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Study of LaFeO₃ perovskite material by high-pressure Raman scattering

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Abstract. We use high-pressure Raman-scattering spectroscopy to study LaFeO₃ synthesized by using the sol-gel method. The structural evolution of the samples under high pressure and at room temperature is monitored via the Raman-scattering spectrum in the pressure range of 0.50 to 22.1 GPa. When the pressure surpasses 12 GPa, the Raman spectra change significantly around 180 cm⁻¹, which indicates a structural phase transition. However, the Raman spectrum remains constant under 5.0 GPa, which indicates that the LaFeO₃ structure is preserved at these pressures.

Keywords: LaFeO₃, high pressure, Raman scattering, structural transition

1. Introduction

Perovskite orthoferrite is a distorted perovskite structure with the chemical formula AFeO₃, space group *Pnma* and/or its derived nonconventional space group, such as *Pbnm*, *Pmma*, *Ibnm*, etc. [1]. In this structure, the *A* cation sits in the interstitial area between the octahedral structure and is coordinated to 12 O anions. In addition, the Fe ion is located at the center of the octahedral and is coordinated to six O anions [2]. The magnitude of the distortion in the orthorhombic perovskite structure is closely related to tilting and rotation of the FeO₆ octahedral, where the tilt angle is very sensitive to substitution at the *A* and/or Fe sites, temperature, and pressure applied to the system [2-3].

LaFeO₃ is a typical orthoferrite perovskite compound with space group *Pbnm* [3]. At ambient pressure, it is an antiferromagnetic insulator [2,3]. The effect of pressure, temperature, and substitution on LaFeO₃ structure has been studied in previous work. For example, Mahapatra *et al.* [1] reported that Ho substitution at La sites causes the Fe-O-Fe angle to depart from 180° and the A-O and Fe-O bond lengths to shorten, which enhances the exchange interaction between A-A and Fe-A, thereby increasing the magnetization. Coutinho *et al.* [2] reported that Y substitution at the La site in LaFeO₃ shifts the vibrational modes to higher frequencies, indicating an increased octahedral distortion and decreased bond lengths. The high-pressure phase transition in LaFeO₃ was studied by Etter *et al.* [3], who prepared LaFeO₃ by using the solid-state method. The material first undergoes a second-order structural phase transition from *Pbnm* to *Ibmm* at 21.1 GPa, and then a first-order phase transition from high-spin to low-spin Fe³⁺ ions at 38.0 GPa.

Building on previous research [1-3], we use high-pressure Raman spectroscopy to understand in more detail the structural evolution of LaFeO₃ under high pressure. The vibrational characterization of LaFeO₃ in this work is detected by using Raman scattering in the pressure range of 0.50 to 22.0 GPa. The Raman shift reveals the atomic vibrations in the crystal lattice. LaFeO₃ was prepared by using the sol-gel method and the samples were used to study how high pressure affects the structural properties of the crystal (i.e., crystal structure and crystallography parameters of LaFeO₃). The



