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FTIR SPECTROSCOPY OF OH^- IONS IN $Pb_5(GeO_4)(VO_4)_2$ APATITE

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Lead germanate vanadate – $Pb_5(GeO_4)(VO_4)_2$ (PGV) – is a promising acousto-optical material, which can be grown from melt by the Czochralski method (YANO et al., 1971). PGV crystallizes in a hexagonal structure characterized by the space group $P6_3/m$ (IVANOV & ZAVODNIK, 1989). It belongs to the general $A_4B_6(XO_4)_6Y_2$ apatite structure, where lead occupies both A and B positions, germanium and vanadium are randomly located in tetrahedral sites, X, and the anionic position, Y, remains empty. In hydroxyapatites Y denotes the OH group. In oxide crystals grown in air atmosphere, however, hydroxyl ions are usually present as impurities occupying oxygen sites (WÖHLECKE & KOVÁCS, 2001). The aim of this paper is to study the vibrational properties of hydroxyl ions possibly incorporated in synthetic $Pb_5(GeO_4)(VO_4)_2$ single crystals, using the Fourier Transform InfraRed (FTIR) absorption technique.

The presence of hydroxyl ions in *as-grown* $Pb_5(GeO_4)(VO_4)_2$ crystals has been confirmed by detecting an absorption band related to the stretching vibration of OH^- ions at $\nu = 3558$ cm^{-1} wavenumber at 300 K, $\Delta\nu \approx 20$ cm^{-1} These values are in relatively good agreement with those reported for $Ca_{10}(PO_4)_6(OH)_2$ hydroxylapatites, $\nu \approx 3572$ cm^{-1}, $\Delta\nu \approx 10$ cm^{-1} (CANT et al., 1971). The OD^- isotopic replica at 2625 cm^{-1} wavenumber has appeared in the crystal after a high temperature treatment at 1073 K in D_2O vapour atmosphere. The anharmonicity of the stretching mode calculated from the frequencies of the OH^-/OD^- ions is $x_e \approx 0.024$, in excellent agreement with those found for hydroxyl ions in other oxides (WÖHLECKE & KOVÁCS, 2001). The stretching mode frequency has shifted to higher energies, while the halfwidth of the slightly asymmetric band has shown an anomalous increase for decreasing temperatures ($\nu = 3561.5$ cm^{-1}, $\Delta\nu = 24$ cm^{-1} at 9 K). Anomalous behaviour has also been observed for the halfwidth of the absorption band using polarized light. At 300 K for light propagating along the *c* axis (ordinary polarization) $\Delta\nu$ is about 20 cm^{-1}, while for extra-ordinary polarization $\Delta\nu = 13$ cm^{-1} The band intensity, however, shows only a slight change for *o* and *eo* polarization directions. The anomalous temperature and polarization behaviour of the OH^- absorption band and the possible lattice sites of the hydroxyl ions in synthetic $Pb_5(GeO_4)(VO_4)_2$ apatite single crystals will be discussed.

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