Stabilizing several anions (F, O, OH, S) in the vicinity of transition metals or rare earths to tune the optoelectronic properties of new materials

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Numerous complex oxides exhibiting mixed valence states of 3d-transition metals from insulating to metallic behaviours have been deeply investigated. For many years, the stabilization of these new oxides contributes to a better understanding of the relationships between the composition, the structural features and the electronic properties. The occurrence in the vicinity of transition metals (3d shell) or rare earth ions (4f and 5d shells) of more than two anions (p shell) with various polarizabilities leads to an alteration of the energetic parameters such as the crystal-field, the polarizing effects leading to affect the bandwidth and the position of p and 3d/5d bands, as well as the position of 4f level in the band gap.

New rare earth Ln-based oxysulfides, fluorosulfides and oxyfluorosulfides have been widely investigated and exhibit interesting optical properties such as luminescence in Ln_2O_2S network or absorption in the visible range in $Ln_{10}S_{14}O$ or LnSF[1]. Rare earth-based mixed anions (O, S, F) compounds have been investigated for the last decades[2] in order to tune the environment of rare earth, than modifying optical absorption properties. Most of rare-earth based mixed anions compounds exhibit 2D-networks due to the presence of anions with various polarizabilities. The building principle of ionic and covalent sheets in these layered structures with the modification of the block size and charge based on competitive bonds around the rare earth will be presented. Finally most of these networks are structurally related to the new generation of superconducting oxypnictides $LnMPO_{1-x}F_x$ (M = Fe, Co, Ni as transition metals and P = P, As, Sb as pnictides) and correspond also to the succession of ionic (O,F) blocks surrounding rare earth and covalent sheets containing transition metal[3,4].

New synthesis routes have been developed to stabilize mixed anions compounds. Then new oxy(hydroxy)fluorides (O/OH/F) with 3D networks have been also obtained and characterized. In addition, anionic and cationic vacancies have been stabilized in these new compounds prepared by hydro-solvothermal routes. Relevant examples will be given in the case of Ce^{4+} (anionic vacancies in Fluorite-type network) and Ti^{4+}/Fe^{3+} (cationic vacancies in ReO_3 and HTB frameworks) where the nature and concentration of anions strongly affect the structural features and the band gap[4,5,6].

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