Structural and Raman Analysis of Double Perovskite La$_2$CoTi$_{0.7}$Ni$_{0.3}$O$_6$

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Abstract: La$_2$CoTi$_{0.7}$Ni$_{0.3}$O$_6$ (LCTNO) double perovskite oxide was synthesized through conventional sol-gel citrate route method. X-Ray diffraction patterns indicated orthorhombic symmetry with Pbnm space group, which is confirm by Rietveld refinement of the XRD patterns for La$_2$CoTi$_{0.7}$Ni$_{0.3}$O$_6$, wherein, only one B site ordering of Ti and Ni cations. The random occupancy of Co^{2+}, Ti^{4+} and Ni^{2+} at the B site in La$_2$CoTi$_{0.7}$Ni$_{0.3}$O$_6$. Average particle size of the sample is about 45 nm. Deconvoluted Raman spectra using Lorentzian function gave 6 first order Raman modes for LCTNO double perovksite. Observed phonon modes were found in good agreement with the corresponding group theoretical predictions for space group Pbnm for sample.

INTRODUCTION

Perovskites are one of the most studied class of compounds due to their high symmetry and the versatile application potentials. Multiple ion substitution in the perovskite structure is used to tailor physical properties and forms complex perovskites. Double perovskites are one among such complex perovskites with general stoichiometry AA' BB' O$_6$ or A$_2$BB'O$_6$ or AA B$_2$O$_6$ with cubic symmetry belong to Fm$\bar{3}$m space group. The versatile properties of perovskites in several technological fields such as superconductors, ferroelectrics, optical materials, magnetodielectric materials, microwave dielectrics etc. are due the feasibility in substituting nearly 80% of elements in the periodic table in simple perovskite lattice [1-9]. Among perovskite-type oxides, cobaltite have attracted a continued attention due to their excellent electronic transport properties and mixed ionic-electronic conductivity which make them a potential alternative to present state-of-art SOFC A$_2$BB'O$_6$. Interestingly, either *n*- or *p* type conductivity can be induced in cobaltites by an appropriate doping or substitution in the B-site. The double perovskite compounds, with chemical formula A$_2$BB'O$_6$, offer more opportunities to established interplay among the constituent ions [1]. The double perovskite with pseudocubic structure and non ideal A – O, B – O bonds can be accounted for tailoring desired properties by means of various ionic substitution at A or B site. This results in octahedral tilts in various possible directions so as to accommodate the mismatch in size of substituted cation. On the other hand, vibrational spectroscopy is one of the easily available as well as sensitive tools to probe the correct symmetry of double perovskites.

Many reports are available in literature, [10-14] showing the reduction in symmetry due to the octahedral tilting in double perovskites viz. Sr$_2$CoTeO$_6$, Ca$_2$CoTeO$_6$, Ca$_2$CoWO$_6$, Ca$_2$MgTeO$_6$, BaLaLiTeO$_6$, SrLaLiTeO$_6$ determined using Raman spectroscopic technique. In continuation, properties of double perovskite type La$_2$CoTiO$_6$ (LCTO) are very sensitive to the relative ratio of Co/Ti ions due to which LCTO have been proposed as promising MIEC materials [15]. The utilization of cobalt in B-positions in A$_2$BB''O$_6$ (Inset to the Fig. 1) structure usually consequences of high electronic conductivity, due to both its ability to present mixed oxidation states and the important covalent character of the Co–O bonds. Such systems allow oxygen-deficient oxides to be obtained under reducing conditions (by reduction of Co^{3+} to Co^{2+}), giving rise to the formation of anionic vacancies and oxygen-ion mobility and inducing oxygen conduction [16-18]. Recently, lanthanum cobalt based oxides have attracted the attention of researchers due to their structural features as well as technological applications in various fields such as SOFC.

