Neutron Powder Diffraction Measurements of the Spinel MgGa$_2$O$_4$:Cr$^{3+}$ - A Comparative Study between the High Flux Diffractometer D2B at the ILL and the High Resolution Powder Diffractometer Aurora at IPEN

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Abstract. Optical materials that emit from the visible to the near-infrared spectral region are of great interest due to their possible application as tunable radiation sources, as signal transmission, display, optoelectronics signal storage, cellulose industry as well as in dosimetry. One important family of such systems are the spinel compounds doped with Cr$^{3+}$, in which the physical the properties are related to the insertion of punctual defects in the crystalline structure. The purpose of our work is two fold. First, we compare the luminescence of the MgGa$_2$O$_4$-Ga$_2$O$_3$ system with the single phase Ga$_2$O$_3$ and MgGa$_2$O$_4$ and relate structural changes observed in MgGa$_2$O$_4$-Ga$_2$O$_3$ system to the optical properties, and secondly, to compare the neutron powder diffraction results obtained using two diffractometers: D2B located at the ILL (Grenoble, France) and Aurora located at IPEN (São Paulo, Brazil). In the configuration chosen, Aurora shows an improved resolution, which is related to the design of its silicon focusing monochromator.
1. Introduction

Solid-state lasers are widely used in various scientific areas as material processing, spectroscopy, medicine, communications, displays, photonics, etc. For all of these applications two types of laser are particularly useful: tunable lasers and micro-lasers adequate for “integration” in an optical circuit. Both types of laser consist on a single crystal host having good optical and thermal characteristics doped with one or more laser-active impurities. The impurities are transition metal ions as Cr$^{3+}$, V$^{3+}$, Ti$^{3+}$, etc. or rare earth ions as Nd$^{3+}$, Er$^{3+}$, Dy$^{3+}$, Yb$^{3+}$. The hosts are double oxides or halide compounds. In order to facilitate the substitution, the host ion must have the same valence and atomic radius value quite close to the impurity one. However, it is not unusual a host which does not satisfy these requirements. In this case the difference of valence and ionic radius are compensated by a new position of the host ions during the synthesis process. When the impurity ion is inserted in the host lattice, the energy levels of the host can be split, in a trend that depends strongly on the potential generated by their neighbourhood (crystal-field). This dependence can be directly associated to small structural differences in the occupation site of the doping ion. However, in many cases, the precise structure of the emitting centres is not well known, even if the determination of such structures is of capital interest for the optimization and application of new lasers systems. For example, Cr ion is a typical laser-active impurity in solid-state lasers and it is its valence and local symmetry in the lattice that completely determine the emitting properties. So, Cr$^{3+}$ coordinated with six O$^{2-}$ ions gives laser emission in the visible range but Cr$^{4+}$ coordinated with four O$^{2-}$ ions gives laser emission in the infrared range. 1,2

Following this idea we have combined neutron powder diffraction (NPD) to X-ray powder diffraction (XPD) and optical measurements to get insight on the structure of MgGa$\textsubscript{2}$O$\textsubscript{4}$: Cr$^{3+}$. The interest in this compound comes from the fact that nowadays the most efficient solid-state lasers emit between 720 and 1010 nm. 3,4 For instance, YAG: Mn$^{2+}$ lasers emit between 600 and 800 nm, with maximum of intensity at 640 nm, but with very low efficiency (<1%) 5, when compared to Cr$^{3+}$ systems. Moreover, Cr$^{3+}$ ions are stable in the crystal synthesis but Mn$^{2+}$ ions are not, originating compounds with Mn$^{2+}$ and Mn$^{4+}$, making its spectral interpretation difficult and more importantly contributing to the laser efficiency decrease. Therefore obtaining a new material with emission located under 700 nm, i.e. in the visible range, having Cr$^{3+}$ as impurity is of great interest.

