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# Effects of divalent dopants on the microstructure and conversion efficiency of $Cr^{4+}$ ions in Cr,Me:YAG (Me – Ca, Mg, Ca/Mg) transparent ceramics

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## Abstract

*The efficiency of $Cr^{4+}$:YAG is directly proportional to the transparency and concentration of $Cr^{4+}$ which can be tuned by changing the divalent dopant. The aim of this study was to investigate the influence of different kinds of divalent dopants on the properties of Cr,Me:YAG (Me = Ca, Mg or Ca/Mg) ceramics made by solid-state sintering in vacuum. Pure YAG phases with an in-line transmittance of 80% at 1064 nm were prepared. It was revealed that the $Cr^{4+}$ concentration is directly proportional to the concentration of divalent dopants and it does not depend on the type of dopant. Our experiment proves that the efficiency of high optical quality $Cr^{4+}$:YAG ceramics prepared by sintering does not change when different kinds of divalent additives are used.*

***Keywords:*** *$Cr^{4+}$:YAG, vacuum sintering, additives, optical properties*

## I. Introduction

Yttrium aluminium garnets doped with tetravalent chromium ($Cr^{4+}$:YAG) are solid-state laser materials used as saturable absorber for the 1.06 mm laser emission [1–6]. Moreover, these materials are employed as tunable mid-IR lasers in the 1.3 to 1.6 μm spectral range [7]. The efficiency of $Cr^{4+}$:YAG as laser materials is directly proportional to the transparency and to the concentration of $Cr^{4+}$ [8–10]. These parameters can be improved by changing the concentration of functional dopants such as Ca and/or Mg. However, up to now, there are few works reporting a systematic study of the influence of these dopants on the properties of $Cr^{4+}$,Me:YAG ceramics and there are questions that still need to be answered [9–14].

$Cr^{4+}$:YAG ceramics are commonly produced by vacuum sintering from the initial oxides and CaO and MgO, which are added as sources of Ca and Mg counterions [12,15–18]. In the YAG crystal lattice, chromium can coexist in different oxidation states as some other elements do [9,10,18–23]. The $Cr^{4+}$:YAG ceramic synthesis requires the use of divalent dopants such as Ca or Mg, as charge compensators for $Cr^{4+}$ ions. Only a small amount of $Cr^{3+}$ ions recharges into $Cr^{4+}$ valence state even when the concentration of divalent dopants is one order of magnitude higher than the $Cr^{3+}$ concentration. The dependence of $Cr^{4+}$ concentration on $Me^{2+}$ doping level [9–12,24] and annealing conditions [13,14,25] has already been investigated, but, to our knowledge, there are not yet published reports discussing the properties of $Cr_4^{+}$,Ca:YAG, $Cr^{4+}$,Mg:YAG and $Cr^{4+}$,Ca,Mg:YAG ceramics sintered in a single technological cycle. Therefore, there is still an open question about which the best divalent dopants for $Cr^{4+}$:YAG ceramics are.

The aim of this study was to investigate the influence of different kinds of divalent dopants on the properties of $Cr^{4+}$,Me:YAG (Me = Ca, Mg or Ca/Mg) ceramics that seem to be promising for use as passive Q-switchers. Optical transparency of $Cr^{4+}$,Me:YAG ceramics strongly depends on the concentration of divalent dopants [12] and therefore, divalent dopants were

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**Table 1. Composition and thermal history/annealing conditions of each sample**

| Sample | Concentration [at.%] | | | Vacuum sintering | | Air annealing | |
|---|---|---|---|---|---|---|---|
| | Cr | Ca | Mg | $T$ [°C] | $t$ [h] | $T$ [°C] | $t$ [h] |
| Cr,Ca:YAG | 0.1 | 0.5 | 0 | 1750 | 10 | 1450 | 15 |
| Cr,Mg:YAG | 0.1 | 0.08 | 0.05 | 1750 | 10 | 1450 | 15 |
| Cr,Ca,Mg:YAG | 0.1 | 0 | 0.05 | 1750 | 10 | 1450 | 15 |

used in order to obtain the high optical qualities of the samples at the same technological cycle.

