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Corresponding Author:	Ashot Petrosyan ARMENIA
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Please submit a plain text version of your cover letter here.	Interstitial Li+ controls the UV transmission and the radiation hardness in YAG M.V. Derdzyan1, K.L. Hovhannesyan1, A. Novikov1, E. Auffray2, A.G. Petrosyan1*, C. Dujardin3 1Institute for Physical Research, 0203 Ashtarak, Armenia 2CERN, 1211, Geneva 23, Switzerland 3Institut Lumière Matière, UMR 5306 Université Lyon 1-CNRS, Villeurbanne, France *) email: ashot.petrosyan783@gmail.com Abstract Absorbance in as-grown and gamma-ray irradiated YAG-undoped, YAG:Li and YAG:Ca is compared for characterization of effects introduced by impurities. The studies are conducted on single crystals grown by the vertical Bridgman method. Basing on Li+ incorporation mechanism, clarification is done on optimal amounts of Li+ for preparation of YAG:Li crystals with low concentration of anion vacancies and related absorption in the UV range due to F-type centers. Differences in behavior are recorded in variously doped crystals subjected to gamma-ray irradiation; in comparison to un-doped YAG, the induced absorption coefficient at 300 nm in YAG:Li of optimal composition is lower by a factor 6. High transmission in the UV and high radiation tolerance are important for most applications of YAG, especially when operated in high radiation fields.
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Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	

First Author:	Marina Derdzyan
First Author Secondary Information:	
Order of Authors:	Marina Derdzyan
	Karine Hovhannesyan
	Artur Novikov
	Etiennette Auffray
	Ashot Petrosyan
	Cristophe Dujardin
Order of Authors Secondary Information:	
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Interstitial Li+ controls the UV transmission and the radiation hardness in YAG

M. V. Derdzyan, K. L. Hovhannesyan, A. Novikov, E. Auffray, A. G. Petrosyan, C. Dujardin*

Abstract

Optical absorption spectra measured in as-grown and gamma-ray irradiated un-doped YAG, Li-doped YAG and Ca-doped YAG single crystals are compared for characterization of effects introduced by impurities. The studies are conducted on single crystals grown by the vertical Bridgman method. Basing on the Li^+ incorporation mechanism, clarification is done regarding the optimal amounts of Li^+ for preparation of YAG:Li crystals with low concentration of anion vacancies and related defects giving rise to absorption in the UV range. Differences in behavior are recorded in variously doped crystals subjected to gamma-ray irradiation; in comparison to un-doped YAG, the induced absorption coefficient in Li-doped YAG of optimal composition is lower more than 6 times. High transmission in the UV and high radiation tolerance are important for most applications of YAG, especially when operated in high radiation fields.

1. Introduction

Since the first report of 1951,[1] yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) has found numerous applications as a laser,[2] phosphor[3] and scintillator[4] host. YAG is a stable compound which can be grown by all classical methods in the form of large single crystals of high optical quality (the melting point is 1935 °C). It is chemically and mechanically resistant material (Moh's value 8.5) and has high thermal conductivity (13 $Wm^{-1}K^{-1}$). The structure is cubic (space group is O^h_{10} - Ia3d) with eight coordinated Y^{3+}, and six and four coordinated Al^{3+}. Transmission range of YAG is from 180 nm to nearly 4 μm. Due to these properties un-doped YAG has also found applications as substrate and optical window material. In the form

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of fibers it is used for the delivery of IR laser radiation and, as expected, can be capable of transmitting very high laser energies.[5] Under high-energy excitation, emission from un-doped YAG associated with intrinsic lattice defects (vacancies and non-equivalent substitutions) is registered in the UV with maximum at around 300 nm; it is believed that modification of the defect states may improve its scintillation properties.[6,7] Because of its rather high index of refraction (n=1.8289 at 632.8 nm), un-doped YAG is presently considered also as a potential Cherenkov emitter. However, the Cherenkov photons are mainly emitted in the UV range, where the optical transmission is low.[4] High transmission in the UV and high radiation tolerance are therefore the most demanding parameters for most applications of YAG.