EXPERIMENTAL PROCEDURE

LCTNO sample were prepared using the citrate route in order to increase the homogeneity of the starting mixture of the elements. The metal nitrate in appropriate ratio mixed together with anhydrous citric acid in deionized water under stirring at a temperature of 90 °C. The amount of citric acid used corresponded to three times the total positive charge of the cations. Titanium (IV) butoxide was thereafter added to the solution, where upon a white precipitate of hydrated titanium oxide formed and then dissolved after a few minutes. The pH was then raised to 8.5–9 by slowly adding ammonium hydroxide and the solution left standing for 1h. The solution was transferred to a porcelain dish on a heating plate and water evaporated at 300 °C until a viscous gel is formed. The gel was then heated in air at 900 °C for 2h in order to burn off the organic parts. The resulting voluminous powder was thereafter grinded, pressed then sintered at 1350 °C for 24h in air. These samples were characterized by X-ray diffraction using a Bruker D8 advance XRD instrument, the value of 2θ is in between 10° to 90° with step size 0.02. The Raman measurements were carried out using LAB- RAM HR-800 single stage spectrometer equipped with a 488nm excitation ,an edge filter,1800g/mm grating monochromator and a CCD detector giving a spectral resolution of ~1 cm^{-1}.
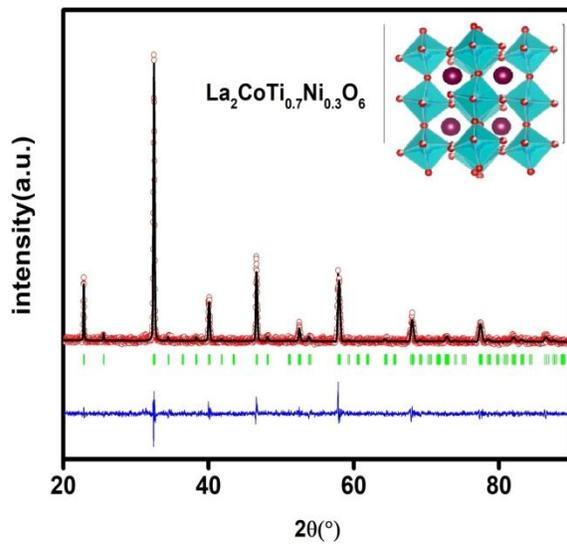

Figure 1. Observed and Rietveld fitted room temperature XRD pattern of the LCTNO sample. Inset show the structure.
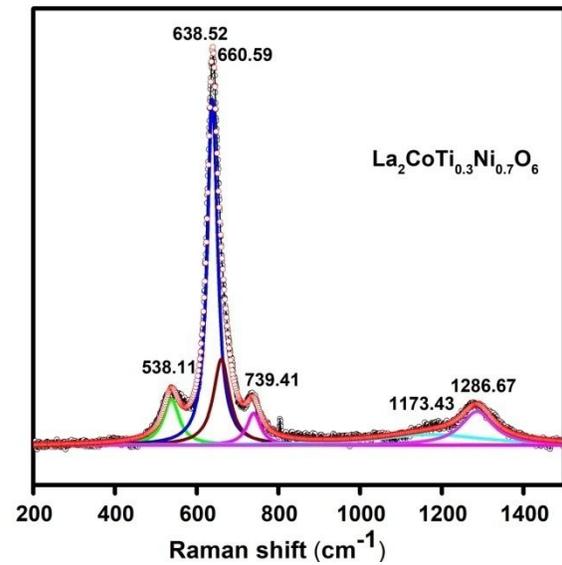

Figure 2. Observed and fitted room temperature Raman shift of the LCTNO sample.

