

materials. Surprisingly, however, during the last decade nearly no interest in the melilites as optical materials is documented in literature. In a recent study of nonlinear-laser properties of $\text{Ba}_2\text{MgGe}_2\text{O}_7$ [1] we found that germanate crystals with non-centrosymmetric melilite-type structure can manifest numerous attractive $\chi^{(2)}$ - and $\chi^{(3)}$ -interactions with good prospects of their use in experiments of modern laser physics and nonlinear optics. In the present contribution we summarize the results of our investigations of linear optical properties and of stimulated Raman scattering (SRS) of further germanates $\text{Ba}_2\text{ZnGe}_2\text{O}_7$, $\text{Sr}_2\text{MgGe}_2\text{O}_7$ and $\text{Sr}_2\text{ZnGe}_2\text{O}_7$, which all possess an unmodulated melilite-type structure. All four melilite crystals allow the generation of a lasing comb of approximately one octave bandwidth on pumping at $\lambda_{p1} = 1.06415 \mu\text{m}$, arising from a SRS-promoting vibration mode at $\sim 770 - 780 \text{ cm}^{-1}$, which corresponds to the symmetrical stretching mode $\nu_3(\text{GeO}_3)$ of the $[\text{Ge}_2\text{O}_7]$ unit. In addition, for $\text{Ba}_2\text{ZnGe}_2\text{O}_7$ a second mode, $\delta_3(\text{GeO}_3)$, acts as a further SRS-promoting mode. For all four investigated germanate melilites numerous rather efficient $\chi^{(2)}$ -, $\chi^{(3)}$ -, and cascaded $\chi^{(3)} \leftrightarrow \chi^{(2)}$ - photon-photon and photon-phonon parametric interactions are observed. While these phenomena are quite similar for the four germanate melilites their $\chi^{(1)}$ -based properties (i.e. refractive indices and their dispersion) depend markedly on the chemical composition of the crystals. Going hand in hand with this, the phase matching possibilities for SHG (second harmonic generation) and SFG (sum frequency generation) processes vary within a range from SHG phase matching (SHG-pm) in the visible range ($\text{Ba}_2\text{MgGe}_2\text{O}_7$) to SHG-pm in near IR ($\text{Sr}_2\text{MgGe}_2\text{O}_7$ and $\text{Ba}_2\text{ZnGe}_2\text{O}_7$) to no possibility for SHG-pm for $\text{Sr}_2\text{ZnGe}_2\text{O}_7$. The latter crystal, however, is characterized by an iso-index point [2-4]. The diversity of optical properties of the germanate melilites, together with their nonlinear optical manifestations classifies this crystal family as an attractive group of optical materials.

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Li_xFeO_2 as battery cathode material: Li^+ /vacancy patterns and reaction energies. Michele Catti, Mercedes Montero-Campillo. *Dept. of Materials Science, University of Milano Bicocca, Italy.*
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More environment-friendly and less expensive cathode materials have been extensively sought to replace LiCoO_2 in lithium batteries. An attractive candidate is LiFeO_2 , showing a complex polymorphism; some of its phases were considered in the past as active electrochemical materials [1,2]. We have undertaken a combined crystallographic (neutron diffraction) and theoretical (ab initio simulations) study of this system, to elucidate some aspects left open by electrochemical measurements. Preliminary results obtained on the β'

(monoclinic) and γ (tetragonal) phases, by neutron diffraction [3] and computational [4] methods, showed that the order-disorder of Li/Fe distribution plays an essential role in determining the mobility of Li^+ ion in the host framework. Now the hollandite-type (tetragonal) and orthorhombic (o- LiMnO_2 -type) polymorphs of LiFeO_2 were examined. In particular, the latter phase was shown by electrochemical measurements to actually transform into LiFe_5O_8 spinel after few cycles of charge/discharge [2], yet preserving the electrode activity, but with no clear indications of the actual chemical and physical processes therein occurring. First-principles quantum-mechanical simulations (CRYSTAL code, all-electron basis set, hybrid DFT-HF functional) were performed to address two points: (i) the structural changes and energy barriers characterizing the Li^+ ion transfer, and (ii) the actual charge/discharge reactions taking place in the electrode. Several kinds of superstructures and Li^+ /vacancy patterns were devised for $\text{Li}_{1-x}\text{FeO}_2$ ($0 \leq x \leq 0.5$) and $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ ($0 \leq x \leq 2$), in order to properly account for vacancy formation and ion mobility during the lithium intercalation-deintercalation processes. The corresponding structures were fully relaxed and their energies were calculated, allowing us to determine the electrochemical potentials for a number of possible cathode reactions. As a result, the processes $\text{LiFeO}_2 \rightarrow \text{Li}_{1-x}\text{FeO}_2 + x\text{Li}$, $5\text{Li}_{1-x}\text{FeO}_2 + 5x\text{Li} \rightarrow \text{LiFe}_5\text{O}_8 + 2\text{Li}_2\text{O}$, and $\text{LiFe}_5\text{O}_8 + x\text{Li} \leftrightarrow \text{Li}_{1+x}\text{Fe}_5\text{O}_8$ are proposed as good candidates to explain the experimental charge/discharge voltage-capacity curves [2]. In the last reaction, both Li and Fe atoms prove to move to octahedral sites on intercalation, changing spinel into a rocksalt superstructure. Thus, the evolution of X-ray powder pattern on cycling is accounted for satisfactorily by simulations based on the least-energy theoretical structures involved in the above series of reactions. Further, pathways of Li^+ ion mobility within the host frameworks are determined, also providing the corresponding activation barriers.

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Metal salts of phosphoric acid have been known for over a century. In 1964, was obtained the first crystalline such compound, $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, which allowed a better understanding of their layered structure and chemical reactivity. Although only two crystalline forms of layered titanium phosphates are known, $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$, many derivatives have been reported, including partially and completely substituted ion-exchanged forms and intercalation compounds. Surprisingly, the γ -layered titanium phosphate is less studied than the α -phase, even though the γ -layers are more rigid, thicker, acidic and amenable to intercalation processes. Now, we revise the structural and thermal data of the γ -titanium phosphate, using