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Evidence of spin-phonon coupling in La_2NiMnO_6 double perovskite

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Abstract Herein, a correlation between B-site cation order and spin-phonon coupling in La_2NiMnO_6 double perovskite has been investigated. Raman spectra of La_2NiMnO_6 double perovskite annealed at 950 and 1400°C have been measured in the 140-598 K range. A substantial softening of the phonon modes has been observed below the Curie temperature, which emphasized the presence of the spin-phonon coupling in the system. The spin-phonon coupling was found to be stronger in relatively more ordered La_2NiMnO_6 double perovskite. Thus, the magnitude of spin-phonon coupling was influenced by the Ni/Mn cation order.

Key words Spin-phonon coupling, Antisite disorder, Cation ordering, Raman spectroscopy, Ferromagnetism

1. Introduction

The La_2NiMnO_6 is a multifunctional material with different coexisting properties, such as ferromagnetic ordering [1], magnetoresistance [2], and magnetodielectric coupling [2,3]. Hence, it has a great prospect for spintronic applications. The rocksalt type ordering for B-site cations (Ni, Mn) was found in La_2NiMnO_6 double perovskite [1,4]. La_2NiMnO_6 double perovskite has a monoclinic $P2_1/n$ structure with an alternate arrangement of corner shared NiO_6 and MnO_6 octahedra in the unit cell as illustrated in Fig. 1. The La ions occupy the voids between the two octahedra. In reality, synthesizing a fully ordered double perovskite with a perfect alternate distribution of Ni and Mn cations at B-site is impossible. Antisite disorder, *i.e.*, partial interexchange of Ni and Mn ions is generally observed in La_2NiMnO_6 [5,6]. In La_2NiMnO_6, the ferromagnetic ordering with the Curie temperature, T_C ~280 K appears due to superexchange interaction between alternatively arranged Ni^{2+} and Mn^{4+} ions [7-9]. For a perfect B-site ordering, the saturation magnetization (M_S) of 5 μ_B/f.u. is expected. However, antisite disorder causes antiferromagnetic Ni^{2+}-O^{2-}-Ni^{2+} and Mn^{4+}-O^{2-}-Mn^{4+} superexchange interactions, thereby decreasing the saturation magnetization [5].

The long-range B-site cation ordering can be assessed by X-ray/neutron/electron diffraction, Raman spectroscopy, and magnetization measurements [1,2,4,10-12]. The superlattice reflections observed in X-ray diffraction patterns due to the doubling of lattice parameters can be used to evaluate the magnitude of B-site ordering in the material. The estimate of B-site ordering can be obtained more precisely from the value of saturation magnetization extracted from the dc field-dependent magnetization measurements. The B-site homogeneous configuration of Ni^{2+} and Mn^{4+} ions leads to the mono-

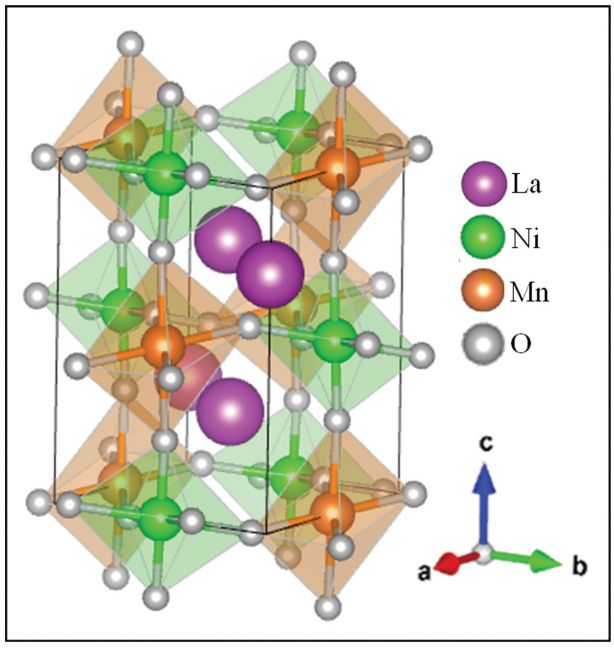

Fig. 1. The unit cell of La_2NiMnO_6 double perovskite having a monoclinic structure.

