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# Raman spectroscopic detection of vacancies in LaFeO<sub>3</sub>

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## ABSTRACT

By coupling Raman measurements and first-principles investigations on bulk lanthanum orthoferrite (LaFeO<sub>3</sub>), we have demonstrated that the Raman peak around 620 cm<sup>-1</sup> usually observed in these samples is a signature of vacancies within the material. This Raman peak can be used as a fast and non-destructive detection test, to determine whether a LaFeO<sub>3</sub> sample contains a non-negligible quantity of vacancies. Finally, using first-principles calculations, we propose an infrared spectroscopic method to differentiate the chemical nature of vacancies (oxygen, iron, or lanthanum).

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## 1. Introduction

Lanthanum orthoferrite LaFeO<sub>3</sub> constitutes a first-choice perovskite material for various industrial applications, because of its moderate cost, non-toxicity, and wide range of physico-chemical properties such as methane combustion catalysis [1], water-splitting photo-catalysis for hydrogen production [2], high-temperature refrigeration [3], superconductivity [4].

However, depending on its synthesis process, LaFeO<sub>3</sub> can spontaneously present a defective structure, with oxygen vacancies that are complementary to iron [5] or lanthanum [6] vacancies in order to ensure electroneutrality. Particularly, oxygen vacancies have major consequences on LaFeO<sub>3</sub> properties, among which polar displacement of Fe ions [7], catalytic power improvement [8, 9, 10] and modification of optical absorption [11]. Thus, an experimentalist working with such a sample needs to know whether that sample is lacunary or not.

In this Letter, we propose a way to detect vacancies in LaFeO<sub>3</sub> by means of Raman spectroscopy, a technique of particular interest seeing its numerous advantages (simple to implement, fast, non-destructive, micrometric resolution). We propose also a complementary infrared protocol to differentiate the chemical nature of vacancies (La, Fe, or O).

This work is organized as follows. In a first part, we will compare our Raman measurements with experimental data from literature. In a second part, we will present first-principles calculations from which Raman spectra could be deduced, which lead to a vacancy identification test. In a third part, we will propose, from first-principles calculations, an infrared (IR) identification criterion to determine the type of vacancies (La-, Fe-, or O-type vacancy).

## 2. Experimental acquisition of Raman spectrum

Our experimental investigations were performed on a polycrystalline bulk LaFeO<sub>3</sub> ceramic (previously purchased in Kurt J. Lesker Company [12]), using a RENISHAW Raman spectrometer with 633 nm laser (10s of time exposure, and 50 long-working-distance objective). Fig. 1 presents three Raman spectra recorded from three different grains. These spectra, exhibiting characteristic Raman modes in ranges 100-200 cm<sup>-1</sup>, 250-350 cm<sup>-1</sup>, 400-450 cm<sup>-1</sup>, 600-650 cm<sup>-1</sup>, are fully consistent with literature data [13, 14].

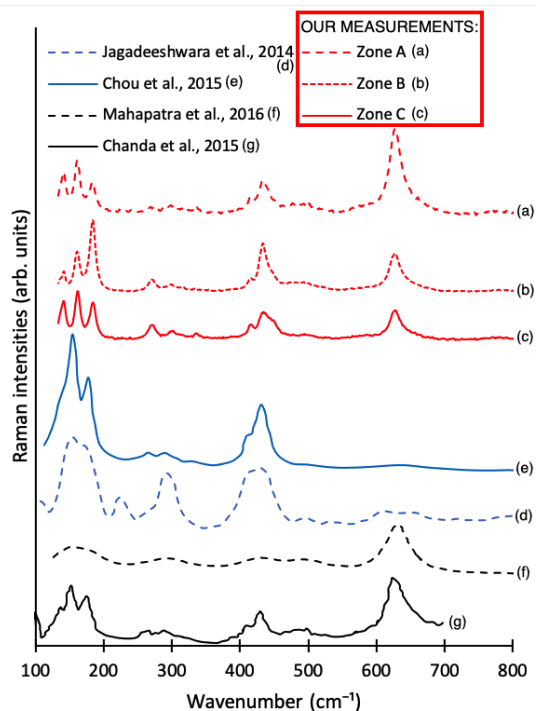
However, one can notice two important facts. First, considering solely the four spectra extracted from the literature, one can see that the peak around 620 cm<sup>-1</sup> present serious intensity variations depending on the sample considered: it appears very intense in ref. [13, 14], moderately intense in ref. [15], and is quasi-inexistent in ref. [16]. Second, considering solely our three experimental spectra, one can note that the intensity of the 620 cm<sup>-1</sup> peak varies depending on the observed grain.