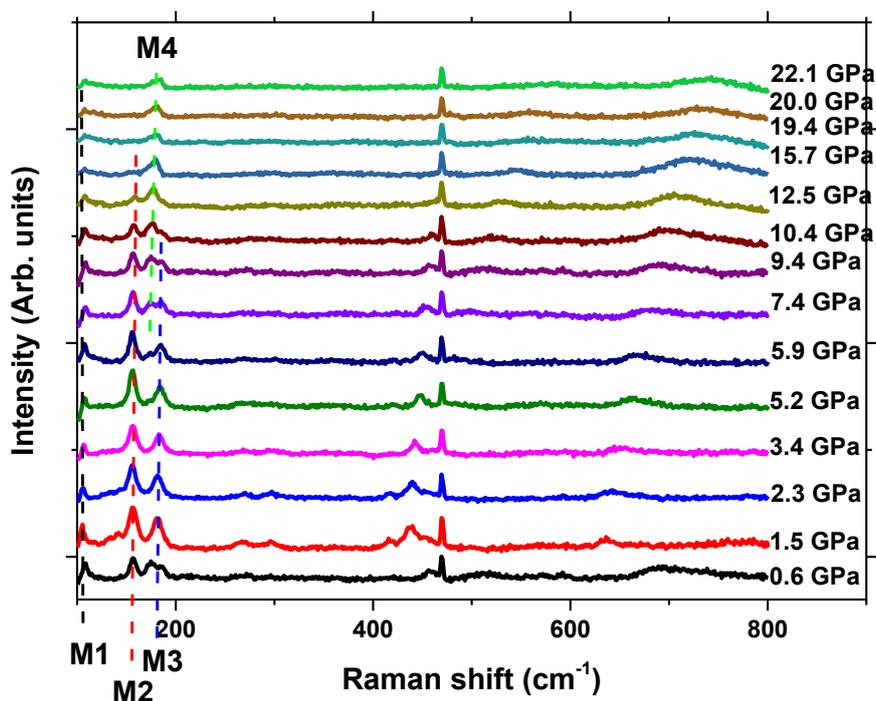


Figure 1. LaFeO₃ Raman-scattering spectra for several pressures.

vibrational modes obtained from Raman scattering spectra were fit by using Peakfit software, which allows us to estimate the pressure-induced changes in the structural properties of LaFeO₃.

2. Experimental details

By using the sol-gel method, LaFeO₃ was synthesized from the precursors lanthanum oxide and ferrite nitrate nonahydrate (all analytical grade). The precursors were balanced stoichiometrically and mixed with citric acid monohydrate and aquadest as solvents. Next, the solvent was stirred and heated with a magnetic stirrer (wisestir MSH-20D) until a brown gel was formed. The gel phase was dried to eliminate water and organic compounds, following which the resulting powder was calcined to obtain LaFeO₃ in powder form.

Raman spectroscopy measurements were made in an inVia Renishaw Raman spectrometer system with an excitation-laser wavelength of 512 nm. The powder was subjected to high pressure by using a symmetric diamond anvil cell consisting of a pair of 500 μm diamond anvil culets. The stainless steel gasket was pre-indented from 250 to ~ 40 μm thick and a 250- μm -diameter hole was laser drilled through the center of the indented area to serve as sample chamber. The powder sample was loaded into the sample chamber along with several ruby spheres for calibrating pressure [4]. Silicone oil was used as a pressure-transmitting medium.

3. Results and discussion

Figure 1 shows the Raman-scattering spectra of LaFeO₃ for several pressures at room temperature. LaFeO₃ has an orthorhombic perovskite structure with the *Pbnm* space group (not shown here). The increasing of pressure broadens the peaks and decreases of intensity, which indicates increased distortion of the crystal structure. In addition, several Raman modes below 200 cm^{-1} and between 400 and 500 cm^{-1} disappear with increasing pressure.

Based on previous research [2], the Raman modes between 100 and 160 cm^{-1} are attributed to an A_g mode associated with the La site vibration. The Raman mode around 180 cm^{-1} is attributed to the A_g mode associated with La rotation. The Raman mode between 400 and 500 cm^{-1} is attributed to the A_g mode associated with O octahedral bending vibration. However, the significant changes are in the Raman modes below 200 cm^{-1} , and these are the focus of the following discussion.

