Experimental report

21/12/2023

Proposal: 5-23-733 **Council:** 4/2019

Title: Structural characterization of luminescent complex oxides:AxGa4+xTin-4-xO2n-2 (A=Na, Li; n=5, 6 and 7 and x≈0.7)

Research area: Materials

This proposal is a new proposal

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Samples: Li0.7Ga4.7Ti2.3O12
Na0.7Ga4.7Ti0.3O8
Na0.7Ga4.7Ti1.3O10
Na0.7Ga4.7Ti2.3O12
Li0.7Ga4.7Ti0.3O8
Li0.7Ga4.7Ti1.3O10

Instrument	Requested days	Allocated days	From	To
D2B	1	1	09/09/2019	10/09/2019

Abstract:

Alkali gallium titanates have attracted the interest due to their physycal properties, such as ionic donduction and photocatalysis. In this sense, we have synthesized a sodium/lithium gallium titanate homologous series with chemical formula: AxGa4+xTin-4-xO2n-2 (A=Na, Li n=5, 6 and 7 and x=0.7) powders (A total of 6 samples). We have carried on a preliminar characterization by XRD and several advanced electronic microscopy techniques. Moreover, this materials have shown very good and tunable luminiscent properties as we describe in the proposal letter. A characterization by neutron diffraction is necessarily required to accurately determine the positions and occupations of oxygen atoms, as well as, sodium and lithium composition present in the structure. The set of results obtained will allow us to know the accommodation of oxygen vacancies and its influence in the photoluminescence properties of these materials.

Transparent semiconducting oxides (TCO) constitute a large field of research due to its applications as transparent electrodes in transistors, flat panel displays, solar cells, sensors, etc. The study of beta-galia-rutile oxides has intensified in recent years due to the interest of its properties, such as ionic conduction and photocatalysis; moreover, the rapid transport of ions through the tunnels present in the structure makes of it a good ionic conductor for its use in batteries [1, 2].

We successfully synthesized the sodium/lithium gallium titanate homologous series with chemical formula: $Na_xGa_{4+x}Ti_{n-4-x}O_{2n-2}$ (n=5, 6 and 7 and x≈0.7) powders, hereafter referred as NGT1 for n=5, NGT2 for n=6 and NGT3 for n=7, respectively. These structures lead to the formation of hexagonal (NGT1) or orthogonal (NGT2 and 3) tunnel network where Na ions are placed.

Due to the scattering lengths of Ga and Ti atoms are too distinct (bGa = 7.288 fm; bTi = -3.438 fm), the structure and composition were solved by neutron powder diffraction (NPD) and thus we obtained the Ga/Ti ratio in each polyhedron of the structure. Moreover, this technique allows determining of the oxygen and the Na content. Neutron powder diffraction (NPD) measurements were performed on D2B diffractometer (λ = 1.594 Å).

For NGT1, the NPD pattern was refined using the monoclinic isostructural oxide, $Na_{0.7}Ga_{4.7}Ti_{0.29}O_8$ [3] with a C2/m space group as a starting structural model. Figure 1a shows the results of the final NPD data fitting. The refinement of occupancy factors of the oxygen atoms does not reveal anionic vacancies; therefore, these factors were fixed during the refinement. The structure, schematically represented in Figure 1b, can be described on the basis of an ordered intergrowth of β-Ga_2O_3 type chains (formed by octahedral and tetrahedral sites, colored in red) and $(Ga/Ti)O_6$ octahedra (colored in yellow). The cell parameters obtained from the NPD refinement are: a = 12.36138(8) Å, b = 3.00098(2) Å, c = 9.36302(4) Å, β = 122.1140(4)°. Additionally, according to NPD refinement, the composition obtained was $Na_{0.80(3)}Ga_{4.66(3)}Ti_{0.34(3)}O_8$ with the complete anionic sublattice.

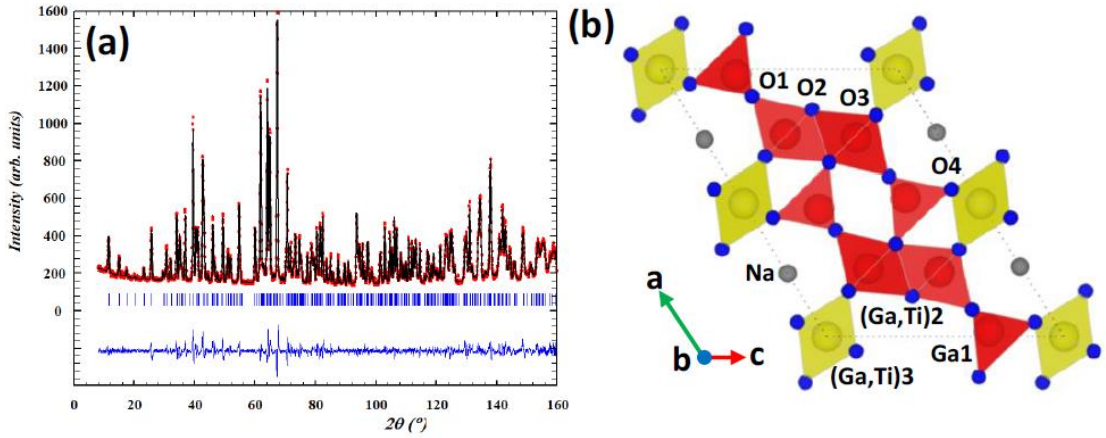

Figure 1. (**a**) Rietveld refinement of the NPD data for $Na_{0.80(3)}Ga_{4.66(3)}Ti_{0.34(3)}O_8$. The observed patterns (red circles), calculated patterns (continuous black line), and difference curves (continuous blue line) are shown. (**b**) Structure model for NGT1 oxide. Color code: red: β-Ga2O3 type chains, yellow: Ga/Ti octahedra, grey: (Na), blue: (O).