Available data from the literature show that there is a considerable variability in UV absorption of un-doped YAG depending on the crystal purity and sample history (applied growth method, ambient atmosphere and surface quality). A comprehensive analysis can be found in,[8] where references and comments to earlier papers are also given. An increase of absorption in the UV-visible range is observed after UV light or γ-ray irradiation, which is accounted for presence of vacancies and trace impurities. [9-11] Methods of control of anion vacancy concentration in as-grown YAG crystals remain thus a critical aspect for most of applications mentioned above. Incorporation mechanisms and the functional role of Li^+ impurity in different garnets have been examined in the recent paper.[12] It was found that, in contrast to isostructural LuAG ($Lu_3Al_5O_{12}$), Li^+ ions in the YAG host do not substitute for any lattice site but reside preferentially at interstitials decreasing the amount of anion vacancies. In this paper, an absorption spectroscopy study performed on as-grown and gamma-ray irradiated YAG:Li^+ crystals with varied Li+ concentration is presented. We confirm the functional role of Li^+ and establish interconnections between Li^+ concentration and the amplitude of UV absorption in YAG:Li crystals. The results show that the UV absorption and radiation tolerance of crystals can be largely controlled by selecting an appropriate concentration of Li^+.

2. Experimental

High purity Y_2O_3 (99.99%) powder and crystalline Al_2O_3 (99.95%) taken in stoichiometric amounts were used as starting components; Li was added in amounts 25÷150 ppm. Growth of single crystals was performed by the vertical Bridgman (or vertical directional crystallization) method in 14 mm diameter Mo tubes of special purity under Ar/H_2 atmosphere and using seed crystals cut parallel to <100> axis; details of the method can be found in.[13,14] The growth

parameters were controlled to provide comparable growth conditions for all crystals including the ambient gas composition, translation rate, thermal field and the cooling rate, since they may affect the concentration of defects and the extent of UV absorption. For comparison, a YAG:Ca single crystal was grown under similar conditions. The Ca^{2+} impurity has been selected because it is known as efficient in promoting anion vacancies and therefore shows the opposite behavior. The obtained crystals (around 70 mm long) of all compositions (un-doped YAG, Li-doped YAG, Ca-doped YAG) were transparent and colorless. Samples of 8x8x2 mm^3 and 8x8x9 mm^3 size were cut from different parts of the boules and polished employing diamond paste with the lowest grit size of 1.5 μm. Optical quality was examined using a green laser light and MPS-2 polarization microscope. Only small peripheral facets and occasional light scattering centers arising from micro-inclusions were found in the samples. Optical absorption spectra were measured with a SPECORD200 PLUS spectrometer in the 190-1100 nm range. Gamma-ray irradiation of the samples was done with a ^{60}Co source of 1.25 MeV photon energy and 468 Gyh^{-1} dose rate. The samples after irradiation acquired different coloration; after measurements they were further kept in a box to avoid any influence by the day light.

3. Results and discussion

Figure 1 shows the absorption spectra in the YAG:Li (0÷150 ppm) series measured in 2 mm thick samples cut from nearly the same positions over the crystal length, as well as in YAG:Ca (100 ppm).
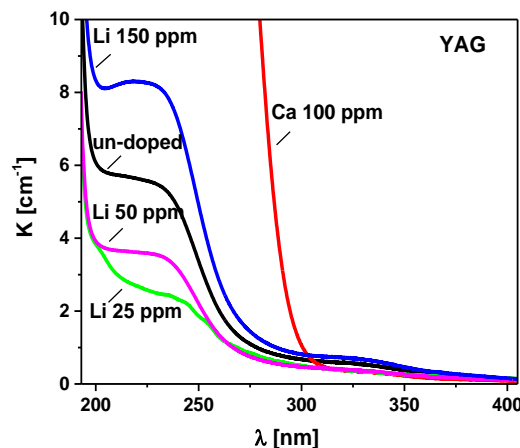

Figure 1. Optical absorption spectra of as-grown samples of un-doped YAG, YAG:Li (25, 50 and 150 ppm) and YAG:Ca (100 ppm) in the UV range.

