Pressure induced amorphization of A-site deficient $La_{0.333}NbO_3$ perovskite – Raman spectroscopic and x-ray diffraction investigations

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ABO_3 type perovskites are one of heavily investigated class of compounds where high pressure (HP) studies relvealed high structural stability and reversibility of the pressure induced changes. Introduction of A-site vacancies are attempted to further tune the properties of these materials -- in several cases with great success as for $La_{1/3}NbO_3$ [1]. Earlier HP x-ray powder diffraction (XRPD) studies showed the occurrence of irreversibile pressure amoprhization (PIA) of $La_{1/3}NbO_3$. Figure 1 (upper panel) demonstrate the reproduction of earlier reported results in our recent measurements. Earlier HP x-ray absorption studies (XAS) has evidenced a two stage process in the PIA process of $La_{1/3}NbO_3$ [2,3]. Recently we have undertaken systematic HP XRPD and HP-Raman spectroscopic investigations of this system to further understand two stage process involved in the PIA. Our HP-Raman data shows that with increasing pressure above 11 GPa, the lattice modes below 400 cm^{-1} of $La_{1/3}NbO_3$ damp quickly. This is in agreement with the disruption of long-range crystalline order above this pressure. Above 11 GPa, Raman spectra of $La_{1/3}NbO_3$ is principally characterized by two large bands around 650 and 830 cm^{-1} unlike the ambient pressure data. Such a spectral structure is retained with further increase in pressure up to 22 GPa. Upon pressure release, the Raman spectra is found to retain such spectral characteristics expect for a small shift and reduction in the width, revealing the irreversibility of the PIA. Raman data from $La_{1/3}NbO_3$ which have undergone a pressure of 16 GPa after a month (Fig. 1 lower panel) showed spectral characteristics similar to the HP-amorphous state (Fig. 1 lower panel). This observation further confirming the stability of the HP induced amorphous state. Our HP-XRPD studies revealed that the pressure induced modifications in the Raman spectra are completely reversible for pressures below 5 GPa. Earlier HP-XRD studies demonstrate that the structural modifications occurring in this pressure regime are completely reversible [2]. However, for pressures above 11 GPa, irreversible changes are observed. These observations provide further inputs to the already reported two stage process in the irreversible PIA of the *A*-site deficient $La_{1/3}NbO_3$ perovskite [2,3]. Using data from several pressure runs with varing maximum pressure of HP-Raman and HP-XRPD, we discuss the irreversible PIA and further HP material tuning opportunities of A-site deficient $La_{1/3}NbO_3$ perovskite.

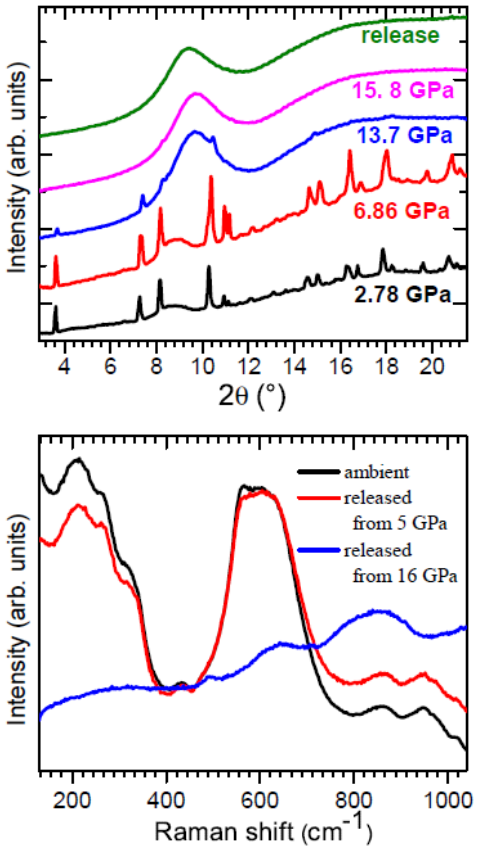

Figure 1. HP-XRPD data evidencing the amorphization and its persistence upon pressure release (upper panel) and HP-Raman data releaving the irreversibility of the amorphization process upon pressure release from 16 GPa and the reversibility of the pressure dependent changes upon release from 5 GPa.

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