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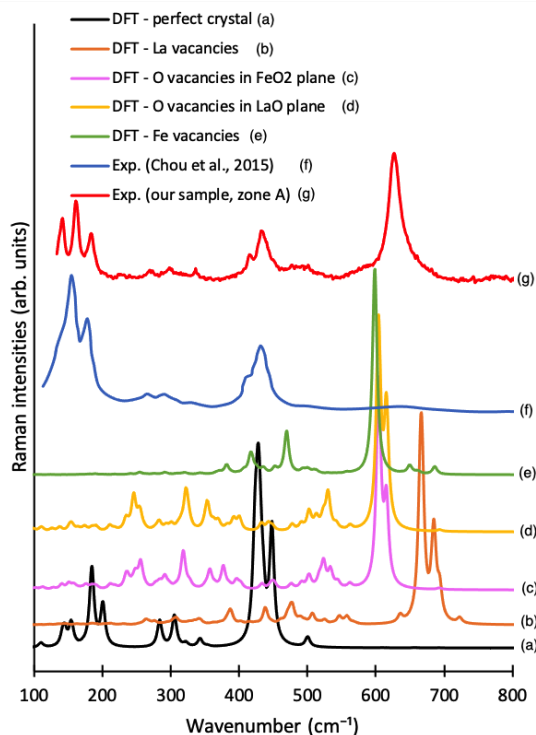
**Figure 1:** Raman spectra measured on three different grains on the LaFeO<sub>3</sub> target (red lines), in comparison with data from experimental literature (blue [15, 16] and black [13, 14] lines).

To attempt to solve this inconsistency on LaFeO<sub>3</sub> Raman peak intensity around 620 cm<sup>-1</sup>, we examined the works of Rusevich et al. [17] and Tenne et al. [18] who both studied different type of perovskites. Using first-principles calculations, Rusevich et al. [17] showed that introducing an oxygen vacancy induces major changes in BaTiO<sub>3</sub> Raman spectrum, switching from a spectrum constituted of modes in range 0-550 cm<sup>-1</sup> for the pure bulk to a spectrum exhibiting a series of modes in range 600-700 cm<sup>-1</sup>. On the other hand, in their experimental investigation, Tenne et al. [18] proved that oxygen vacancies in SrTiO<sub>3</sub> cause the appearance of a Raman peak around 700 cm<sup>-1</sup>. Considering both results, it is very likely that the Raman peak towards 620 cm<sup>-1</sup> detected experimentally in several LaFeO<sub>3</sub> samples is related to oxygen vacancies. Such assumption is compatible with Raman measurements by Blanck et al. on LaFeO<sub>3</sub> [19], showing that the intensity of the 620 cm<sup>-1</sup> peak is decreasing during temperature-controlled hydration at 500°C. In order to verify this conjecture that vacancies are the origin of the 620 cm<sup>-1</sup> Raman peak, we will then compare the perfect and lacunary LaFeO<sub>3</sub> spectra using first-principles calculations.

### 3. First-principles calculations: Raman detection of vacancies

Our calculations have been performed in the framework of Density Functional Theory (DFT) with CRYSTAL17 code [20] (details of implementation are given in Supplementary Material). We have computed the LaFeO<sub>3</sub> Raman spectrum in the perfect bulk case, and in the lacunary cases 8.3% (resp. 12.5%) vacancies in O (resp. in Fe or La), which is realistic with respect to the compositions found in literature (for instance, LaFe<sub>0.82</sub>O<sub>3-δ</sub> in Ref. [5], determined by X-energy dispersive spectroscopy).

Our DFT spectra are represented on Fig. 2 with experimental data for easy comparison. The pure bulk spectrum computed in DFT (without vacancies) matches well with the experimental data from Ref. [16]. For a perfect crystal, the DFT Raman modes in range 590-700 cm<sup>-1</sup> are only detectable in logarithmic scale. However, DFT supercells with either an oxygen vacancy (either in LaO or FeO<sub>2</sub> plane), an iron vacancy, or a lanthanum vacancy, induce high intensity peaks in the range 590-700 cm<sup>-1</sup>. It is clear that our experimental spectra are a combination of the undefective and lacunary DFT spectra. Contrary to the sample studied by Chou et al. that is clearly non-lacunary, our sample exhibits all the characteristics of a lacunary sample.