## II. Experimental details

Three different compositions of Cr,Ca:YAG (with 0.1 at.% of Cr and 0.5 at.% of Ca), Cr,Mg:YAG (with 0.1 at.% of Cr and 0.05 at.% of Mg) and Cr,Ca,Mg:YAG (with 0.1 at.% of Cr, 0.5 at.% of Mg and 0.08 at.% of Ca) ceramics were prepared by reaction sintering in vacuum using high-purity precursors: $Al_2O_3$, $Y_2O_3$, MgO, CaO and $Cr_2O_3$ powders. The amount of each oxide powder was calculated based on the YAG stoichiometry, whereas $Cr^{3+}$ and $Me^{2+}$ concentrations were regulated to substitute $Al^{3+}$ and $Y^{3+}$ ions, respectively. The homogenization of the obtained mixture was carried out in a planetary mill for 15 h using high-purity aluminium oxide balls. The resulting mixture was dried in a drying cabinet for 24 h and then compacted by isostatic pressing at 250 MPa. The solid-phase synthesis was carried out in a vacuum oven at a temperature of 1750 °C for 10 h. This procedure is described in more detail in our previous reports [26–28]. The $Cr^{3+}$ oxidation to the tetravalent state was achieved by annealing the samples in air at 1450 °C for 15 h. The composition and the temperature used during the manufacturing of each sample are presented in Table 1.

Optical studies were carried out using a Perkin Elmer Lambda 35 optical spectrophotometer in the wavelength range of 190–1100 nm. Microstructure of the ceramics was investigated using a scanning electron microscope (SEM, JEOL JSM-6390LV). X-ray diffraction analysis was performed on a DRON-3 X-ray diffractometer.

## III. Results and discussion

### *3.1. Microstructure*

XRD study (Fig. 1) of the phase composition of the Cr,Me:YAG ceramics confirms the presence of the cubic yttrium aluminium garnet phase according to the ICSD Card N170158. The diffraction data were refined with the cubic $Ia\bar{3}d$ space group for $Y_3Al_5O_{12}$ by using the Rietveld analysis (Fig. 2). The analysis gives lattice parameter 12.0002 ± 0.0002 Å, 11.9962 ± 0.0004 Å, 11.9987 ± 0.0003 Å for the Cr,Ca:YAG, Cr,Mg:YAG and Cr,Ca,Mg:YAG samples, respectively. As shown in Fig. 1, all the diffraction peaks are ascribable only to YAG phase, and impurities were not detected. There is no essential displacement of the XRD peaks after addition of $Ca^{2+}$ and/or $Mg^{2+}$ ions in comparison to the pure YAG. The minor changes of the lattice parameter of the ceramics with different dopants can be explained by the difference between $Ca^{2+}$ and $Mg^{2+}$ radii, but the other reasons also can affect. Due to the complicated process of intercalation of $Me^{2+}$ ions into YAG, the XRD results are not enough to determine the location of $Me^{2+}$ incorporation into YAG structure. For example, recently the microstructure of Cr,Ca:YAG ceramics was investigated by means of high-resolution electron microscopy [27]. Inhomogeneous distribution of $Ca^{2+}$ ions in YAG grains was shown, caused by the formation of Ca-rich layer of the same crystal structure and crystallographic orientation as the original grains. The concentration of Ca in this layer was higher than the solubility of $Ca^{2+}$ ions in YAG. So high concentration of Ca might cause the

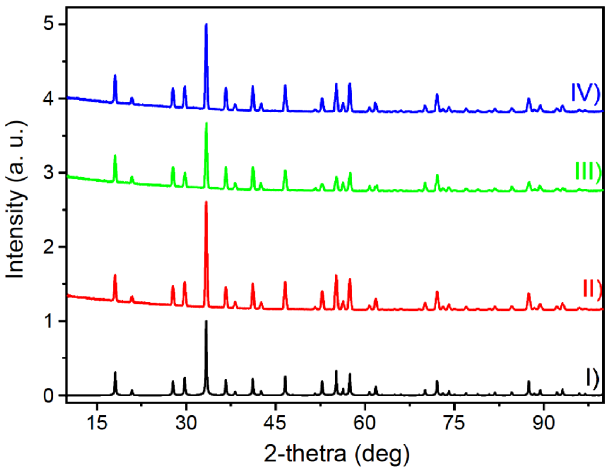


**Figure 1. X-ray diffraction patterns of ICSD Card N170158 of YAG (I) and the samples Cr,Ca:YAG (II), Cr,Mg:YAG (III) and Cr,Ca,Mg:YAG (IV)**

