Thermodynamic and kinetic model of point defect distributions during Ti:sapphire growth

Lingling XUAN

Supervisor: T. Duffar

Thursday, October 28th 2021 – 1:30 p.m.

Amphi Jean Besson (Phelma Campus)

Jury :
Detlef KLIMM, Dr. Rer. Nat. Habil., Leibniz Institute for crystal growth, Berlin, Rapporteur
Loïc FAVERGEON, Maître de Recherche, École des Mines de St-Étienne, Rapporteur
Elisabeth SIEBERT, Directrice de Recherche CNRS, LEPMI, Présidente
Fiqiri HODAJ, Professeur à Grenoble INP-UGA, Examinateur
Kheirreddine Lebbou, Directeur de Recherche CNRS, Institut Lumière Matière, Lyon, Examinateur
Guillaume ALOMBERT-GOGET, Docteur-Ingénieur à RSA Le Rubis SA, Invité

Abstract: Ti:sapphire is outstanding for producing ultra-short pulse laser due to the presence of doping Ti3+ ions. However, the crystal laser efficiency is decreased by the residual absorption caused by harmful Ti4+. The valence conversion mechanisms between the two Ti ions during crystal growth are not completely understood and no theoretical model is available to explain the experimental distributions of both ions in the crystals. In this thesis, a physico-chemical model is established by taking into account the diffusion and chemical reaction of point defects and the validity of the model is checked through numerical simulation.

Ti ion concentrations in the solid phase are determined by their concentrations in the liquid phase and their segregation coefficients. First, FactSage software is used to thermodynamically calculate these values using updated database with respect to experimental solubility data. Then, the Ti ion concentrations and segregation coefficients are calculated and analyzed as function of the partial pressure of O2 (PO2). The influence of Mo and C on P_O2 is studied and results show that graphite elements surrounding the growing crystal have much more influence on P_O2 than the Mo crucible.

Further, a physico-chemical model is proposed to study the conversion mechanisms between Ti3+ and Ti4+ in the solid phase during Ti:sapphire growth. The model assumes that the conversion between Ti3+ and Ti4+ is controlled by the diffusion and chemical reaction of point defects, likely Al vacancies and holes. The boundary condition for the concentration of Al vacancies on the crystal surface is described as function of PO2 and temperature. This affects the final distributions of Ti ions in grown crystal.

The proposed model is implemented in COMSOL Multiphysics software to study its relevance during Ti:sapphire growth process. Simulation of annealing experiments are performed to obtain unknown physical parameters related to the model: Diffusion coefficient of Al vacancies and reaction rate constant. Then, previously calculated concentrations, segregation coefficients, boundary conditions and parameters are introduced into the numerical model. Simulation results for a simplified growth

configuration are performed. They show a qualitative agreement with the experiments. The effect of crystal growth rate, temperature gradient and PO2 on the Ti ion distributions is studied.