MICRORAMAN ANALYSIS OF CORUNDUM CRYSTALLIZED BY CRYOLITE FLUX

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Corundum is crystallized by different methods, among them Verneuil, Czochralski and flux growth give the crystals with the better quality. The Vernueil method allos the obtention of crystals with size and quality optimal for jewelry applications. Czochralski corundums give high quality crystals for technological applications. The flux method produces crystals very similar to natural corundum.

The choice of the growth methods depends on several factors. Our choice of the flux method was due to the availability of different phases formed with the components involved in the corundum growth by this procedure.

Usually the fluxes used to crystallize corundum are lead, bismuth and boron oxides and/or fluorides (PbO, PbF_2, Bi_2O_3, B_2O_3), the proportions of which can be varied. Also other mixtures can be used, the components of which are sodium carbonates, sulphates, fluorides and aluminates and cryolite (Na_3AlFe). The high solubility of the Al_2O_3 in melted cryolite is the principle of the Hall-Heroult process for the fabrication of aluminum. This process takes place at temperatures well below the melting point of pure alumina, this is the reason why the cryolite is an ideal solvent to obtain corundum crystals with the flux method.

A mixture of commercial alumina and cryolite with Cr_2O_3 as dopant and dye (in a 01.7:15.0:00.5 g. proportion) has been used in the present work. A platinun crucible (h = 4 cm and ∅ = 3,6 cm) covered with a glass fiber cap was used. The fussion was performed in a muffle kiln at 1200° C. The mixture was allowed to cool down to room temperature in 24 hours. The identification and preliminary characterisation of the products were performed by optical trasmission and reflection optical microscopy (OM), scannig electron microscopy (SEM), x-ray dispersed energy qualitative chemical analysis

(SEM+XDE), and x-Ray diffraction (XRD). This has been complemented with a detailed microRaman study of the differents identified phases ohf the melt.

Micro-Raman spectra were recorded on a DILOR X-Y raman spectrometer attached to a metallographic microscope. The excitation was done with either 488.0 or 514.5 nm lines of an Ar^+ laser, focuse by the microscope objective. The scattered light was also colleced by the microscope objective. The Raman signal spectrally resolved with the spectrograph and the detection was done with a liquid nitrogen cooled CCD. The Raman spectra were obtained in backscattering with the laser perpendicular to the sample plane. The samples were two thin layers cut along planes parallel and perpendicular to the crucible axis.

Corundum plates were identified on the crucible walls near the edge. These plates were pink colored; they can be isolated or forming bunches with small rose shape up to 5 mm diameter with micrometric thickness and (0001) crystal orientation. At the optical microscope they show helicoidal dislocations and small crystals spared over the surface, which were identified as sodium heptaluminun eleventhoxide ($NaAl_7O_{11}$) by microRaman and DRX. The residual melt exhibits an intense yellow color (dark green in some specific points). It is formed of fibers with radial distribution and optically isotrope round grains in between the fibers. The morphology of these grains can be associated with a vitreous phase, with a poor crystallinity, the Raman spectrum reveals the presence of corundum beneath these grains. Higher magnification of the fibers reveals that they are formed of a tangle of aligned thin plates. The space in between plates is filled with a granular material with vitreous aspect. This materiall has been identified as a cryolite, the characteristic Raman modes of the Corundum are also observed, though very weak. One observed as well the presence of octaedric structures on the crucible walls, which were associated with villiaumite (NaF). Also, some thick plates with hexagonal shape, identified as corundum and small hexagonal prisms, probably related to a sodium oxifluoride. The dark green colored material was cryolite, eskolaite (Cr_2O_3) and Na_5AlO_4.

In conclusion, a full identification of the different solid phases resulting of the cryolite flux grown corundum has been achieved using microRaman spectroscopy.

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