In comparison to un-doped YAG, absorption in the 200-270 nm range in YAG:Li (25 ppm) and YAG:Li (50 ppm) is remarkably lower. Following,[12] Li$^+$ ions, when taken in small amounts, do not substitute for any lattice site but are accomodated in interstitials. The process is accompanied by a charge compensation *via* reduction of anion vacancies and of associated defect centers (mainly of F-type), which are responsible for absorption in this range. In the range above 290 nm reduction of O$^-$ centers is also possible. In comparison to un-doped YAG, absorption in YAG:Li (150 ppm) in the 200-270 nm range is higher evidencing that a part of Li$^+$ ions is forced into lattice sites accompanied by creation (for charge balance) of additional anion vacancies. As expected, absorption in YAG:Ca is significantly higher due to a larger amount of anion vacancies present in the lattice, since Ca^{2+} ions substitute for Y^{3+} sites due to the small (~10%) size difference (Ca^{2+} - 1.12 Å, Y^{3+}- 1.02 Å, in eight-fold coordination) and the charge misfit of only unity. Increase of absorption in the UV range was observed also in LuAG:Li (in comparison to LuAG), in which Li$^+$ ions are incorporated at Lu^{3+} sites (Li$^+$ - 0.92 Å, Lu^{3+} - 0.977 Å; size difference ~6 %).[12] Thus, the preference for site substitution by Li$^+$ becomes less favorable, when going to larger cations in place of Lu^{3+}. The size difference between the host and impurity ions is therefore much more critical in the case of charge misfit equal to two.

The values of absorption coefficient at 224 nm measured over the crystal length in four examined compositions (including un-doped YAG) are given in **Figure 2**.
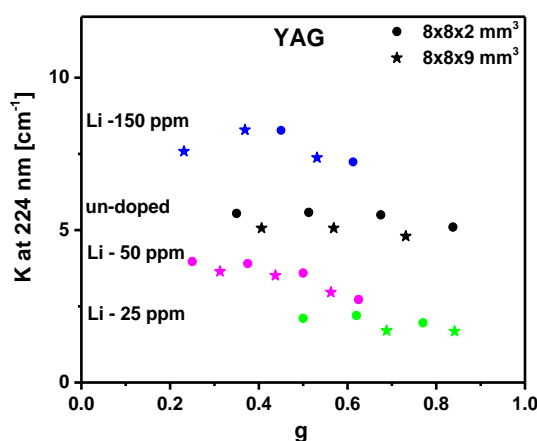

Figure 2. Absorption coefficient at 224 nm in un-doped YAG and YAG:Li (25, 50, and 150 ppm) measured in different parts over the crystal length (g is the portion of crystallized melt).

While absorption in un-doped YAG remains almost constant, there is some decrease towards crystal end in the YAG:Li series, which may be caused by gradual loss of Li from the melt.

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Absorption in YAG:Ca increases towards the crystal end (**Figure 3**), since the distribution coefficient of Ca^{2+} is less than unity leading to segregation and gradual increase of the Ca^{2+} concentration over the crystal length, which, in turn, results in formation of higher amounts of anion vacancies and related centers. Contribution of various types of lattice defects and trace impurities to absorption in the 190-350 nm range in as-grown crystals is possible including F-type centers,[15,16] Fe^{3+} (at 255 nm) and Fe^{2+} (at 312 nm).[9]
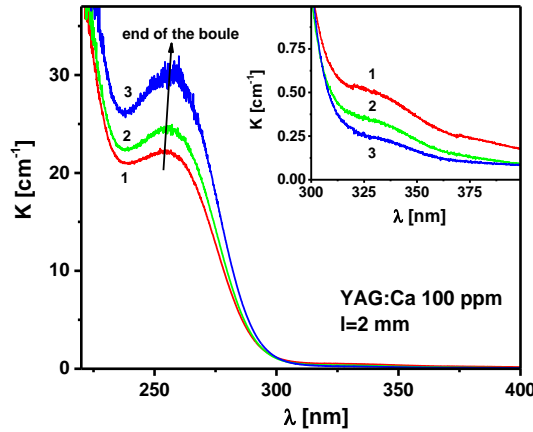

Figure 3. The Ca-doped YAG: optical absorption spectra measured in different parts over the crystal length of (inset: zoom of the 300-400 nm range).

