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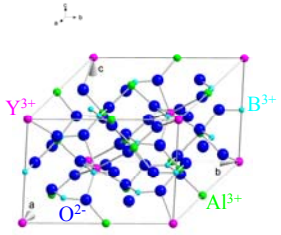
$YAl_3(BO_3)_4$ (YAB)



Hexagonal space group R32 with trigonal symmetry: $a = 9.293(2)$ Å, $c = 7.236(8)$ Å

- High radiation hardness
- high non-linear optical coefficient → self-frequency doubling (SFD)
- broad optical transmission range (2500-50000 cm^{-1}) → self-frequency summing (SFS)
- Cr^{3+} substitutes for Al^{3+}: O_h local symmetry
- RE^{3+} substitutes for Y^{3+}: D_3 local symmetry
- charge compensation not required → high RE^{3+} solubility

- YAB: Nd^{3+}: IR-to-visible up-conversion [1].
- YAB: Yb^{3+}: tunable green and yellow outputs [2,3].

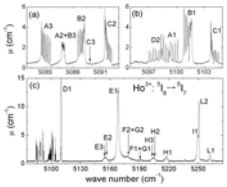
Experimental Details

YAB single crystals are grown by the TSSG from the $K_2O/MoO_3/B_2O_3$ mixed flux and intentionally doped with Ce^{3+}, Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}. Pure samples are studied as references.

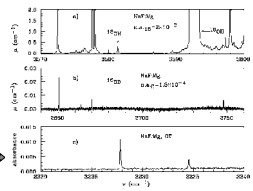
Optical absorption spectra are measured by means of a Fourier Transform (FT) spectrometer

- spectral range: 500-25000 cm^{-1}
- resolution: 0.01 cm^{-1} (non apodized)
- temperature range: 9-300 K.

High resolution FT spectroscopy was proved as powerful tool to monitor even fine spectra details.



⇐ Nuclear hyperfine interaction in YAB: Ho^{3+} [4].



Isotopic effects in alkali halides [5]: OD concentrations down to 3×10^{12}/cc. ⇒

Practically all samples are affected by traces of other RE^{3+}

Examples are supplied in Figs. 1, 2 and 3 by the spectra measured mainly at 9 K on YAB samples either **pure** or intentionally doped with different RE^{3+} (**Yb^{3+}**, **Ho^{3+}**, **Er^{3+}**, and **Dy^{3+}**) in the regions of Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$, Er^{3+} $^4I_{15/2} \rightarrow {}^4I_{13/2}$, $^4I_{11/2}$, and Dy^{3+} $^6H_{15/2} \rightarrow {}^6H_{9/2}$+$^6F_{11/2}$ crystal field transitions.

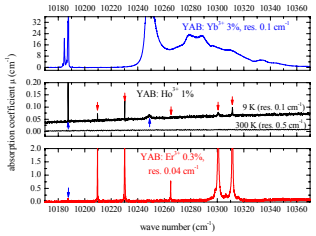


Fig. 1 – 9 K optical absorption spectra of YAB samples doped with different RE^{3+} (**Yb^{3+} 3%**, **Ho^{3+} 1%**, **Er^{3+} 0.3%**). The RT spectrum (res.=0.5 cm^{-1}) is also displayed. The traces of unwanted impurities are indicated by arrows.

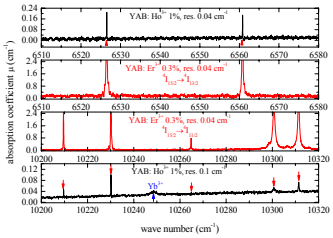


Fig. 2 – 9 K absorption spectra measured in the regions of Er^{3+} $^4I_{15/2} \rightarrow {}^4I_{13/2}$, $^4I_{11/2}$ transitions on YAB samples doped with different RE^{3+} (**Ho^{3+} 1%**, **Er^{3+} 0.3%**). The traces of unwanted impurities are indicated by arrows.

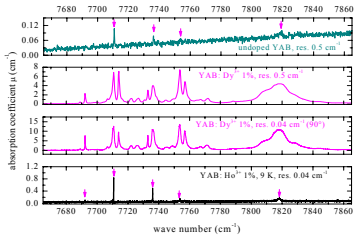


Fig. 3 – 9 K absorption spectra measured in the regions of Dy^{3+} $^6H_{15/2} \rightarrow {}^6H_{9/2}$, $^6F_{11/2}$ transitions on YAB samples **undoped** and doped with different RE^{3+} (**Dy^{3+} 1%**, **Ho^{3+} 1%**). The traces of unwanted impurities are indicated by arrows.