Magnesium gallate, MgGa$\textsubscript{2}$O$\textsubscript{4}$, has a partially inverted spinel structure belonging to the AB$\textsubscript{2}$O$\textsubscript{4}$ class of materials in which there are two positions for the A$^{2+}$ and B$^{3+}$ cations. It crystallizes in the Fd3m cubic space group with cell parameter $a = 8.286$ Å, with 16±2% of the Mg$^{2+}$ population in tetrahedral and 81±1% in octahedral sites. 6,7 Phase diagram studies 8 have indicated the possibility of some amount of beta-gallium, β–Ga$_2$O$_3$, together with the principal compound MgGa$_2$O$_4$, which was indeed confirmed by XPD and optical measurements 9,10. Interestingly, the presence of the β–Ga$_2$O$_3$ compound in the MgGa$_2$O$_4$ samples certainly introduces an additional perturbation on the observed spectra since Cr$^{3+}$ optical spectroscopic properties depend on the environment of the dopant ion. In fact the β–Ga$_2$O$_3$ presents a monoclinic structure 11,12 crystallizing in the C2/m space group with lattice parameters $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å and $\beta = 103.7^\circ$, with distorted octahedral Ga$^{3+}$ sites that can be occupied by Cr$^{3+}$ ions. It has been shown 9 that the MgGa$_2$O$_4$: Cr$^{3+}$ systems presents a broad emission band in red and near infrared spectral region between 670 nm and 850 nm, which is attributed to Cr$^{3+}$ ions in octahedrally coordinated sites, and in reality produced by variations in the crystal field due to the inverse nature of this spinel.

In this work we demonstrate that the optical characteristics of MgGa$_2$O$_4$: Cr$^{3+}$ are enhanced when MgGa$_2$O$_4$: β–Ga$_2$O$_3$: Cr$^{3+}$ is formed. This fact is directly related to the structural characterization using the combination of x-rays and neutron diffraction data. The diffraction pattern shows that the compound is a mixture of the inverted spinel and the monoclinic phase. The calculated percentages show that the dominant phase is the spinel arrangement. Finally we confirm that for the determination of structures with lower symmetry and larger unit cells, the resolution of the spectra has great importance.
2. Experimental details

2.1.1. Sample preparation
Powder samples of the system MgGa$_2$O$_4$ - β-Ga$_2$O$_3$ with 0.1, 0.5, 1 and 5% (in mass) Cr$^{3+}$ substituting the Ga$^{3+}$ ions were produced by a solid-state reaction of PA oxides, MgO, Ga$_2$O$_3$ and a desired amount of Cr$_2$O$_3$, by sintering at 1300°C using a Jung 5713 oven. After the thermal treatment the samples presented the characteristic green variation obtained for similar doped Cr$^{3+}$ samples.

2.1.2. Optical measurements
Photoluminescence measurements were performed at ambient condition at the Optical Spectroscopy Laboratory at Pontifícia Universidade Católica (PUC-RIO) using a QuantaMaster$^{TM}$ UV VIS, with a 3 nm resolution.

2.1.3. Short description of the neutron powder diffractometers (NPD): D2B and Aurora
The neutron powder diffractometer D2B is located at the Institut Laue Langevin (ILL, Grenoble) and is characterised by the very high take-off angle (135°) for the monochromator, which is 300 mm high, focusing vertically onto about 50 mm and has a relatively large mosaic spread of 20°. In addition, 200 mm high detectors and collimators match the large incident vertical divergence. In this particular study a wavelength of 1.2307 Å was used. Such a configuration allows for fast measurements time due to higher neutron flux on the sample.

Aurora is a high-resolution neutron powder diffractometer installed on the IAEA-R1 research reactor located at Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP, São Paulo). This diffractometer is equipped with a position sensitive detector (PSD) and a double-focusing perfect single crystal silicon monochromator. Installed in a take-off angle of 84°, the monochromator can be positioned to produce 4 different wavelengths, namely 1.111, 1.399, 1.667 and 2.191 Å (nominal values). In this study an adjusted value for the wavelength equal to 1.4119 Å was used, allowing for improved resolution in the q-range of interest.

2.1.4. X-ray powder diffractometer - XPD
Room temperature XPD measurements were performed using a X’Pert PRO Panalytical Diffractometer located at the Crystallography and X-ray Diffraction Laboratory at the Centro Brasileiro de Pesquisa Físicas (CBPF, Rio de Janeiro), with 40 KV and 40 mA and CuK$\alpha$ radiation, $\lambda = 1.5418$Å in Bragg-Brentano geometry. A $2\theta$ range from 10° to 100° was covered using a step of 0.05 ° and a count time of 1 sec. NPD and XPD data were analyzed using the program FullProf.15