To establish the correlation between the composition and the extent of radiation damage, the optical transmission spectra in un-doped YAG (a), YAG:Li (50 ppm) (b) and YAG:Li (25 ppm) (c) before and after irradiation were measured and shown in **Figure 4**.
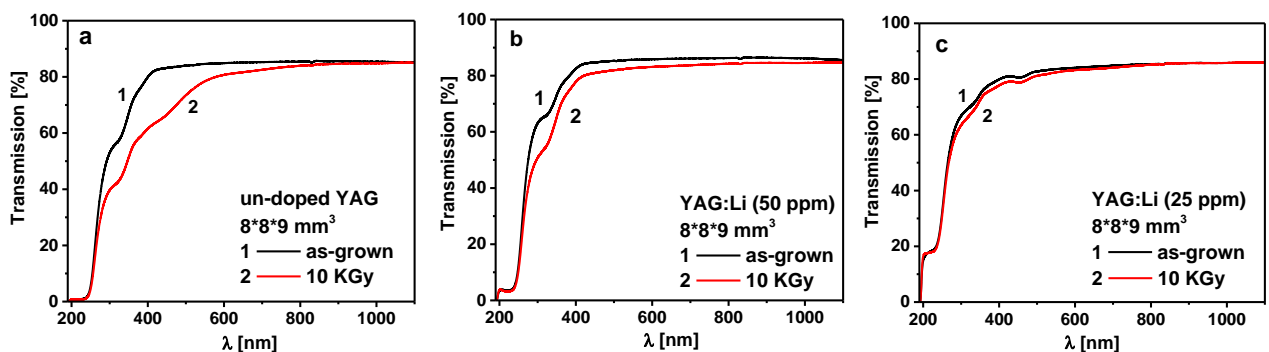

Figure 4. Transmission spectra of as-grown and gamma-ray irradiated samples:
(a) un-doped YAG, (b) YAG:Li (50 ppm) and (c) YAG:Li (25 ppm).

The corresponding radiation induced absorption spectra are shown in **Figure 5**; for comparison, the radiation induced absorption spectrum in the Ca-doped YAG is also shown in **Figure 5**. The lowest radiation damage is observed in the YAG:Li (25 ppm) sample. The induced absorption bands peaking at around 220 nm, 240 nm, 315 nm and the wide band at around 405 nm with a tail extending to 700 nm are seen in un-doped YAG and in Li-doped YAG samples, as shown in **Figure 5b**. The bands appearing in the 190-450 nm range were previously assigned to different F-type centers, [15-20] traces of Fe^{3+} (at 255 nm) and Fe^{2+} (at 312 nm), [9] and O^- centers at 312-345 nm [20] and 390 nm.[21] In addition to intense bands at 250 nm and 300 nm **(Figure 5a)**, the band in the 480-500 nm range is seen in the Ca-doped YAG **(Figure 5b)**. Its origin is not finally clear but following [21] (and references sited therein) may be related to electron F^+ centers.
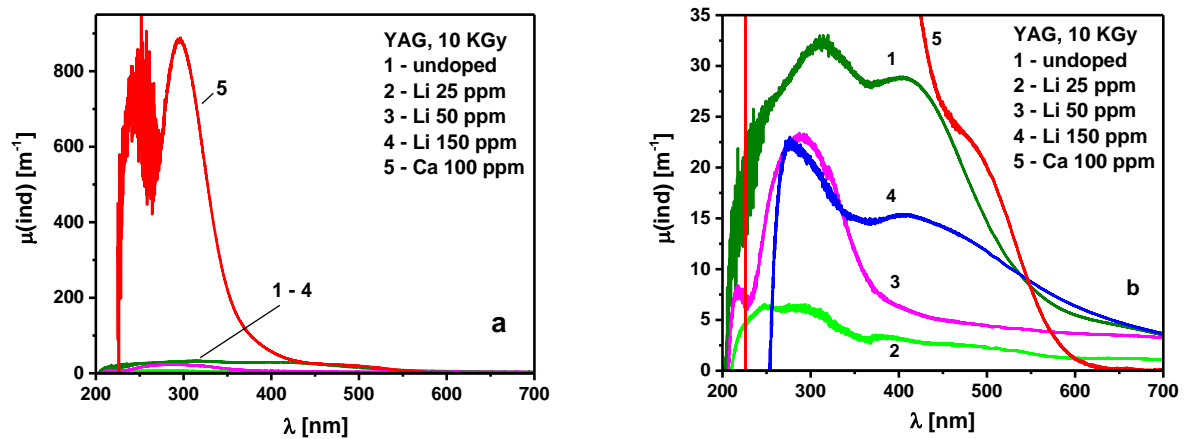

F**igure 5**. Gamma-ray radiation induced absorption spectra of un-doped YAG, YAG:Li (25, 50, 150 ppm) (size: $8 \times 8 \times 9$ mm^3), and YAG:Ca (100 ppm) (size: $8 \times 8 \times 2$ mm^3) (a); zoom of the same spectra (b).