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clinic structure, while a random arrangement of the same results in an orthorhombic symmetry [6,13,14]. Therefore, polarized Raman spectroscopy can be utilized to characterize the B-site ordering in double perovskites. Polarized Raman spectroscopy has been previously performed on La_2NiMnO_6 and other related double perovskites [11,15-17]. Raman spectroscopy has also been widely employed to examine the spin-phonon coupling in many ferromagnetic double perovskites [11,17-19]. The effect of B-site ordering on the spin-phonon coupling was elucidated previously for La_2CoMnO_6 double perovskite thin films [17].

In this work, the possibility of spin-phonon coupling in La_2NiMnO_6 double perovskite is explored by temperature dependent Raman spectroscopy. Further, the role of cation order on the spin-phonon coupling is evaluated.

2. Experimental

Polycrystalline La_2NiMnO_6 double perovskite was synthesized using the sol-gel method as reported elsewhere [7]. Briefly, a homogenous solution is prepared from the stoichiometric amounts of high purity La_2O_3, $Ni(NO_3)_2{\cdot}6H_2O$, and $Mn(NO_3)_2$ in deionized water. It is to be noted that La_2O_3 was first dissolved in the solution of deionized water and dilute HNO_3. The ethylene glycol and citric acid were added to the precursor solution in the 1:1 ratio. The final solution was heated at 80°C, yielding a viscous gel, which was further dried at 200°C. The as-prepared powder was ground to achieve a fine powder. The powder was calcinated at 500°C for 12 h followed by heating at 900°C for 12 h. Then the pellets were fabricated using a uniaxial press and annealed at 950 and 1400°C for 12 h. Raman spectroscopy measurements were performed on both La_2NiMnO_6 double perovskites annealed at 950 and 1400°C using a micro-Raman spectrometer (Jobin-Yvon Horiba LABRAM-HR) in the temperature range 140~598 K range. The 633 nm line He-Ne laser was used to excite the vibrational modes of the samples.

3. Results and Discussion

In our previous report on La_2NiMnO_6 double perovskites, the role of annealing temperature on antisite disorder was explored [7]. Also, the influence of antisite disorder on saturation magnetization was elucidated. It was observed that antisite disorder increases as the annealing temperature was increased, thereby it resulted in the decrease of saturation magnetization. The sample annealed at 950°C exhibited the highest saturation moment (Ms) with a mere 0.6 % antisite disorder. On the other hand, the lowest saturation magnetization was obtained for the sample annealed at 1400°C with 15 % antisite disorder. Hence, La_2NiMnO_6 double perovskite annealed at 950°C is highly ordered, while the one annealed at 1400°C is relatively low ordered. However, all samples revealed the same paramagnetic to ferromagnetic transition, 280 K, irrespective of the annealing temperature.

Here, temperature-dependent Raman spectroscopy has been performed to evaluate the effect of Ni/Mn ordering on the spin-phonon coupling in both high and low-ordered La_2NiMnO_6 double perovskites. Raman spectroscopy was performed in the temperature range, 140~598 K for both samples. Figure 2 shows the Raman spectra at different temperatures for La_2NiMnO_6 annealed at 950 and 1400°C. The spectra exhibit two intense bands ~530 and 670 cm^{-1} as observed previously [11]. The modes at ~530 and 670 cm^{-1} are described with B_g and A_g symmetry, respectively [11]. The stretching vibrations associated with the (Ni, Mn)O_6 octahedra result in A_g mode [11,15,16]. While B_g mode appears due to both anti-stretching and bending vibrations. Both B_g and A_g modes get broadened with increasing temperature for both samples.

Below the room temperature, the intensity of both modes increases for both the samples, while the intensity of Raman modes gradually decreases above room temperature because of the line broadening. It is also

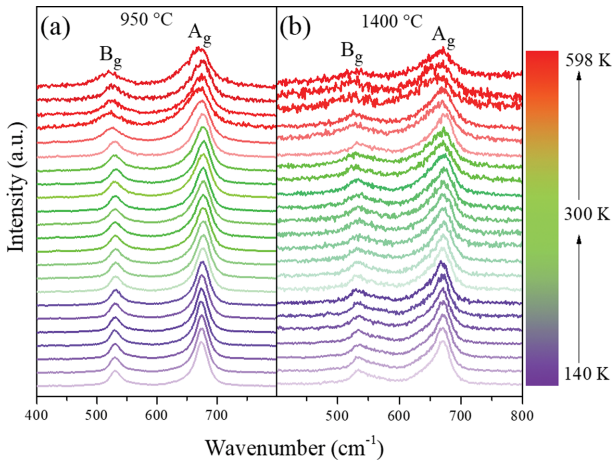

Fig. 2. Temperature-dependent Raman spectra of La_2NiMnO_6 double perovskite annealed at 950 and 1400°C. A_g and B_g denote the modes at ~530 and 670 cm^{-1}, respectively.

observed that the peak broadening in 1400°C is larger than in 950°C sample.

