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Structural Transition Induced Enhancement of Magnetization and Magnetoresistance in Epitaxial $(Pr_{0.5}Ba_{0.5}MnO_3)_{1\text{-}x}$:$(CeO2)_x$ Vertical Aligned Thin Films

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Energy-dispersive X-ray spectroscopy (EDS) Mapping

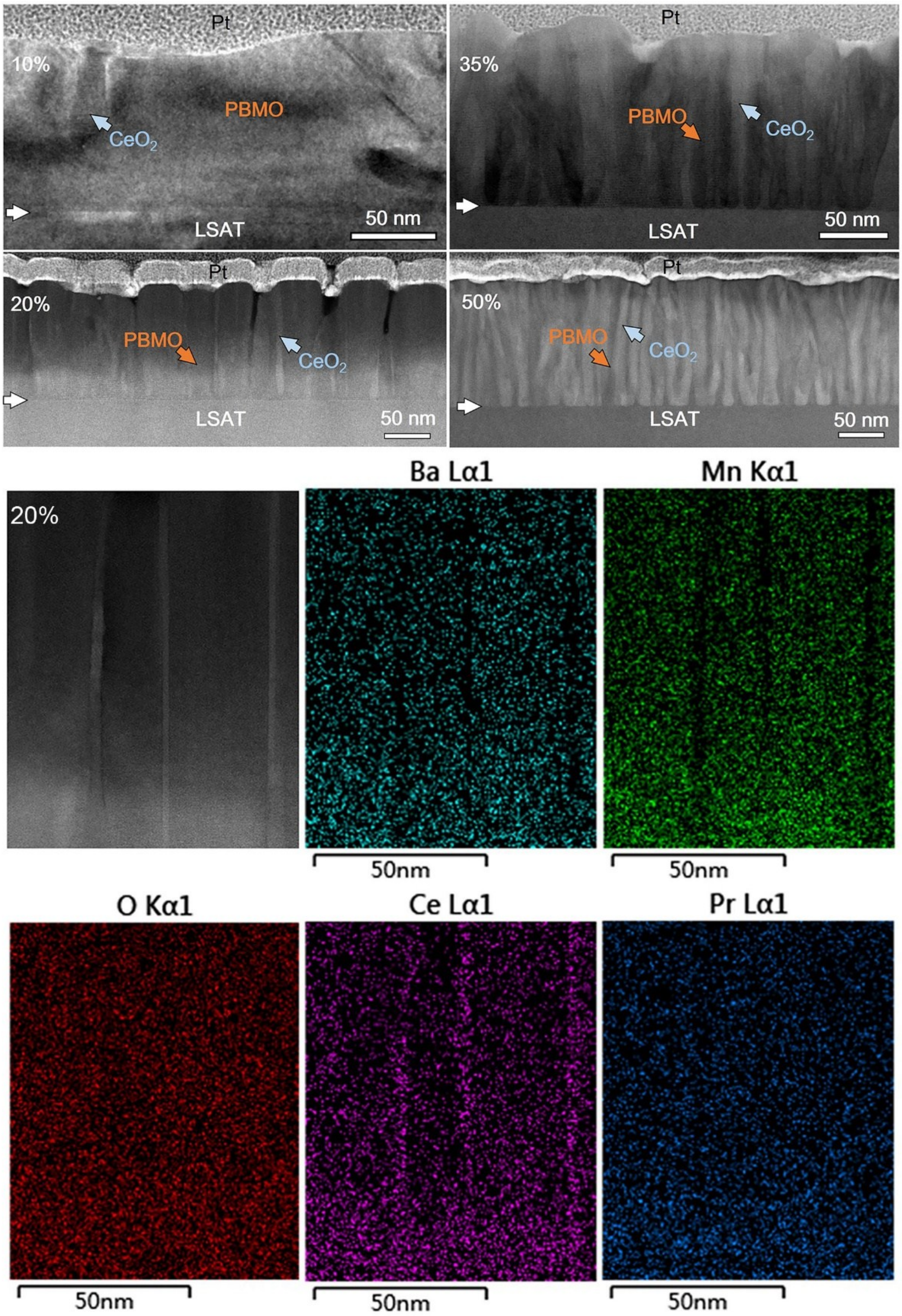

Figure S1 Low magnification cross-sectional STEM images of $(Pr_{0.5}Ba_{0.5}MnO_3)_{1-x}$:$(CeO_2)_x$ (x=10%, 20%, 35%, 50%) samples and the EDS mapping of the x=20% sample.

X-ray photoelectron spectroscopy

In order to identify the oxidation state of Mn, X-ray photoelectron spectroscopy (XPS) measurement was carried and the Mn 2p3/2 line was selected to do analysis. Theoretically, Mn cations in $Pr_{0.5}Ba_{0.5}MnO_3$ should be at the mixed state of 50% Mn^{3+} and 50% Mn^{4+}. From the Figure S2, it could be clearly seen that the all the Mn 2p3/2 peaks were well fitted by the sum of Mn^{3+} and Mn^{4+} [1]. The atomic concentration for each state could be calculated from the area of corresponding peak as shown in the lower right panel. Taking the possible errors into consideration, we could conclude that the oxidation state of Mn is $Mn^{3.5+}$, and it doesn't change with the structural transition.

