Hydrothermal growth and characterization of rare earth vanadate polyscale crystals

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Hydrothermal method is one of the best routes to grow polyscale crystals covering an entire range of sizes from bulk single crystals to fine, ultrafine and nano- single crystals. There are several advantages in the hydrothermal method due to highly controlled diffusion, which helps in obtaining defect free bulk single crystals. In recent years, organic ligands, capping agents, chelating agents and surfactants are used extensively in the hydrothermal growth of crystals to achieve a desired shape and size for the crystals. Also these organic ligands can provide the desired surface charge for the crystals, which in turn assist in obtaining a crystal surface either hydrophobic or hydrophilic.

In the present work, the authors discuss systematically the growth of rare earth vanadate polyscale crystals under hydrothermal conditions within a wide range of PT conditions starting from mild hydrothermal ($T \sim 100\,^\circ\mathrm{C}$ and $P < 30$ bars) to supercritical hydrothermal conditions ($T \approx 400\,^\circ\mathrm{C}$ and $P = 30\,\text{MPa}$). The mechanism of the growth of rare earth vanadate polyscale crystals has been discussed in detail. The morphology of the rare earth vanadates has been studied in detail with respect to the experimental conditions. Rare earth vanadates are the potential materials used as diode pumped laser materials, bio-imaging, neutron capture therapy, photocatalytic, etc. The hydrothermal technique is highly suitable for the growth of such polyscale rare earth vanadate crystals. In this work, a systematic characterization of these polyscale rare earth vanadate crystals has been discussed.

Keywords: hydrothermal synthesis, rare earth vanadate, optical properties

Structural phase transition in a super protonic conductor KHSO$_4$

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Insitu high temperature structural phase transitions and dehydration of a super fast proton conductor have been analyzed by single crystal X-ray diffraction. The room temperature structure is orthorhombic, space group $Pbca$, $a=8.415(7)\,\AA$, $b=9.790(8)\,\AA$, $c=18.967(2)\,\AA$, on heating to 475K the structure convert to more symmetric, space group $Cmca$, $a=8.4290(9)\,\AA$, $b=9.8938(10)\,\AA$, $c=19.1950(2)\,\AA$. At 475K dehydration takes place and the compound become K$_3$HSO$_4$ ($S_2O_7$) with space group $P2_1/c$ and cell parameters $a=13.1960(5)\,\AA$, $b=13.1960(5)\,\AA$, $c=9.6560(5)\,\AA$, $\beta=97.056(5)\,^\circ$. The room temperature structure is perfectly ordered but at 463K there are disordered oxygen and hydrogen atoms with a S-O bond distance $1.753(4)\,\AA$ The crystal structure exhibits O-H...O hydrogen bonds forming zero dimensional dimer and infinite polymeric chain at both room temperature and 463K. The presence of hydrogen bond is only responsible for the proton conduction. It was suggested that at high temperature the dimer breaks and forms chains resulting in the observed high proton conductivity [1]. It is shown in our analysis for the first time that the structure of the dimer and infinite polymeric chain of hydrogen bond remain intact, however, disorder in both oxygen and hydrogen atoms resulting in the lengthing of S-O bond length could be the cause of increased proton conductivity. It is of interest to note that the structure at 475K has only dimeric hydrogen bond and not chains.

Reference

Keywords: phase transition, proton conductor, dehydration