MS15-P40 New luminescent materials based on ortho-phenylenediboronic acid – from crystal engineering to spectroscopic properties

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Arylboronic acids have already found many applications in diverse areas of chemical science, such as organic synthesis, catalysis or crystal engineering. Quite recently we have worked on para- and ortho-phenylenediboronic acids.[1,2] In the present study, we focus our attention on a new class of adducts based on the latter compound.

It occurred that a simple one-pot reaction of ortho-phenylenediboronic acid with 8-hydroxyquinoline results in a new photoactive species. The reaction proceeds smoothly even in solvent-free conditions (mechanochemistry) and allows obtaining many modifications of such complexes (regarding both the acid and N-donor compound) in high yield. It was possible to crystallize and structurally characterize many of these systems, including several fluorinated derivatives and various solvatomorphs.

Additionally, luminescent properties of the studied complexes were investigated using the time-resolved spectroscopy, both in solution and in the solid state. The recorded emission spectra indicate the possibility of tuning the colour of the emitted light in the visible regime (from blue to orange). The determined lifetimes are of nanosecond order (9 – 15 ns), which suggests that the main contribution to the emitted light comes from the fluorescence process (singlet-to-singlet transition) what is further supported by the DFT calculations. Theoretical results show also that the charge transfer processes occur mostly in the quinoline ring fragment. The emission quantum yields determined in solution are in the range of 10 to 30%. The lifetimes and quantum yield values are highly dependent on the number of fluorine substituents in the acidic part of the molecule. The more the F-substituents present, the lower the corresponding values.

[1] K. Durka, K. N. Jarzembska, R. Kamiński, S. Luliński, J. Serwatowski, K. Woźniak *Cryst. Growth Des.* **2012**, *12*, 3720.

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Keywords: phenylenediboronic acids, quinoline derivatives, crystal engineering, fluorescence

MS16. Physical properties through lattice distortions: structure of perovskites & Co studied by electron microscopy and diffraction

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MS16-P1 Molecular dynamics modeling of radiation stability of $Ca(Zr,Ti,Sn)O_3$ perovskites

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The aim of this work was to investigate the relation between the radiation stability and the composition of $Ca(Zr,Ti,Sn)O_3$ solid solution using method of molecular dynamics (MD). This compound with perovskite structure (space group *Pbnm*) is one of the promising matrices for utilization of high level radioactive waste. Note that a new mineral *lakargiite*, which represents the $Ca(Zr,Ti,Sn)O3$ solid solution with the maximal molar fraction $x(CaZrO_3) = 0.93$ and maximal fractions $x(CaTiO_3) = 0.22$ and $x(CaSnO_3) = 0.20$, was registered in 2007. Our original approach, described in [1] makes it possible to simulate the solid solutions using representative supercell of limited size with optimal atomic distribution. Thus, for MD simulation we used a supercell with different compositions with sizes $310×210×315$ Å, which contains 1.4 million atoms with a maximally disordered distribution of Zr, Ti, and Sn. As an analog of the recoil atom the knocked out Th atom with energy of 20 keV was used. After the formation of the atomic displacement cascade at instant $t=0.71$ ps the structure starts to be "restored" and displaced atoms partially return to their sites or equivalent crystallographic sites. At the end of the simulation ($t=20$ ps), the total number of Frenkel pairs is minimal (figure 1). In contrast to some other tested materials defects in $Ca(Zr,Ti,Sn)O3$ are mainly of the point character, which indicates the high stability of this solid solution to the radioactive effect. We evaluated parameter a, which characterized susceptibility to amorphization of material under radiation damage. This parameter numerically equal to a part of the energy of Th atom, which is consumed for the formation of Frenkel pairs in a cascade of displaced atoms. It was shown that the dependence of a-parameter on the solid solution composition is lowest for Sn-Zr compositions, whereas Ti-riched compositions exhibit poorer performance. Thus the radiation stability of Sn-Zr-riches matrices can be of unquestionable interest

when solving both fundamental and applied problems associated with the isolation and burial of highly active radioactive wastes.

