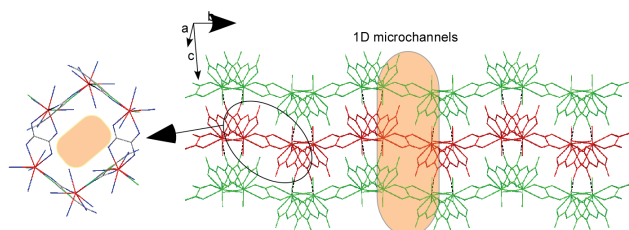


One of the goals of crystal engineering is to make it possible to design and synthesize MOFs with predetermined topology and properties, usually through judicious selection of multitopic organic ligands as the spacers and metal ions or clusters as the junctures [1]. As functional metal centers, rare earth metals are attracting more and more attention due to their fantastic coordination properties and special chemical characteristics arising from 4f electrons [2], [3]. Many coordination polymers based on rare earths have been synthesized, and most of them exhibit amazing optical and magnetic properties, enabling them as fluorescent probes and electroluminescence devices [4], [5].

We report herein a family of 11 isostructural 3D metal-organic compounds,  $\{[\text{Ln}(\mu_3\text{-pmdc})(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})_2] \cdot 2.25\text{H}_2\text{O}\}_n$  (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er; pmdc = pyrimidine-4,6-dicarboxylate, ox = oxalate). The most striking feature of these structures is that they undergo a phase transition from the monoclinic  $P2_1/n$  space group at room temperature towards a modulated commensurate structure upon cooling up to 100 K with the superspace group  $P2_1/n(\alpha 0 \gamma)0s$  and  $t = (0 \ 0 \ 1/3)$ , in such a way that the modulated commensurate unit cell is related to the room temperature one as being three unit cells piled up along the  $c$  axis. The dimension of the channel and the occupancy of the water molecule placed in these channels are modulated. The metal centers are joined by means of bis-bidentate pmdc and ox ligands to lead to neutral Shubnikov hexagonal plane nets, which are joined together through the coordination of the non-chelating carboxylate oxygen atom belonging to the adjacent layers. The overall three-dimensional open framework possesses channels along the crystallographic  $a$  axis that are filled by solvent water molecules. The available space within these channels of approximate dimensions of  $5 \times 7 \text{ \AA}$  represents a 20.1% of the unit cell volume. The topological analysis of the crystal structure carried out by means of the TOPOS program package indicates a *ins* like 3D network (3,4-c net), the Schläfli symbol being  $\{6^3\} \{6^5.8\}$ .

Europium and terbium compounds exhibit bright red and green luminescence under excitation at 488 nm, respectively.



**Figure 1.** View of the overall 3D open framework showing the microchannels.

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**Keywords:** commensurate, lanthanide, luminescence

## MS88.P11

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### Thermally Induced Structural Changes in Modulated $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$ (CBN28)

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The incommensurately modulated crystal structure of relaxor ferroelectric CBN28 was refined at elevated temperatures up to 330°C in the 3+2 dimensional superspace group  $P4bm(pp1/2, -pp1/2)$ . Single crystals grown by the Czochralski method were used.

The crystal structure of  $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$  is isotypic with the tetragonal tungsten bronzes. Corner-sharing octahedra form a framework, which leaves space for three types of cavities. The Me1 site is coordinated by 12 oxygen atoms, the Me2 site by 15 O atoms and the Me3 position by nine oxygen atoms. The latter is not occupied in the tetragonal bronze type and the Me1 and Me2 sites are incompletely filled with the larger cations ( $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ ). The X-ray single crystal diffraction patterns of  $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$  exhibit weak first order satellite reflections in addition to the main reflections indicating the existence of a two dimensional structural modulation like in isotypic  $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  with  $x$  ranging from about 0.25 to 0.75. The wave vectors are  $q_1 = \alpha a^* + \alpha b^* + \frac{1}{2} c^*$  and  $q_2 = -\alpha a^* + \alpha b^* + \frac{1}{2} c^*$  with  $\alpha \sim 0.3$  [1], [2].

The modulation consists of a wavy distribution of barium and calcium atoms as well as vacancies on the incompletely occupied Me2 site with 15-fold oxygen coordination. The occupational modulation is coupled with a modulation of the atomic displacement parameters and a very weak modulation of the positional parameters of Me2. The surrounding oxygen atoms show strong positional modulations with an amplitude up to ca. 0.4 Å resulting in a cooperative tilting of the  $\text{NbO}_6$  octahedra. The Me1 site and the octahedrally coordinated niobium atoms are hardly affected by the modulations.

With increasing temperatures, the electric polarization is reduced by way of approaching 0 or 1/2 of the  $z$  parameters of all atoms, which are special positions in the centrosymmetric space group  $P4/mbm$  (no. 127). However, not all atoms arrive exactly at these equipoints at the Curie temperature near 270°C. Above  $T_C$ , the average structure can better be described in  $P4bm$  (no. 100) or in the non-polar space group  $P-4b2$  (no. 117) [3] than in  $P4/mbm$ . The modulations persist above  $T_C$ . The intensities of the satellite reflections, however, can only be refined in the superspace group  $P4bm(pp1/2, -pp1/2)$  indicating that no true change of symmetry takes place at 270°C. The amplitudes of the positional modulations decrease at temperatures above  $T_C$  while the atomic displacement parameters increase indicating enhanced vibrational motions at the expense of the static displacements. Lattice parameters and the wavelength of the modulation change only slightly upon heating.

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**Keywords:** incommensurate, modulation, ferroelectricity

## MS88.P12

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### Anion deficient perovskites $(\text{Pb,Bi})_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$ modulated by crystallographic shear planes

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$\text{BiFeO}_3$  is one of the rare perovskites combining ferroelectric and magnetic ordering in a single phase material. Being a room-temperature multiferroic,  $\text{BiFeO}_3$  is a playground for the investigation of the physical phenomena behind multiferroicity [1]. The main instability