3. Structural results based on X-rays and neutron powder diffraction
Both XPD and NPD experiments were used to take advantage of the different scattering lengths ratios, which should facilitate the determination of the different site occupancies. Moreover, by sampling small amounts of the different pellets by XPD, it was possible to check for sample inhomogeneities in the larger samples produced for the NPD measurements. The powder patterns were initially modeled for all samples (Cr$^{3+}$ concentration = 0.1%, 0.5%, 1% and 5%) employing the cubic spinel structure described by the space groupFd$\bar{3}$m with Ga or Mg in the Wyckoff position 16d (0.5, 0.5, 0.5) (center of the octahedra) and Ga or Mg ions at the Wyckoff position 8a (0,125, 0.125, 0.125) (center of the tetrahedra). The O atoms reside on Wyckoff position 32e (x, x, x), with the x-value being the only variable parameter to be determined. The initial value x=0.256(5) obtained for MgGa$_2$O$_4$ was used as initial parameter. However all attempts of indexing the diffraction peaks in this structure failed indicating that the system under study is a mixed phase. Therefore, a second phase described by the β-Ga$_2$O$_3$ structural model was introduced into the refinement. In β-Ga$_2$O$_3$ the atoms are in five sets of 4i special positions, (0, 0, 0, 0.5, 0.5, 0) ± (x, 0, z), with two crystallographically different Ga atoms in the asymmetric unit, one with tetrahedral and the
other with octahedral coordination geometry. The results of the Rietveld refinements using NPD and XPD of the crystalline structure of the system MgGa$_2$O$_4$-$\beta$-Ga$_2$O$_3$:0.1Cr$^{3+}$ are shown in Figure 1.

![Figure 1](image)

**Figure 1.** Comparison of NPD and XPD diffraction patterns at RT room temperature for MgGa$_2$O$_4$-$\beta$-Ga$_2$O$_3$ with 0.1% Cr$^{3+}$ measured using D2B-ILL, $\lambda = 1.2307$ Å (a) and a X’Pert PRO Panalytical Diffractometer with CuK$\alpha$ radiation, $\lambda = 1.5418$ Å (b). The red line is the Rietveld refinement, the blue line is the difference between the experimental data and the calculated one; the marks are (i) the upper mark is related to MgGa$_2$O$_4$ and (ii) the lower mark is related to the $\beta$-Ga$_2$O$_3$.

The calculated inverted spinel phase percentages are 72%, 77%, 72% and 79% for the 0.1%, 0.5%, 1% and 5% Cr$^{3+}$ concentrations respectively. Figure 2 shows the behavior of the lattice parameter, $a$, and the occupation of Ga and Mg in the A and B sites in the spinel structure as a function of Cr$^{3+}$ concentration. We observed a distinct influence of the Cr$^{3+}$ cation in the structure, and in fact when the concentration of Cr$^{3+}$ cation increases there is a reversion of the occupancy between the Ga and Mg atoms in the B site (the octahedral site) as shown in the Figure 2 (b). These findings corroborate with luminescence results showing a distinct difference between the lines as a function of concentration. As the crystalline arrangement of the spinel system studied here contains highly symmetric atomic arrangement the resolution of the powder pattern is of great interest. Therefore, the experiments for the crystal structure were also carried out using the NPD Aurora for selected compositions. An example is given in Figure 3 showing the measurement for the MgGa$_2$O$_4$-$\beta$-Ga$_2$O$_3$:0.1Cr$^{3+}$ at both neutron powder diffractometers. It is observed that the average separation between adjacent Bragg reflections is improved using Aurora, for instance the shoulder around 1.45Å, attributed to the $\beta$-Ga$_2$O$_3$ phase related to the (0 2 4) reflection, can be clearly distinguished due to the instrumental higher resolution. Moreover, an asymmetric peak shape can noticeably be observed and explained by the fact that overlapping peaks are discriminated. For instance, the peak around 1.6 Å related to the reflections (3 3 3) from MgGa$_2$O$_4$ and the peak (-3 1 3) from $\beta$-Ga$_2$O$_3$, follow in this category see Figures 3 (c) and 3 (d).
Figure 2. a) Lattice parameter $a$ and b) the occupation of the Ga and Mg atoms in the B sites of the spinel structure (as shown in the insert figure) as a function of Cr$^{3+}$ concentration.