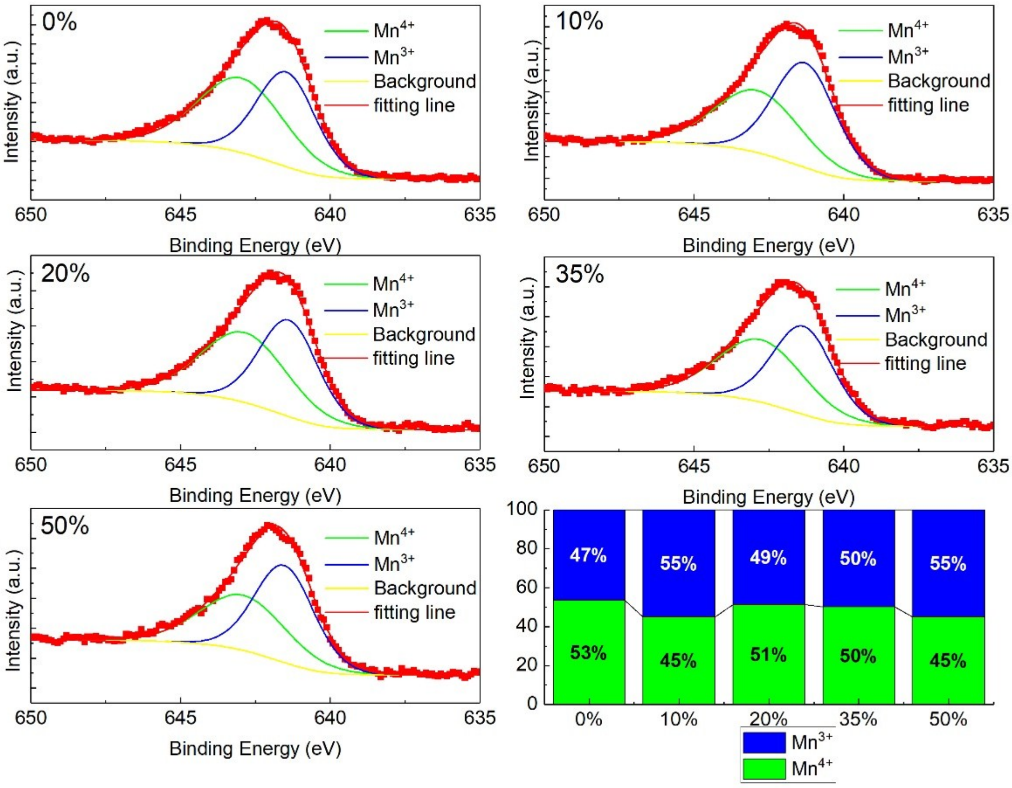

Figure S2 XPS spectra of the Mn2p3/2 line and the atomic concentration of Mn^{3+} and Mn^{4+} for $(Pr_{0.5}Ba_{0.5}MnO_3)_{1-x}$:$(CeO_2)_x$ (x=0, 10%, 20%, 35%, 50%) samples.

Raman spectroscopy

Raman spectra for $(Pr_{0.5}Ba_{0.5}MnO_3)_{1-x}:(CeO_2)_x$ (x=0, 10%, 20%, 35%, 50%) samples have been collected as shown in the Figure S3. The 532.8 nm line for an Ar^+ was used for excitation and the spectra from 75cm^{-1} to 600cm^{-1} was measured at room temperature. Three main peaks which were labeled as ω_1, ω_2, and ω_3, could be observed. Based on previous reports[2-4], ω_1 is related to (Pr, Ba)-O vibrational modes, ω_2 is associated with the tilting of oxygen octahedral and ω_3 is attributed to the O-Mn-O bending modes. However, it should be noticed that the ω_3 mode could also be attributed to the Ce-O vibrational unit[5] in CeO_2. That's why the ω_3 mode is enhanced with the introduction of CeO_2.

Now let's focus on the ω_1 mode and ω_2 mode. It seems that the frequency of these two peaks is insensitive to epitaxial strain[4], which coincide with previous report. We notice that the ω_2 mode was a little bit reduced with the increase of the content of CeO_2, which may indicate that the oxygen octahedral tilting was suppressed by the strain induced by CeO_2 columns. As a result, the double exchange interaction will be enhanced so as the magnetization in Figure 4(b) in the main text.

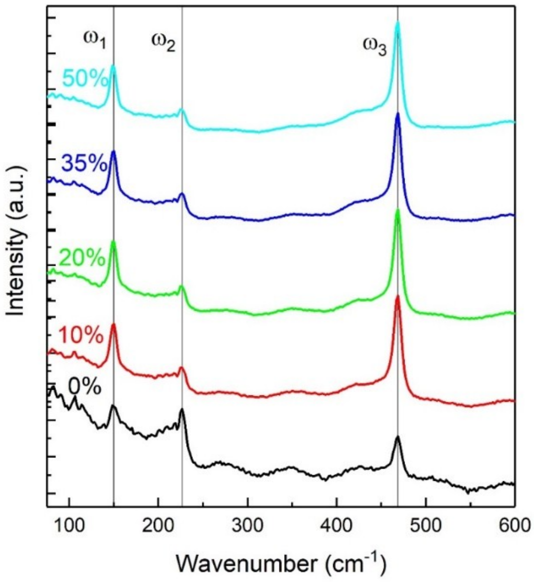

Figure S3 Raman spectra for $(Pr_{0.5}Ba_{0.5}MnO_3)_{1-x}:(CeO_2)_x$ (x=0, 10%, 20%, 35%, 50%) samples.

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