The NPD study of the NGT3 was performed assuming, as an initial model, the orthorhombic isostructural oxide $Na_{1-x}Ti_{2+x}Ga_{5-x}O_{12}$ (x = 0.2) with Pbam space group[4]. The result of the final NPD data fitted is depicted in Figure 2a. The crystal structure, depicted in Figure 2b, can be described by both edge-sharing and corner-sharing MO_6 octahedra, as well as corner sharing

GaO_4 tetrahedra. As can be observed, large channels are extended parallel to the c-axis in which Na+ ions are delocalized occupying 35% of the 4e positions. The chemical composition, obtained after refinement of the Ga and Ti occupancies in each polyhedron, corresponds to $Na_{0.70(1)}Ga_{4.72(1)}Ti_{2.28(1)}O_{12}$ with the anionic sublattice complete. The cell parameters obtained from the NPD refinement for this member of the series are: a = 15.8046(12) Å; b = 9.33302(7) Å; c = 2.998228(18) Å.

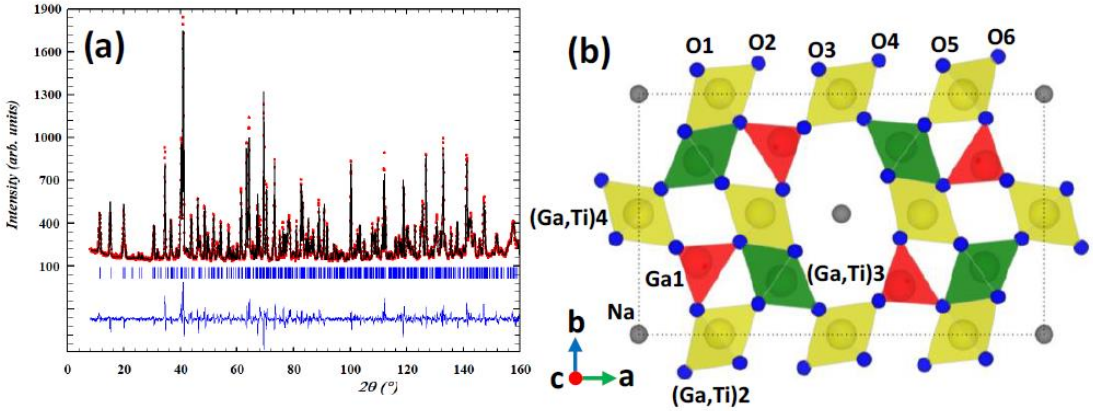

Figure 2. (**a**) Rietveld refinement of the NPD data for $Na_{0.70(1)}Ga_{4.72(1)}Ti_{2.28(1)}O_{12}$. The observed patterns (red circles), calculated patterns (continuous black line), and difference curves (continuous blue are shown. (**b**) Structure model for NGT3 oxide. Color code: red: Ga tetrahedra, yellow: M2 and M4 Ga rich-octahedra, green: M3 Ti rich-octahedra, grey: (Na).

Unfortunately, the NPD pattern of NGT2 prepared for the neutron diffraction experiment shows a very weak presence of NGT1 and $NaTi_2Ga_5O_{12}$ [5] as impurities. The LeBail-type refinement, shown in Figure 3, allowed us to obtain the lattice parameters a = 12.091(1) Å, b = 3.013(2) Å, c = 10.385(2) Å and β = 92.199(3)° in space group C2/m.

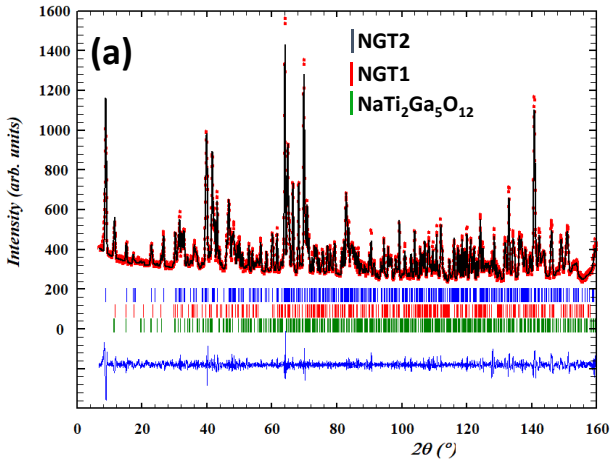

Figure 3. (a) Lebail refinement of the NPD data for NGT2 oxide. The observed patterns (red circles), calculated patterns (continuous black line), and difference curves (continuous blue line) are shown. For the case of NGT2 oxide, NGT1 and $NaTi_2Ga_5O_{12}$ were included as impurities.

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