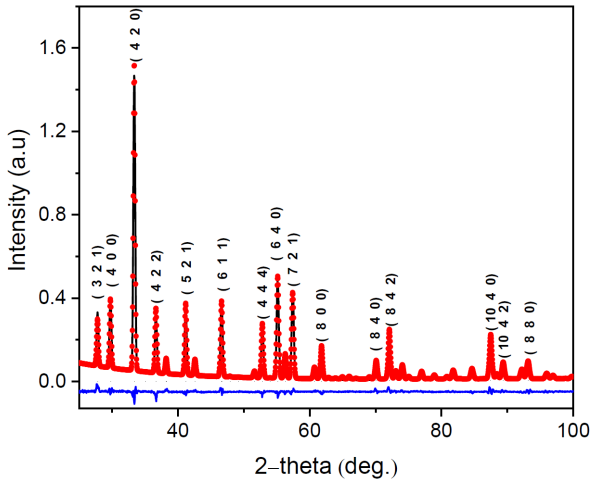


**Figure 2. The Rietveld analysis of the Cr,Ca:YAG X-ray diffraction pattern with the main (*hkl*) values**

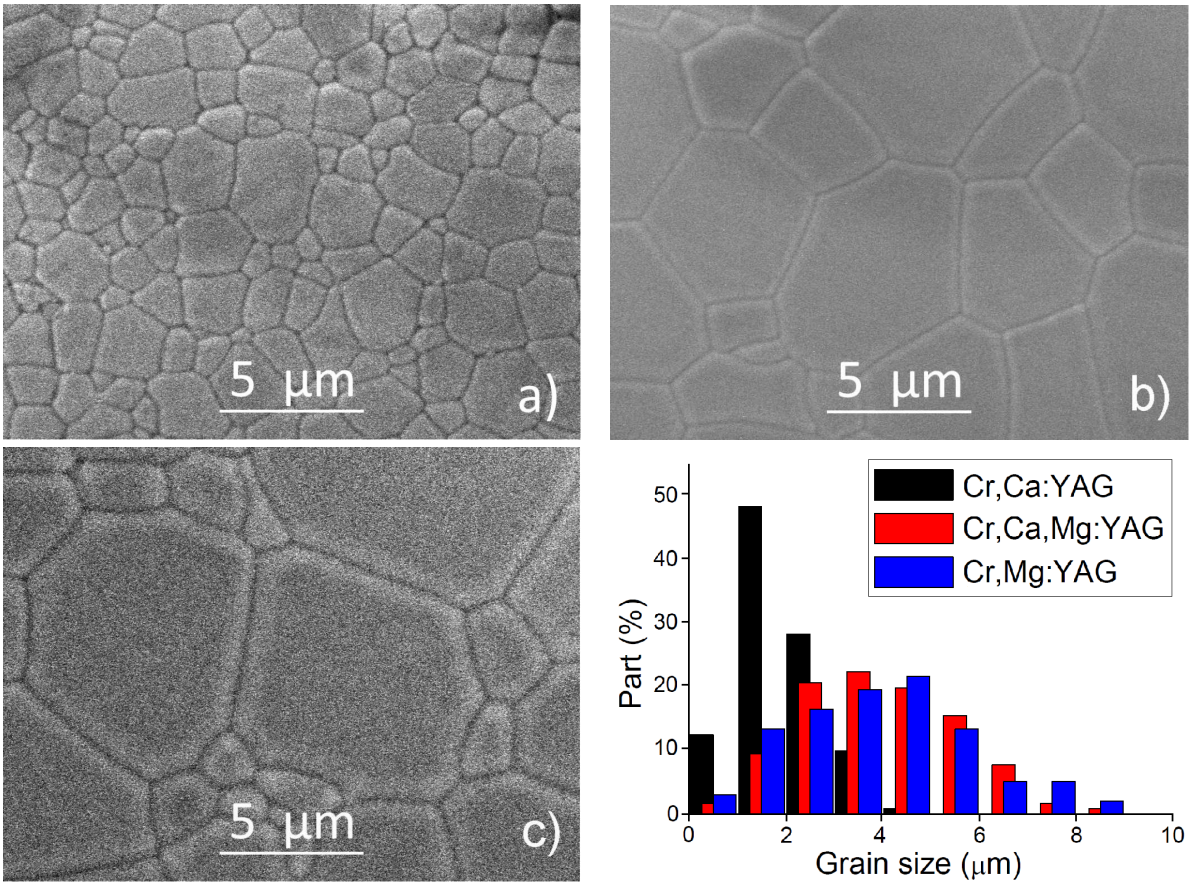


**Figure 3. SEM images of the thermally etched surface of $Cr^{4+}$:YAG ceramics: a) Cr,Ca:YAG, b) Cr,Mg:YAG, c) Cr,Ca,Mg:YAG and d) grain size distribution in the samples**

lattice distortion in this layer. In contrast to $Ca^{2+}$ ions, no similar research has been provided for $Mg^{2+}$-doped YAG ceramics.