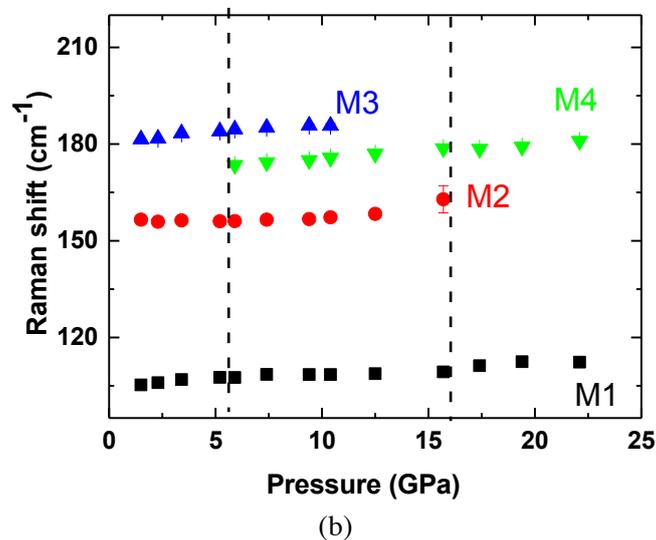
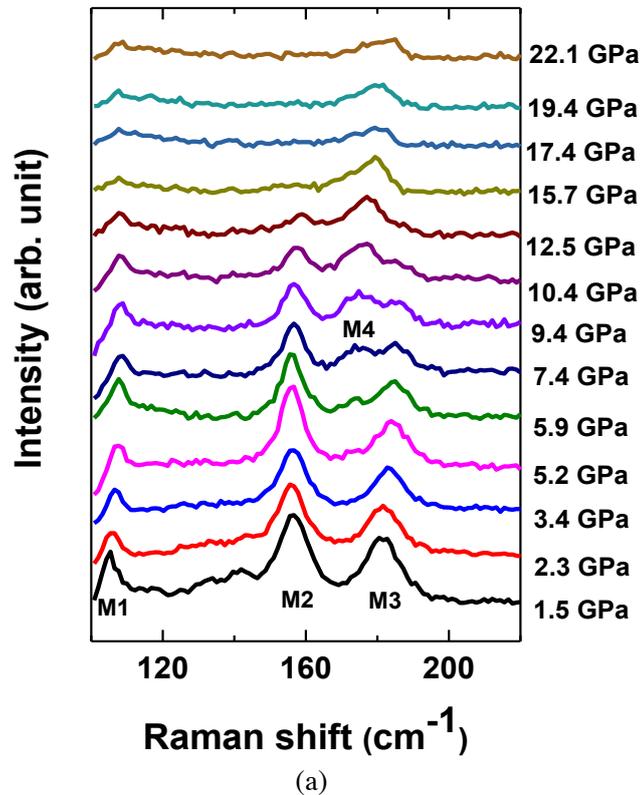


Figure 2. (a) Raman-scattering spectra in the range of 100 to 200 cm^{-1} and for several pressures. (b) Raman shift as a function of pressure based on fits to Raman modes below 200 cm^{-1} .

Figure 2a plots the Raman-scattering spectra from 100 to 200 cm^{-1} . The Raman modes near 110, 160, 180, and 170 cm^{-1} are labeled M1–M4, respectively. In accordance with previous studies [1,2], the Raman mode near 130, 150 and 180 cm^{-1} are associated with A_g mode. The band near 180 cm^{-1} is assigned to an E_g mode. The Raman modes below 200 cm^{-1} are closely related to rotation and vibration at La sites [3].

Based on previous research by Etter *et al.* [3], LaFeO₃ preserves its crystal structure at least up to 48.0 GPa. However, the space group changes from *Pbnm* to *Ibmm* around 21.1 GPa because the La *y* coordinate decreases from 0.029 to 0.0 and the Wyckoff factor changes from 4c to 4e [3].

Figure 2b shows the Raman shift of several modes as a function of pressure as determined by fitting the Raman modes below 200 cm⁻¹. The significant change in the Raman modes is the disappearance of M3 above 12.0 GPa and the appearance of the new Raman mode M4 around 6.0 GPa. As previously reported [2,3], the mode around 180 cm⁻¹ indicates rotation at the La site. The disappearance of M3 and appearance of M4 reflect the change in the rotational state of the La site and its coordinates in the crystal lattice. This allows the possibility of the structural transition at the given pressure (12.0 GPa) from the *Pbnm* space group to the *Ibmm* space group [3]. Compared with previous research [3], the difference in transition pressure may be due to the method in which the samples were prepared and the sample environment. Thus, chemically synthesized LaFeO₃ has inferior stability under high pressure compared with LaFeO₃ synthesized by the conventional solid-state method. However, the characterization of the structural under high pressure should be confirmed to verify the changes in the crystallographic parameters. Finally, the M2 Raman mode completely disappears at 16 GPa. Under 5 GPa, the structure of LaFeO₃ does not change with pressure.

4. Conclusions

A vibrational analysis of LaFeO₃ reveals the disappearance of the M3 Raman-scattering mode at 180 cm⁻¹ and the appearance of the M4 Raman-scattering mode at 170 cm⁻¹ when the pressure surpasses 12.0 GPa, which indicates the possibility of a structural phase transition from the *Pbnm* space group to the *Ibmm* space group. The M3 and M4 Raman modes are closely related to the rotational state of the La site and its crystallographic coordinates. However, the structural changes should be confirmed by another structural characterization under high pressure to confirm this result. Under 5.0 GPa, the Raman modes do not change with pressure, which indicates that the stability of the LaFeO₃ structure is preserved at these pressures.

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