**Figure 2:** Raman spectra computed in DFT (perfect crystal, O vacancy in LaO plane, O vacancy in FeO<sub>2</sub> plane, Fe vacancy, La vacancy) compared to experimental results (zone A of our target, and data from Ref. [16]).

Consequently, Raman spectroscopy is a rapid and non-destructive way to detect vacancies in LaFeO<sub>3</sub>. Starting from the considered LaFeO<sub>3</sub> sample, one can acquire the Raman spectrum, then look at the 600-700 cm<sup>-1</sup> zone: if a peak is present, this means that the sample presents vacancies. However, this technique does not allow to clearly differentiate the nature of those vacancies (La-, Fe- or O-vacancies). We will thus propose differentiation criteria, based on IR spectra analysis.

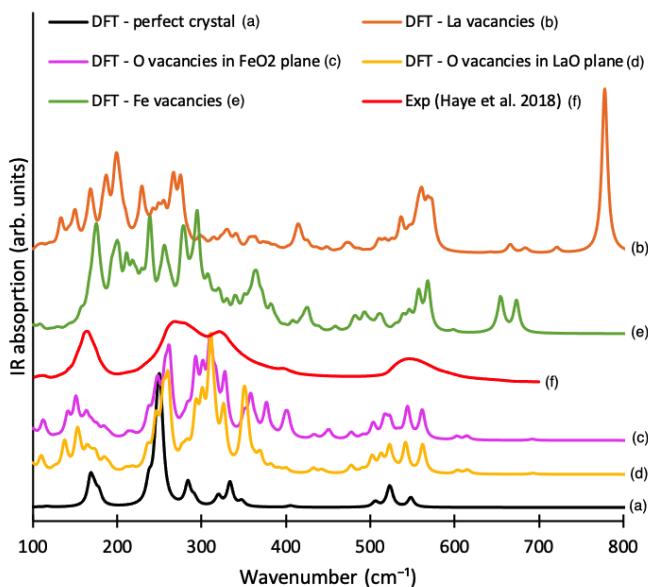
#### 4. First-principles calculations: infrared differentiation of vacancies

Our DFT calculations, presented on Fig. 3, revealed that: (i) the computed perfect and oxygen-deficient IR spectra are in good agreement with the experimental results from Ref. [21] (obtained by Fourier-transform infrared spectroscopy), (ii) contrary to the perfect and O-deficient spectra, the La-deficient and Fe-deficient spectra exhibit characteristic intense modes beyond 610 cm<sup>-1</sup>, respectively two intense peaks in range 600-700 cm<sup>-1</sup> for Fe-deficient case and one intense peak in range 750-800 cm<sup>-1</sup> for La-deficient case.

#### 5. Conclusion

To conclude, from the previous considerations, one can draw the following identification protocol of vacancies for any LaFeO<sub>3</sub> sample. First, one needs to acquire the Raman spectrum, and consider the zone between 600 and 700 cm<sup>-1</sup>: a peak in this zone means that the sample is lacunary. Second, to distinguish the chemical nature of vacancies, one can acquire the IR spectrum in 600-800 cm<sup>-1</sup> region using mid-IR techniques: (i) if there is no intense peak in range 600-800 cm<sup>-1</sup>, there are O vacancies only, (ii) else, there are also Fe vacancies if two intense peaks are detected in range 600-700 cm<sup>-1</sup>, and/or La vacancies if one intense peak is detected in range 750-800 cm<sup>-1</sup>.

Similar Raman-based procedures of vacancies detection can be developed for others materials, such as SrTiO<sub>3</sub> [22], PbTiO<sub>3</sub> [23], ZnO [24], or CeO<sub>2</sub> [25].



**Figure 3:** IR spectra computed in DFT (perfect crystal, O vacancy in LaO plane, O vacancy in FeO<sub>2</sub> plane, Fe vacancy, La vacancy) compared to experimental data from Ref. [21].

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The data that support the findings of this study are available from the corresponding author upon request.

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