The SEM investigation did not show the presence of impurity phases, in agreement with the XRD analysis. The addition of MgO led to an increase in grain size. This phenomenon could be recognised from Figs. 3a, 3b and 3c, i.e. two samples with Mg have larger grains than the sample with Ca as the only dopant. The grain size distribution of the Cr,Ca:YAG sample is in the range from 0.5 to 5 μm, whereas grains in the Cr,Mg:YAG and Cr,Ca,Mg:YAG samples have similar sizes, i.e. in the range from 0.5 to 11 μm (Fig. 3d). The average grain sizes of the Cr,Ca:YAG, Cr,Mg:YAG and Cr,Ca,Mg:YAG samples are 1.9 ± 0.2, 3.9 ± 0.3 and 3.9 ± 0.3, respectively. It should be noted that the concentration of $Mg^{2+}$ in the two later ceramics is the same, while in one of them is lack of $Ca^{2+}$. The addition of $Ca^{2+}$ in the amount under the threshold of solubility does not affect the average grain sizes and size distribution of the Cr,Mg:YAG and Cr,Ca,Mg:YAG ceramics. It means that there is no mutual effect of $Ca^{2+}$ and $Mg^{2+}$ on the morphology of the ceramics. Regarding the influence of calcium ion, it was mentioned [29] that when $Ca^{2+}$ concentration was increased to 0.5 at.%, the inhibition of the grain growth by Ca-rich layer took place.

According to our knowledge, no papers reporting the influence of Ca/Mg ratio on the average grain size of Cr-doped YAG ceramics were published before. Zhou *et al.* [30] reported the rising average grain size with decreasing Ca/Mg ratio in YAG ceramics. This is consistent with our results though in the reported work [30] the YAG ceramics was sintered using TEOS as sintering aid and without Cr-additives. Some discrepancies with our results can be explained by the presence of Cr additives, not using TEOS, different concentration of $Ca^{2+}$ and $Mg^{2+}$, and peculiarity of the sintering conditions. As it has been established earlier, the $Cr^{3+}$ additive changed the sintering process of YAG ceramics [18] and redistributed divalent additives in the grain volume [29].

### *3.2. Optical properties*

The in-line transmission spectra of the Cr,Me:YAG ceramics after vacuum sintering are presented in Fig. 4 (solid line). After vacuum sintering, all samples contained Cr only in its trivalent state. The two absorption bands responsible for $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ transitions, with maximum absorption at 590 and 430 nm, respectively, give a characteristic green colour to the Cr,Me:YAG ceramics [31–33]. The transparencies of the samples were comparable and the in-line transmissions were about 80% at 1064 nm and 72–75% at 375 nm (Fig. 4) indicating a high optical quality of the sintered samples.

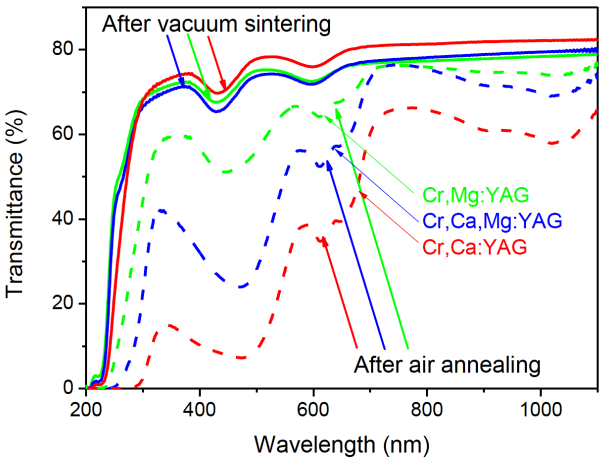


**Figure 4. In-line transmission spectra of Cr,Ca:YAG (red line) Cr,Ca,Mg:YAG (blue line) and Cr,Mg:YAG (green line) samples after vacuum sintering (solid line) at 1750 °C for 10 h and air annealing at 1450 °C for 15 h (dash line)**