Although no Ho^{3+}-related lines are expected to fall in these regions, the high resolution applied at low temperature allowed detecting some weak and extremely narrow (down to 0.13 cm^{-1}) lines in the spectrum of the **Ho^{3+}** doped sample. By comparing the spectrum with those measured on samples doped with **Yb^{3+}** , **Er^{3+}**, and **Dy^{3+}** the unexpected lines could be attributed to small traces of **Yb^{3+}**, **Er^{3+}**, and **Dy^{3+}** [4,6]. The presence of Er^{3+} in the Ho^{3+} doped sample is confirmed by simultaneous presence of crystal field lines in the regions of $^4I_{15/2} \rightarrow {}^4I_{13/2}$ and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transitions of Er^{3+} in YAB (see Fig. 2). Evidences of Dy^{3+} traces are also observed in the nominally **pure** sample (see Fig. 3).

In the case of Nd^{3+}, the presence of traces in a YAB: **Pr^{3+}** sample is confirmed by the observation of the absorption lines within three crystal field transitions: $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$+$^2H_{9/2}$, and $^4F_{7/2}$+$^4S_{3/2}$.

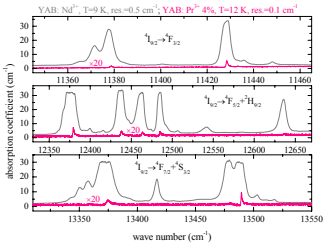


Fig. 4 – Low temperature absorption spectra measured on two YAB samples (doped with Nd^{3+} and **Pr^{3+}**) in the regions of Nd^{3+} $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$+$^2H_{9/2}$, $^4F_{7/2}$+$^4S_{3/2}$ transitions.

The quantitative evaluation of the unwanted RE^{3+} concentration from the related absorption line intensity is not an easy task. It was found for fluoride single crystals doped with Er^{3+} [7] that the line intensity does not linearly scale with the concentration due, not only to cluster formation, but also to the oscillator strength modification: the random distribution of an increasing amount of dopant lowers the crystal field symmetry probed by the RE^{3+}.

The impurity content can be evaluated if YAB samples intentionally doped with low concentrations of RE^{3+} are available as references, e.g. Er^{3+} (0.3%). ⇒ The Er^{3+} concentration in the Ho^{3+} doped sample is estimated to be ~20 ppm

Traces of Cr^{3+} are revealed

The two weak lines at about 14633 and 14690 cm^{-1} (R1 and R2 respectively), originated by the $^4A_2 \rightarrow {}^2E$ transition [6], are detected in almost all the samples. The high resolution and low temperatures allow to observe in a few samples the splitting of the **Cr^{3+}** lines into two components [8] of varying amplitude and separation (see Figs. 6 and 7).

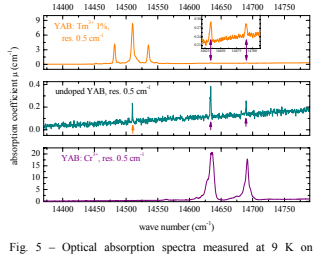


Fig. 5 – Optical absorption spectra measured at 9 K on different YAB samples: **undoped** and intentionally doped with **Tm^{3+} 1%** and **Cr^{3+}** . The traces of unwanted impurities are indicated by arrows.

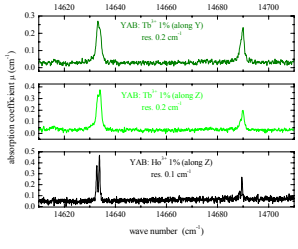


Fig. 6 – Optical absorption spectra measured at 9 K on different YAB samples: **Tb^{3+} 1% (beam travelling along Y axis)**, **Tb^{3+} 1% (beam along the Z axis)**, and **Ho^{3+} 1%**.

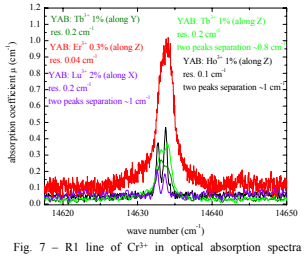


Fig. 7 – R1 line of Cr^{3+} in optical absorption spectra measured at 9 K on different YAB samples: **Tb^{3+} 1% (beam travelling along Y axis)**, **Tb^{3+} 1% (beam along the Z axis)**, **Er^{3+} 0.3%**, **Lu^{3+} 2%**, and **Ho^{3+} 1%**.

The high resolution Fourier transform spectroscopy is an effective tool to investigate the impurities present in crystals, even in very small amounts.

This might give some hints about the purity of the raw materials and the possible improvements in the growth technique and procedures.

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