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References: [1] Eremin N.N. et al, Glass Phys. Chem. 34 (1), 9 (2008).
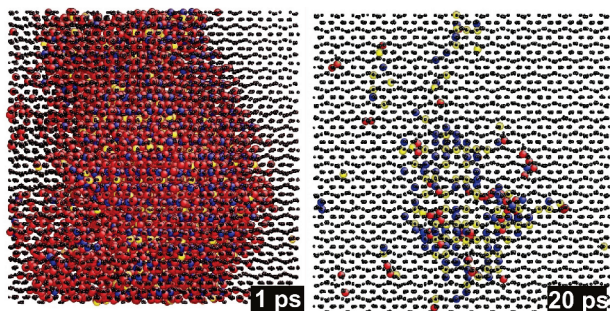
Figure 1. Radiation damage, produced by 20 keV Th recoil in Ca(Zr,Ti,Sn)O$_3$ solid solution at the peak of the damage (left) and after structure relaxation (right).

MS16-P2 Structure relations of the sub-solidus phases in the CaO–La$_2$O$_3$–TiO$_2$ system

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Sub-solidus phase relations in the ternary CaO–La$_2$O$_3$–TiO$_2$ system at 1400 °C in air were determined. The multi-phase samples were prepared by a solid-state reaction method, whereas the single-phase samples for the structure analysis of selected solid solutions were prepared by a wet-precipitation method in order to provide good homogeneity of the starting mixtures. The phases in the prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The oxides form seven ternary compounds in the equilibrium state, many solid solutions (which extend across a broad concentration region), and a large, single-phase area based on the CaTiO$_3$ solid solution. The structures of several new phases – solid solutions on the tie lines CaTiO$_3$–Ca$_3$La$_4$Ti$_3$O$_{15}$ and La$_2$TiO$_5$–Ca$_3$La$_4$Ti$_3$O$_{15}$ – were determined in detail.

The phases studied are denoted with black dots in Fig. 1 and he labels are explained in the figure caption. It was found that the majority of identified ternary phases belong to the perovskite group of structures. The exception is is 232, which is isostructural with LT.

The remarkable single-phase region (marked grey in Fig. 1) is due to an extensive solid solubility of lanthanum titanates and the 323 compound in the perovskite CaTiO$_3$. Interesting composition-dependent distortions of the perovskite structure were found. The compositions Ca$_{1-x/2}$La$_x$Ti$_{1-x/2}$O$_3$ with x > 0.353 have a monoclinic perovskite structure and those with x < 0.353 an orthorhombic perovskite structure. The origin of such behaviour will be discussed in detail.
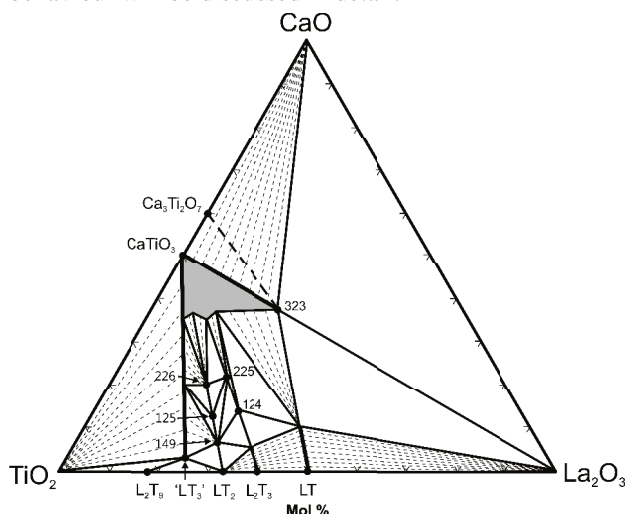
Figure 1. Sub-solidus phase diagram of the ternary system CaO–La$_2$O$_3$–TiO$_2$ in air, at 1400 °C (L$_4$T$_9$: La$_4$Ti$_9$O$_{24}$, 'LT$_3$': La$_{2/3}$TiO$_{3(STAB)}$, LT$_2$: La$_2$Ti$_2$O$_7$, L$_2$T$_3$: La$_4$Ti$_3$O$_{12}$, ^{4}LT: La$_2$TiO$_5$, 149: CaLa$_4$Ti$_9$O$_{31}$, 125: CaLa$_4$Ti$_5$O$_{17}$, 226: Ca$_2$La$_4$Ti$_6$O$_{20}$, 124: CaLa$_4$Ti$_4$O$_{15}$, 225: Ca$_2$La$_4$Ti$_5$O$_{18}$ and 323: Ca$_3$La$_4$Ti$_3$O$_{15}$).