RESULT AND DISCUSSION

Figure 1 shows the Rietveld refinement of X-ray diffraction data for polycrystalline LCTNO sample. XRD analysis reveals a orthorhombic phase having space group *Pbnm*. The diffraction peaks of XRD pattern confirms the formation of pure phase compound which is also evident from the obtained goodness of fit data ($\chi2 = 1.05$). Generally, in the double perovskite structure, the superlattice diffraction peak formed by the periodical arrangement of B-site appears at near 32°. In Fig. 1, an apparent superlattice peak could be observed at 32.2°. As known, the grain refinement is the main cause of the broadening of diffraction peaks in XRD, and the crystalline size can be calculated by Scherrer equation with the aid of the full width at half maximum (FWHM, rad) of the diffraction peak: $P=(0.9*\lambda)/(\beta*\cos\theta)$ where λ is the X-ray wavelength (nm), θ is the diffraction angle (deg), and P is the average crystalline size (nm). In the double perovskite, if FWHM is taken from the superlattice peak formed by the ordering of B-site, P can be considered as the ordered domain size (ODS). According to the XRD patterns of samples the crystalline sizes and the calculated values of the B-ordered size are shown in Table 1. Inset of figure 1 shows the crystal structure of LCTNO, therein, along c-axis the B ions are held interchangeably and La^{3+} ion is interspaced between planar layers. Both Co^{2+} and Ti^{4+} ions are surrounded be six O^{2-} ions forming CoO$_6$/TiO$_6$ octahedra. The refined room temperature structural parameters of LCTNO are listed in table 1.

TABLE 1: Structural parameter obtained from Rietveld refinement analysis of the $La_2CoTi_{0.7}Ni_{0.3}O_6$ (LCTNO) sample.

LCTNO	a(Å)	b(Å)	c(Å)	V(Å3)	$\chi2$	Cystalline size(nm)	Ordered domain size(nm)
Pbnm	5.5014	5.5223	7.7905	236.6769	1.48	35.34	41.50

Atom	x/a	y/b	z/c	Occ.
La	-0.0055	0.4749	0.25	1.83
Co	0	0.2513	0.7523	0.98
Ti	0	0	0	0.69
Ni	0	0	0	0.29
O1	0.04559	0.00802	0.25	3.65
O2	0.21157	0.27820	-0.03530	2.81

By considering the symmetries and the Wyckoff site occupations in the LCTNO structure within the Pbnm (#62) space group and point group D_{2h}(mmm), group theoretical tools help us to predict, in terms of the irreducible representation of the D_{2h} factor group, 30 Raman-active modes ($8A_g+7B_{1g}+8B_{2g}+7B_{3g}$) and 47 infrared-active (IR) modes ($16B_{1u}+15B_{2u}+16B_{3u}$). Usually, the highest wave-number mode is the so-called Axe mode, which is due to the oxygen vibrations in the BO_6 octahedra framework, while the two lowest-wave number modes are the Slater-type mode, which involves mainly B ion motion against oxygen vibrations, and the Last-type mode, which is mainly due to the A ion motion against oxygen vibrations [19-20]. Concerning the complex perovskite of general formula $A_2BB'O_6$ with tilts (Glazer notation $a^-b^+a^-$), the pbnm (D_{2h} or #62) space group is usually observed[21]. In the irreducible representation of the D_{2h} point group as obtained from the site-group method, the total modes in the sample is given by

$\Gamma=8A_g+16A_u+ 7B_{1g}+8B_{2g}+7B_{3g} +17B_{1u}+16B_{2u}+17B_{3u}$

therein, $\Gamma_{acoustic}=B_{1u}+B_{2u}+B_{3u}$ and $\Gamma_{optic}= 8A_g+16A_u+7B_{1g}+8B_{2g}+7B_{3g} +16B_{1u}+16B_{2u}+17B_{3u}$