The formation of $Cr^{4+}$ ions in the Cr,Ca:YAG ceramics takes place during annealing in an oxidizing ambient where the tetravalent impurities can be stabilized through the formation of structural defects in the lattice [34–37]. To recharge chromium into the tetravalent state, the samples were annealed in air at 1450 °C for 15 h. The air annealing provides the rise of the absorption bands belonging to $Cr^{4+}$ ions that lead to the drop in transparency of the samples (Fig 4 dash line). As a result, the crystals' colour changed from light green, typical of $Cr^{3+}$, to dark-brown, typical of $Cr^{4+}$ doped YAG. Since no absorption of $Cr^{4+}$ ions was detected after vacuum sintering, the observed change in the absorption of the samples after air annealing originates only from the formation of $Cr^{4+}$ ions. Absorption of $Cr^{3+}$ is weaker than of $Cr^{4+}$ as seen from Fig. 4. Therefore, subtraction of the absorption spectra of the sample before air annealing from that after annealing may then be assigned to $Cr^{4+}$ ions alone [38].

Figure 5 represents the absorption spectra of $Cr^{4+}$ ions in the samples. The absorption coefficients

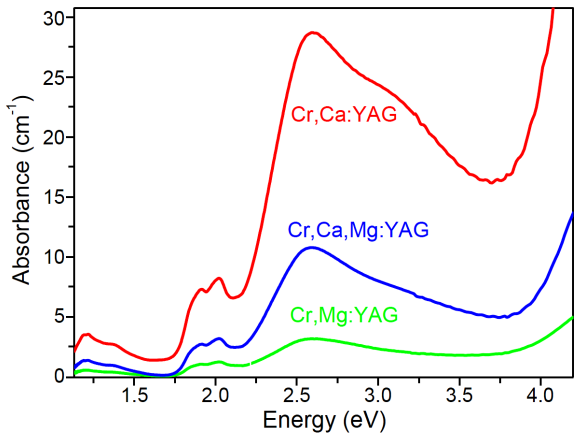


**Figure 5. Absorption spectra of $Cr^{4+}$ in Cr,Ca:YAG (red line), Cr,Ca,Mg:YAG (blue line) and Cr,Mg:YAG (green line) ceramics after vacuum sintering and oxidation annealing**

of $Cr^{4+}$ ions in the Cr,Ca:YAG, Cr,Mg:YAG and Cr,Ca,Mg:YAG samples were approximately 3.6, 0.55 and 1.3 $cm^{-1}$ at 1030 nm after annealing. The concentration of $Cr^{4+}$ ions was calculated from the absorption of $Cr^{4+}$ ions in the samples (see Fig. 5) according to the methodology described in the literature [12]. The concentrations of Cr ions are presented in Table 2. The concentration of $Cr^{3+}$ and $Ca^{2+}$ ions was taken from the initial powder mixtures. The sample Cr,Ca:YAG had the highest concentration of $Cr^{4+}$ ions, both in the octahedral and in the tetrahedral sites. The ratio between $Cr^{4+}$ and the total Cr in the samples Cr,Ca:YAG, Cr,Mg:YAG and Cr,Ca,Mg:YAG was 24.4, 3.3 and 8.6%, respectively. Up to 10% of the divalent additives compensated Cr of its tetravalent state. The distribution of $Cr^{4+}$ ions between octahedral and tetrahedral sites slightly depends on the divalent impurities: the relative population of tetrahedral sites occupied by $Cr^{4+}$ ions was a little bit higher in the sample doped only with Mg.

## IV. Discussion

As it can be expected, different compositions lead to different properties of the Cr,Me:YAG ceramics. The peculiarity of $Cr^{4+}$:YAG materials is the requirement of divalent additives to stabilize $Cr^{4+}$ ions; these can be Ca, Mg or both. The presence of these additives has an influence on the $Cr^{3+}$ to $Cr^{4+}$ ions transformation as well as on the microstructure and the transparency of the ceramics. Early, we have shown that the different behaviour of the Ca:YAG and Mg:YAG ceramics is due to a different kind of interaction between CaO and MgO with the basic components of YAG, i.e. $Al_2O_3$ and $Y_2O_3$ [34]. Therefore, it can be assumed that the Cr,Me:YAG ceramics, where Me stands for Ca, Mg or a mixture of Ca and Mg, has dissimilar characteristics.

