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A Demourgues

University of Bordeaux, France

The world of fluorine-based nano-materials: Past, present and future

The aim of this presentation is to illustrate, considering various new 'nano' oxy(hydroxyl)fluorides prepared by hydrothermal routes, the key role of cationic/anionic vacancies allow relaxing the structure (bond distances and angles) which explain outstanding physical-chemical properties (reactivity, UV-Vis-NIR absorption and electrochemistry). Nanoparticles of crystallized phases have been obtained by microwave assisted solvothermal routes using HF, various solvents and precursors leading to control the composition, the crystal structure, the nanosize particles and the surface area. The case of Ti-based oxy(hydroxy)fluorides with Ti vacancies and unexpected UV shielding properties with band gap around 3.2eV and small refractive index around 1.9 will be presented. Al fluoride hydrate also with cationic vacancies, structural water and fluorine as ligands of Al^{3+} ions, has been synthesized and exhibits Lewis-Brönsted acidities. The strong acidic behavior highlights the effect of water molecules/cationic vacancies on the surface structure. Both these compounds adopt also derived ReO_3 frameworks. Ti vacancies can be also stabilized in derived Hexagonal Tungsten Bronzes (HTB) and anatase form containing O^{2-}, OH^- and F^- species but the cationic vacancies rate remains smaller in these last cases than in the previous ReO_3 form. The more complex case of trivalent Fe-based oxyfluorides will be presented by outlining the occurrence of cationic and anionic vacancies in this network where these compounds adopt the HTB used as cathodes in Li-ion battery. Finally, nanoparticles of tetravalent Ce-based oxyfluorides with fluorite-type structure where anions are in tetrahedral sites, have been prepared by co-precipitation in basic (pH=12) medium. The presence of Ca2+ partially substituted for Ce^{4+} and F- for O^{2-} allows tuning the optical band gap at the UV-Visible frontier and obtaining new UV absorbers with low refractive index. The role played by fluorine substituting for O^{2-}/OH^- ions will be highlighted which allows creating cationic and anionic vacancies in these nano-materials and contributes to tune the optical absorption properties as well as the acidic and redox properties.

Biography

A Demourgues is working at ICMCB-CNRS-UPR9048 since October 1993 as Research Fellow. He became Research Director at CNRS in October 2008. He received IBM-France award in 1993 (Young Scientist in Materials Science) and SFC (Société Française de Chimie) award in 2003 (Solid State Chemistry division). He is Consulting Scientist since 1998 at RHODIA-SOLVAY in the field of Solid State Chemistry, Redox and Opto-electronic properties.

alain.demourgues@icmcb.cnrs.fr

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