After gamma-ray irradiation with 10 KGy dose the un-doped YAG sample acquired a yellowish coloration, while the Li-doped YAG samples remained colorless. After irradiation with the same dose, the Ca-doped YAG sample acquired a pale yellow-orange coloration, but over time the coloration disappeared. The photographs of all crystals taken a month after the irradiation are shown in **Figure 6**. The induced absorption spectra measured in un-doped YAG and Ca-doped YAG $8 \times 8 \times 2$ mm^3 plates immediately after the irradiation and 6 months later are shown in **Figure 7.** The wide band in the range around 480-550 nm responsible for the coloration of the Ca-doped YAG has disappeared evidencing that the corresponding

centers are unstable. An accurate assignment of all observed bands to particular centers requires additional studies.
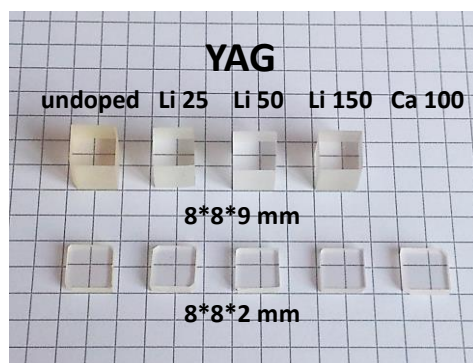

Figure 6. Photographs of single crystal samples of un-doped YAG, Li-doped YAG and Ca-doped YAG (see the text).
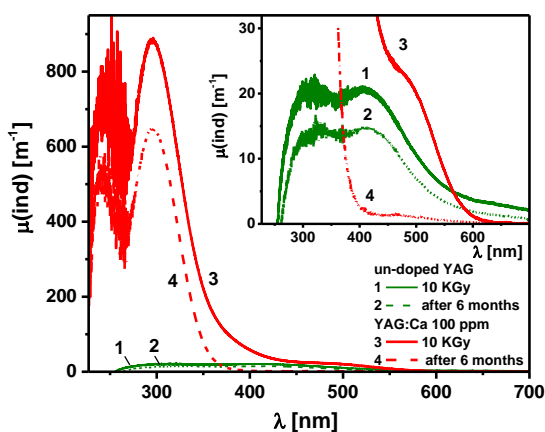

Fig. 7. Decay of the gamma-ray induced absorption bands in un-doped YAG and YAG:Ca (plates 8x8x2 mm^3); inset: zoom of the spectra.

The present contribution demonstrates the importance of preparation of YAG crystals with different aliovalent dopants and understanding of their functional role. Among the studied compositions, the YAG:Li (25 ppm) exhibits the lowest absorption in the UV range in both as-grown and gamma-ray irradiated samples and can therefore be considered as a potential material for Cherenkov emitters. The Ca-doped YAG shows very intense absorption in the UV range after irradiation however, the transmission above 600 nm is retained and is higher than of other studied compositions. It can therefore be considered as a potential material in applications requiring conservation of a high transparency above 600 nm, e.g. in solid state

lasers that use intracavity elements (optical windows, Fabry-Perot elements, etc), since, unlike the widely used technical sapphire, YAG is birefringence free.

Conclusions

Un-doped YAG, YAG:Li (25÷150 ppm) and YAG:Ca (100 ppm) single crystals were grown by the vertical Bridgman method and studied for UV absorption in as-grown and gamma-ray irradiated samples. It is shown that absorption in the UV range can be efficiently controlled by appropriate selection of the Li^+ concentration. The results confirm that Li^+ ions, when taken in low concentrations, occupy preferentially interstitials and decrease the amount of anion vacancies and related F-type centers, as well as of O^- centers. In comparison to un-doped YAG, absorption in the UV range in both as-grown and gamma-ray irradiated YAG:Li (25 and 50 ppm) single crystals is much lower. The Ca-doped YAG exhibits very intense absorption bands in the UV range due to creation of a large number of anion vacancies resulting from substitutions by Ca^{2+} for Y^{3+} sites. However, after gamma-ray irradiation, it remains highly transparent in the range above 600 nm.

Acknowledgements

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