and **2** are related by rotation around one C-C bond which reduces the symmetry of the network. This is easy to see through the topology as the six-connected node reduces to a four-connected node. **2** is found to have the square and tetrahedron four-connected $(4^2.8^4)(4^2.8^4)$ -**pts** net. **3** has the unprecedented four-, five- and six-connected $(4^4.6^2)(4^6.6^4)(4^8.6^6.8)$ network (Figure 1). The four-connected node of **3** is the same as that square four- node of the **pts** net while the six-connected node is the same as that of the **pcu** net.