The full width at half maxima (FWHM) is related to the B-site cation ordering, hence, it is relatively higher for the low ordered sample. To examine the possibility of spin-phonon coupling, the position, ω(T), of most intense mode ~670 cm^{-1} as a function of temperature is analyzed. Figure 3 shows ω(T) for both the samples. The A_g mode is modeled using an anharmonic model [16,19]:

$$\omega_{anh}(T) = \omega_o - C\left[1 + 2/\left(e^{\frac{\hbar\omega_o}{kT}} - 1\right)\right] \quad (1)$$

where C is a constant, ω_o temperature-independent line width and k is Boltzmann constant ω(T) fit nicely for $T_C < T < 598$ K as displayed in Fig. 3. However, it deviates from anharmonicity model in the ferromagnetic state, $T < T_C$ for both samples. In fact, A_g mode shows a clear softening in the ferromagnetic state.

It is observed that softening is large in the ordered La_2NiMnO_6 double perovskite (annealed at 950°C) and is less in the slightly disorder La_2NiMnO_6 double perovskite (annealed at 1400°C). This means that cation ordering has a strong influence on the softening of A_g mode. The anomalous softening is the result of phonon renormalization because of the ferromagnetic ordering [16]. The phonon renormalization results in a coupling between the spin and phonon. This kind of behavior was also observed for ferromagnetic La_2NiMnO_6 films and La_2CoMnO_6 double perovskites [15,16]. The phonon renormalization $\Delta\omega(T) = \omega(T) - \omega_{anh}(T)$ is related to the spin-spin correlation function <Si·Sj> between the i^{th} and j^{th} spin states for the nearest neighbor spin-spin interaction. The phonon renormalization function scales with the normalized magnetization $M^2(T)/M^2_{Max}$ under the mean-filed approximation. Hence, the Ni/Mn ordering determines the degree of the spin-phonon coupling. A relatively lesser softening was noticed for the sample annealed at 1400°C as compared to the 950°C annealed sample. This signifies that the inhomogeneous arrangement of Ni and Mn ions prevents the softening of A_g mode, and thus, decreases the spin-phonon coupling.

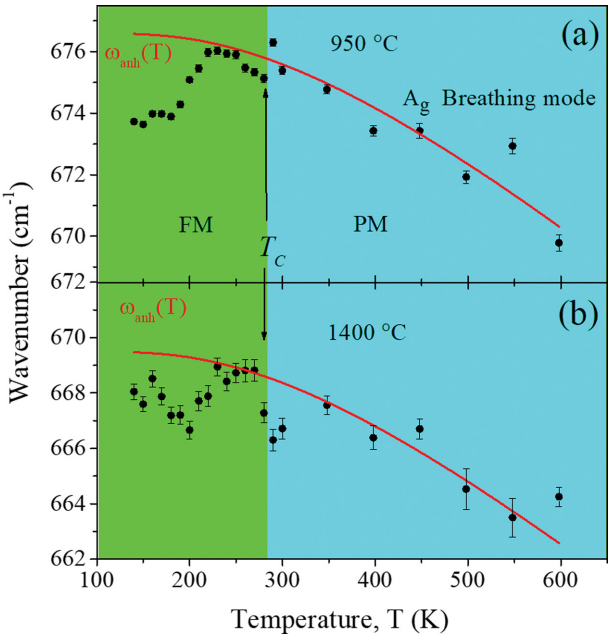

Fig. 3. Temperature dependences of the position of breathing A_g mode for La_2NiMnO_6 double perovskite annealed at 950 and 1400°C. Solid lines denote the temperature evolution of the anharmonic three-phonon models.

4. Conclusion

Temperature dependent Raman spectroscopy was performed on La_2NiMnO_6 double perovskite from 140 to 548 K. An anomalous softening of the symmetric stretching vibrations associated with the (Ni, Mn)O_6 octahedra was found below the ferromagnetic ordering temperature, indicating the presence of spin-phonon coupling. The strength of phonon coupling was observed to be diminished as the degree of cation order in La_2NiMnO_6 double perovskite got reduced.

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