Solution growth of α-GeO_2 and Herbertsmithite $ZnxCu_{4-}OH)6Cl_2$ crystals: towards the identification of defects formation and growth mechanisms

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ECOMARCh seminar room (SIMaP)

Jury :
Joan JOSEP CARVAJAL, Associate Professor, Universitat Rovira i Virgili, Taragona, Spain (Reviewer)
Nathalie MANGELINCK- Noël, CNRS Director of research, IM2NP, Marseille, France (Reviewer)
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Abstract: The growth mechanism study of two functional single crystals grown from solution, Herbertsmithite (ZnxCu4-x(OH)6Cl2) and Germanium oxide), have been investigated in order to determine the growth conditions leading to good quality crystals. ZnCu3(OH)6Cl2, stoichiometric Herbertsmithite crystals, are needed to study the physics of quantum spin liquids and -GeO2 ones are promising piezoelectric crystals that could be used at high temperature conditions and as nonlinear optical crystals in optical parametric devices.During this work ZnxCu4-x(OH)6Cl2 crystals were grown by varying experimental conditions such as growth temperature, pH and initial ZnCl2 concentration of the solution. A selection of some of the crystals obtained by using different parameters were characterized to determine their chemical composition, their structure, the surface topography and the magnetic properties. Two techniques, Laser Induced Breakdown Spectroscopy (LIBS) and micro-X-Ray Fluorescence spectroscopy (μ-XRF), have been used to map the Cu and Zn concentrations in order to determine the x value of the crystals obtained in different growth conditions. LIBS technique allows mapping Cu and Zn contents with very good statistics and at several depths from the surface of the crystal. A quantitative measure of the x value was possible by using well-defined reference samples. Accurate x values have also been obtained by mapping the Cu and Zn contents by μ-XRF experiments. Thanks to the use of a diffraction multi-tool on BM32 at the European Synchrotron Facility (ESRF) we have been able to discriminate between intrinsic triangular moods and extrinsic microcrystallites on the crystals' surface, as they have different x values. μ-XRF is coupled with a micro Laue mapping which allowed to orient the macro steps distributed on crystals' surface. The growth solutions have also been investigated in order to identify the Cu and Zn based species present. Thermochemical calculations based on updated database have been performed as a function of the experimental conditions changed in the different growth runs (T, pH and concentration of Zn, Cu, Cl and O). The obtained results, concerning Zn species, were compared with in situ Raman spectroscopy experiments that allowed us to follow the ZnxCu4-x(OH)6Cl2 formation reaction. Furthermore, a systematic analysis of the height correlation function of the Atomic Force Microscopy (AFM) images of large terraces and

macrosteps present in the crystal surfaces is done in order to determine the growth mechanisms involved in the crystal growth process.In bulk α-GeO2 crystals grown by Top Seeded Solution Growth –Slow Cooling (TSSG-SC) in the ternary system GeO2 – K2Mo4O13 – K6P4O13 and by using seeds oriented along [001] it has been observed the presence of optical twins. In this work a deep study of their propagation, from the beginning until the end of the growth process, and the orientation of twin boundaries have been done by x-ray Topography. One {110} and several {001} oriented thin slabs were studied by using a "Lang technique". The obtained topographies show whether contrast only along the twin boundaries or between different twinned regions depending on the orientation of the slab and the used reciprocal lattice vector g. Apart from twins no other structural defects were observed by x-ray topography, attesting the high crystalline quality of crystals grown by Top Seeded Solution Growth. This x-ray technique along with chemical etching allowed us to determine the orientation of twin boundaries as well as to determine the extension of twinned zones. Moreover, the surface of the as grown natural faces, {010} and {101}, has been investigated by AFM to determine the growth mechanism and to differentiate the domain walls from the growth steps. In addition to these ex situ characterizations, in situ microscopy studies are under development to elucidate the origin of twin formation during crystal growth process