However, elastic distortions coming from the B-site occupation, along with tilts for accommodating the rare earth ion and A-O distance optimization, lead to crystal symmetry lowering, with the consequent increase of the number of first-order Raman and infrared-active normal modes. Note that although the Wyckoff sites occupied by Co ,Ti and Ni ions in orthorhombic LCNTO were same, they have the same local symmetry (-1), which do not contribute to the Raman spectra, but participate uniquely in the IR-active polar modes. The room temperature Raman spectrum of LCNTO is displayed in Fig. 2. A multiple splitting of the Raman peaks at low wavenumbers may support the structure orthorhombic the material as obtained by the XRD analysis. The zone-center vibrational modes of LCTNO can be represented by D_{2h} point group due to its Pbnm symmetry, where Co ,Ni and Ti ions occupy the 4a Wyckoff sites of -1 symmetry and La and O1 ions are at the 4c sites of general .m. symmetry. Deconvoluted Raman spectra of LCTNO using Lorentzian function are carried out to interpret the exact number of modes, results are shown in Fig. 2. The spectrum shows the characteristic spectrum of a cobaltate double perovskite, in which the stronger phonon corresponding to (BO_6) octahedral symmetrical stretching (S) at 638.52 cm⁻¹ and the bands observed around 660 cm⁻¹ is assigned to the asymmetric stretching vibrations of BO_6 octahedral, whereas a mode at 538.11 cm⁻¹ is assigned as a combination of both antistretching (AS) and bending motions. Low-intensity modes were also observed at 410 cm⁻¹, which correspond to the octahedra bending with La moves in xz plane, and octahedra out-of-phase tilt along x axes with La and apical O move in xz plane, respectively. Also, two modes at high wavenumbers, at 1160 and 1283 cm-1, were observed and correspond to symmetrical stretching and bending combination, and symmetrical stretching overtone, respectively. Polycrystallinity of sample, the overlapping of bands, lack of intensity of bands and poor resolution of the instrument are the difficulties in observing all the expected modes. Since experimentally we obtained six first order Raman modes which gives strong evidence that LCTNO would belong to the orthorhombic Pbnm symmetry.

CONCLUSION

A-site ordered double perovskites LCTNO are synthesized in single phase and Rietveld refinement also confirms the orthorhombic symmetry and the lattice parameters crystalline size and structural parameter are obtained. Further

in vibrational spectra there are total of 6 Raman modes are observed for sample which are in good agreement with group theoretical calculations for orthorhombic structure with Pbnm space group.

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REFERENCES

1.   S. Vasala and M. Karppinen, J. Solid State Chem. **43**,1-36 (2015).
2.   G. A. Samara, J. Phys.: Condens. Matter **15**, R367–R411 (2003).
3.   H. A. Blackstead and D. B. Pulling, Phys. Rev. B **6**, 214412 1-11 (2001).
4.   A. A. Bokov and Z. G. Ye, J. Mater. Sci. **41**, 31-52 (2006)
5.   A. J. Wojtowicz and J. Kisielewski, Opt. Mater. **28**, 85-93 (2006).
6.   F. E. Osterloh, Chem. Mater. **20**, 35-54 (2008).
7.   I. M. Reaney and D. Iddles, Microwave, J. Am. Ceram. Soc. **89**, 2063–2072 (2006).
8.   G. Subodh and R. L. Moreira, , Chem. Mater. **19**, 4077-4082 (2007).
9.   M. C. Knapp and P. M. Woodward, J. Solid State Chem. **179**, 1076-1085 (2006).
10. B. Amrithakrishnan and G. Subodh, Mater.Res. Bull. **93**, 177-182 (2017).
11. V. L. Vilesh and G. Subodh, Ceram. Int. **43**, 12718–12723 (2017).
12. A. Dias, G. Subodh and R. L. Moreira, Vibrational, *Chem. Mater.* **20**, 4347–4355 (2008).
13. A. P. Ayala, and J. C. Pedregosa., *J. Appl. Phys.* **101**, 12351 (2007).
14. R. Mukherjee and T.P. Sinha, J. Alloys Compd*s.* **651**, 222-229 (2015).
15. E. Rodrigue and M. L. Lopez, J. Mater. Chem. **12**, 2798–2802 (2002).
16. J. H. Kim and L. Mogni, J. Electrochem. Soc.**156**, B1376–B1382(2009).
17. J. H. Kim and Y. Kim, J. Power Sources **194**, 704–711(2009).
18. M. Jin and X. Zhang, J. Alloys Compd. **494**, 359–361 (2010).
19. M. D. Fontana and F. Gervais, J. Phys. C: Solid State Phys. **17**, 483 (1984).
20. J. Hlinka and T. Ostapchuk, Phase Trans.**79**, 41 (2006)
21. R. Zurmueuhlen and N. Setter, J. Appl. Phys. **77**, 5341 (1995).