It was shown that the sample microstructure is determined by the nature of the dopants. The average grain size of the Cr,Ca:YAG sample was 1.9±0.2 μm, whereas it was 3.4±0.2 μm in the Ca:YAG ceramics [34] with the same concentration of CaO; moreover, the Ca:YAG ceramics was totally opaque. The discrepancy in the grain size and optical behaviour between these samples is due to the presence/absence of $Cr_2O_3$ additives. As we have discussed in our previous work [12], the grain size in the final ceramics depends on the interaction between CaO and $Cr_2O_3$ in the early stages of sintering. The Cr,Mg:YAG and Mg:YAG [34] ceramics did not show any difference in the transparency and microstructure (except for the presence/absence of $Cr^{3+}$ ions absorption bands). This means that MgO and $Cr_2O_3$ do not interact during sintering, in contrast with what was observed for CaO.

The nature of divalent additives does not have an influence on the transparency and the $Cr^{4+}$ ions formation efficiency of Me,Cr:YAG ceramics. The in-line transmittance of the three samples is very similar in the range of 300–1100 nm. This indicates the possibility to pre-

**Table 2. Parameters of Cr,Me:YAG ceramics after oxidizing annealing at 1400 °C for 15 h ($N_D$ and $N_A$ correspond to the concentrations of $Cr^{4+}$ ions in tetrahedral and octahedral positions, respectively)**

| Sample | $N_D \times 10^{17}$ [$cm^{-3}$] | $N_A \times 10^{17}$ [$cm^{-3}$] | $N_D/N_A$ | $Cr^{4+}/(Ca^{2+} + Mg^{2+})$ | $Cr^{4+}/(Cr^{3+} + Cr^{4+})$ |
|---|---|---|---|---|---|
| Cr,Ca:YAG | 19.3 | 36.9 | 0.52 | 0.081 | 0.244 |
| Cr,Mg:YAG | 2.9 | 4.6 | 0.65 | 0.109 | 0.033 |
| Cr,Ca,Mg:YAG | 7.0 | 12.9 | 0.54 | 0.111 | 0.086 |

pare highly transparent ceramics with CaO, MgO or the two of them. The concentration of $Cr^{4+}$ ions is directly proportional to the concentration of divalent additives and it does not depend on their nature, as it can be seen from $Cr^{4+}/(Ca^{2+} + Mg^{2+})$ ratio in Table 2. After air annealing, the Cr,Ca:YAG sample demonstrated the highest concentration of $Cr^{4+}$ ions among the tested compositions. In the Cr,Ca:YAG ceramics, about 25% of $Cr^{3+}$ ions recharge into $Cr^{4+}$, whereas for the Cr,Mg:YAG only less than 4% does so; however, the efficiency of divalent additives is approximately 10% for all samples.

To our knowledge, it was the first time that Cr,Ca:YAG, Cr,Ca,Mg:YAG, and Cr,Mg:YAG ceramics were sintered under the same conditions and their properties were systematically compared. It was demonstrated that high-quality $Cr^{4+}$:YAG ceramics with similar efficiency can be prepared by using different kinds of divalent additives (CaO, MgO or both). The experiments showed that these materials are free from impurities, highly transparent and have analogous concentrations of $Cr^{4+}$ ions. Our results suggest that it is possible to prepare composite structures such as $Cr^{4+}$:YAG/Nd:YAG using either CaO or MgO as additives.

However, there are some limitations that have to be taken into account: i) the concentration of divalent additives in the samples is not the same; ii) using equal concentrations of CaO and MgO additives requires different sintering parameters; iii) the same sintering conditions necessitate different concentrations of divalent additives, making it impossible to correctly compare their properties. Future work should, therefore, include sintering of Cr,Me:YAG ceramics with various concentrations of Cr and Me.

## V. Conclusions

$Cr^{4+}$:YAG ceramics with different divalent dopants was sintered by solid-state reaction at 1750 °C in a vacuum. Our experiment reveals that the efficacy of $Cr^{3+}$ to $Cr^{4+}$ transformation under air annealing does not depend on the type of divalent dopant. X-ray and SEM analyses showed the formation of pure YAG phases, without the presence of any impurity. The in-line transmittance of the samples in the range of 300–1100 nm is comparable. This indicates the possibility to prepare highly transparent ceramics using CaO, MgO or both as additives. The efficiency of the transformation of $Cr^{3+}$ to $Cr^{4+}$ under air annealing is directly proportional to the concentration of divalent dopant and it does not depend on its nature. This paves the way towards the use of either Ca or Mg as a divalent dopant to prepare $Cr^{4+}$:YAG ceramics of high optical quality.

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