CRYSTAL GROWTH BETWEEN 1250°C AND 1100°C OF CUBIC RARE-EARTH SESQUIOXIDES BY THE FLUX METHOD

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Developing large optical grade cubic rare-earth sesquioxides (RE_2O_3, RE=Sc,Y,Gd,Tb,Lu) single crystals, pure or doped with Yb^{3+} ions, stands as one of the most challenging endeavours of today's crystal growth [1,2]. In recent years, we have unveiled a new flux method for growing such crystals, mainly for optical applications (lasers, scintillators, Faraday rotators).The obvious challenge to their growth in bulk single crystalline shape is imposedby the high melting point of these compounds (~2400-2500°C) and, in some of them like Gd_2O_3 or Tb_2O_3, it is rendered more difficult bya series of structural phase transitions occurring upon cooling from the melting point.The case of Tb_2O_3 turns out to be complicated by its mixed valence character which results in an easy oxidation at intermediate and high temperatures. In this work, we will present large dimensions (several mm^3) of pure Tb_2O_3 crystals,$Lu_{1.56}Gd_{0.41}Eu_{0.03}O_3$ scintillation crystaland highly Yb^{3+}-doped Gd_2O_3, Y_2O_3 and Lu_2O_3 single crystals of the cubic phase which were recently grown by a newly designed high-temperature solution growth method [3]. Furthermore we will report on their characterization by means of X-ray diffraction, visible, near infrared and Fourier transformed infrared (FTIR) spectroscopy, electron probe microanalysis (EPMA) coupled with wavelength dispersive spectroscopy (WDS),chemical analysis by GDMS, specific heat measurements and Squid magnetometry. Our method uses an original and nontoxic solvent with a growth setup operating in air and at half the melting temperature of rare-earth sesquioxides. The high-temperature solution growth conditions will also be discussed. Yb^{3+}-substitution levels as high as $Gd_{1.61}Yb_{\mathbf{0.39}}O_3$, $Y_{1.69}Yb_{\mathbf{0.31}}O_3$ and $Lu_{1.86}Yb_{\mathbf{0.14}}O_3$ were reached. In addition to the demonstration that this flux growth process allows achieving optimal doping for high-power laser applications, we will emphasize that it impedes the dissolution of OH^- groups in the crystals,avoids the reduction of Yb^{3+} ions into $Yb^{2+}$and last but not least favours broader absorption and emission bands. These uncoated new Yb^{3+}-doped cubic Gd_2O_3 and Y_2O_3 crystals have been successfully tested in different laser cavities under Ti:Sapphire and diode pumping, and the main laser performances will be shown. Our hydrogen free and controlled atmosphere flux method, which uses a heavy metal free solvent working between 1250°C and 1100°C, was also found to remarkably stabilize the Tb^{3+} oxidation state in Tb_2O_3 and the first Verdet constant measurements in the NIR spectral range suggest that these crystals have great potential as Faraday rotators as compared to well-known TGG crystal [4].

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