Table 1 gives the values for the typical Caglioti resolution parameters accounting for the angular dependence of the width of the Bragg reflections obtained from the Rietveld analysis for ILL-D2B, conventional XPD and the IPEN-Aurora diffractometers.

Figure 3. (a) Data obtained at ILL-D2B, $\lambda=1.2307$ Å and (b) data obtained at IPEN-AURORA, $\lambda=1.4119$ Å. (c) and (d) show details of the resolution of both instruments.

Figure 4 shows a resolution curves for both diffractometers D2B and Aurora. The optimized conditions of Aurora allows for a better resolution than D2B, for angles below 70°. These results are quite stimulating as they show that despite the lower flux Aurora suits well studies related to magnetic structures, as well as small structural distortions.
Figure 4. Resolution curves (FWHM) vs. scattering angles (2θ) for ILL-D2B and IPEN-AURORA for MgGa₂O₄ obtained from the Rietveld refinement. The lines are only guide for the eyes.

| Table 1. Typical Caglioti resolution parameters. |
|------------------------------------------------|
| ILL-D2B                  | XPD                  | IPEN-AURORA          |
| λ=1.2307 Å               | λ=1.5418 Å           | λ=1.4119 Å           |
| (°)                      | (°)                  | (°)                  |
| U                       | 0.066832             | 0.060727             | 0.254962             |
| V                       | -0.202147            | -0.098025            | -0.384117            |
| W                       | 0.181029             | 0.085859             | 0.006255             |

4. Photoluminescence of the Cr³⁺ ion in Ga₂O₃, MgGa₂O₄, Ga₂O₃ and MgGa₂O₄

Figure 5 exhibits the room temperature photoluminescence spectra for samples doped with 0.1% of Cr³⁺ (in mass) excited with 450 nm. The luminescence of the impurity ion in MgGa₂O₄ (dotted line) presents a maximum intensity at 708 nm and is assigned to the spin forbidden ²E(²G) → ⁴A₂ (⁴F) electronic transition of Cr³⁺ octahedral. The luminescence of β-Ga₂O₃ presents a peak at 689 nm, due to the emission associated with the ⁴T₂(⁴F)→ ⁴A₂(⁴F) spin-allowed transition of Cr³⁺ octahedrally coordinated to oxygen ions. Finally, we can see the spectrum of the system MgGa₂O₄+β-Ga₂O₃ showing the broader band, with barycentre at 697 nm (full line). Most likely, a host distortion was generated with the presence of β-Ga₂O₃ leading the Cr³⁺ ions to an intermediate crystal field. Therefore, the ⁴T₂ (⁴F)→ ⁴A₂(⁴F) energy transition originates the broad observed band.

Figure 5. Room temperature photoluminescence of the Cr³⁺ ion in Ga₂O₃ (dashed line), MgGa₂O₄ (dotted line) and MgGa₂O₄+Ga₂O₃ (solid line).

5. Conclusion

XPD and NPD Rietveld refinements were used for quantitative phase analysis to determine the amount of MgGa₂O₄ and β-Ga₂O₃ in the system MgGa₂O₄-β-Ga₂O₃:Cr³⁺ at room temperature. The precursor phases were found to present similar unit cells in all composition studied. Moreover, to assess the
quality of the powder diffraction method, the bulk properties of system analyzed by an optical study are also presented. From the luminescence data, we observe the broadest band emission for the mixed system in comparison with those individual phases. As tunable materials should offer broad emission and intense bands this finding is extremely important. Besides, the samples synthesis process is easy and cheap, leading us to conclude that the system is a promising material for technological applications.

High-resolution NPD obtained using the instrument Aurora allowed to confirm the presence of $\beta$-Ga$_2$O$_3$. In the particular configuration chosen for this study, the higher resolution of Aurora can be attributed to the combination of the focusing silica monochromator to the ensemble of collimation setup in addition to the placement of a sapphire filter. This result places Aurora as a potential NPD diffractometer to be used to determine magnetic structures as well as to perform phase analysis.

Acknowledgments

The results presented in this work were obtained during the development of the PhD thesis of MAFMS under the supervision of LPS at the Universidade do Estado do Rio de Janeiro, and financially supported by FAPERJ. MAFMS acknowledges the partial financial support given by the Berlin Neutron Scattering Center (BENSC) for a visit to discuss on his XPD and NPD results. Support given by the Institut Laue-Langevin (ILL) for the NPD experiments is also acknowledged.

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