EFFECTS OF Sr SUBSTITUTION ON CRYSTALLINE STRUCTURE AND RAMAN SPECTRA OF $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$

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ABSTRACT

Effects of Sr^{2+} substitution for La^{3+} on oxygen concentration and structure of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ have been observed by X-ray diffraction and Raman scattering. Oxygen concentration and unit cell volume of the material decrease monotonously in dependence of x . The vibration modes were calculated for La_2NiO_4 in K_2NiF_4 type structure with the group symmetry of $I4/mmm$. The Raman active modes for this symmetry were also theoretically identified. Raman back scattering spectra have been carried out for all the ceramic polycrystalline samples at room temperature. Two Raman lines at 224.6 cm^{-1} and 433 cm^{-1} , assigned to E_g and A_{1g} vibration modes of oxygen O(II) in bonding La/Sr-O were observed for all the samples. The lower mode 224.6 cm^{-1} shifts down to 208 cm^{-1} , whereas the upper mode 433 cm^{-1} shifts up when concentration of the Sr substituting for La increases.

Keywords: X-ray diffraction, Perovskite layers, Multiferroic, Raman scattering.

1. INTRODUCTION

After the discovery of superconductivity in the La-Ba-Cu-O system by Bednorz and Muller [1], various high- T_c superconductors have been found. In aim to clarify the mechanism governing in the cuprates, layer structure compounds containing other 3d transition metal oxides were investigated. For this purpose, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ has been regarded as a good one among candidates. Crystal structure of La_2NiO_4 belongs to the K_2NiF_4 type, similar to structure of La_2CuO_4 that is a first founded high- T_c superconductor, containing a single CuO_2 layer. Therefore a comprehensive study on structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ in comparison with $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is interested and needed for understanding the superconductivity mechanism in high- T_c cuprate.

As was reported in [2] the charge and spin ordering have been observed in $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$ at the temperature of $T_{co} \sim 240\text{ K}$ and $T_{so} \sim 180\text{ K}$, respectively. Kajimoto et al. [3] reported an observation of rearrangement of the checkerboard charge order to the stripe one in $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ by neutron diffraction. Spin state of the Ni ion has a role in governing the transport and magnetic properties of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compound, and it depends strongly on the concentration of Sr. As was shown the transition from the high spin to low spin state of Ni ions occurs somewhere with x laying between zero and 1.0 [4]. At room temperature, most authors concluded that the crystal structure of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system is tetragonal with the symmetry of $I4/mmm$ [5, 11]. Kato et al [7] systematically investigated influences of the substitution of Sr on structure, unit cell parameters and oxygen deviation in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. They also observed

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the $I4/mmm$ tetragonal structure for all the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ samples. Besides they recorded an increase of valence value of Ni as well as a change in the lattice parameters a , c and their ratio c/a at x in a range of (0.5 - 0.6). However, some other authors described it as the orthorhombic $Fmmm$ [6, 8]. This difference has been explained by a change in structure due to the deviation from the oxygen stoichiometry in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. Hiroi et al. [6] reported quite recently that the structure of La_2NiO_4 varies with δ , from orthorhombic ($\delta \sim 0.02$) to tetragonal ($0.04 \leq \delta \leq 0.12$) and subsequently to monoclinic ($\delta \sim 0.2$). As was shown in [7], the oxygen deviation δ in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ sensitively depends on x , δ was equal to 0.14 ± 0.01 when $x = 0$ and it decreases rapidly to zero as increasing x . As known Raman scattering is a suitable tool for evaluation of the structure of materials, especially in identification of the phonon modes of materials. La_2NiO_4 with the tetragonal K_2NiF_4 -type structure, which has two 4e sites where are located La and O(II), in sites 2a and 4c are located ion Ni and O(I), respectively. Theoretical calculation based on the structure symmetry of La_2NiO_4 suggests that among its vibration modes only two A_{1g} and $2E_g$ modes are raman active, and they could be observed in its Raman spectra. Udagawa et al. [14] observed Raman spectra of the $(\text{La}_{1-x}\text{Sr}_x)_2\text{NiO}_4$ with the concentration x changing in a range of (0.0 - 0.4) at temperatures of 10, 77, 300 and 500 K. They detected two Raman modes at 220 cm^{-1} and 460 cm^{-1} , which are assigned to an apical-oxygen motion along the a axis with E_g symmetry and an apical-oxygen motion along the c axis with A_{1g} symmetry, respectively. As reported the Raman shift of these two modes exhibits a non-monotonous dependence on the concentration of Sr, and it was explained by the change of the force constants.

In this paper we present the recent results of our research on $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ compound by means of the X-ray diffraction and Raman scattering at room temperature, especially the research was focused on effects of the substitution of Sr for La on crystalline structure and phonon modes.

2. EXPERIMENTAL

The samples of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ with $0.0 \leq x \leq 1.0$ were prepared by a solid state reaction method. Powder of $\text{La}(\text{OH})_3$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with a purity of 3N was used as starting materials. The starting materials were mixed and ground for 4h in ethanol and then annealed at a temperature of 500°C for 10h. After that, the samples were mixed and reground again for 4h in ethanol. The obtained powder was pressed in pellets with diameter of 13 mm and height of 0.5 mm. The pellets were annealed at 1100°C for 40h in air, cooled down to 500°C and subsequently annealed at this temperature for 10h. Finally the samples were cooled down to room temperature with turning off furnace. Phase structure of all the samples was checked by powder X-ray diffraction spectra by means of a SIEMENS D5000 diffract-graph equipped with a $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. Based on X-ray diffraction data of the sample of $x = 0.0$, crystal structure of the compound has been constructed by means of the crystal modeling method. Using Win-Metric program we have calculated the lattice parameters of structure for all the samples. Raman scattering spectra at room temperature in the energy region between 100 and 1000 cm^{-1} were recorded by a micro-Raman spectrograph LABRAM-1B equipped with a He-Ne laser ($\lambda = 632.817 \text{ nm}$) with a power of 11 mW.

Fig. 1: Unit cell of La_2NiO_4

3. RESULTS AND DISCUSSION

Powder X ray diffraction patterns recorded at room temperature indicate that all the samples are of a single phase with the K_2NiF_4 structure. Structure refinement shows that the La_2NiO_4 sample has tetragonal structure with the $I4/mmm$ (139) of the space group (Fig. 1). Unit cell of the La_2NiO_4 has oxygen in two positions O(I) and O(II). The Ni ion at (0,0,0) sites at position 2a, locating in the center of the NiO_6 octahedral. The La/Sr and O(II) ions at (0,0,z) sites, which is noted as 4e and the O(I) ions at (1/2,0,0), (0,1/2,0) sites, which is noted as 4c. At room temperature, all the samples are of the tetragonal. Using the obtained X-ray diffraction powder data, the a and c parameters of unit cell of the samples were calculated by the Win-Metric program. Fig. 2 presents the variations of the lattice parameters and c/a ratio of the $La_{2-x}Sr_xNiO_{4+\delta}$ samples. The obtained results completely agree with those reported by [7, 11]. It shows a non monotonous dependence in x with a clear change of a , c parameters, c/a ratio around the values of x equal to 0.5 and 0.6. The a parameter decreases with x below 0.6 and increases for x above, whereas the c parameter increases first with x below 0.5 and decreases for the greater values of x . Consequently the c/a ratio has a maximum value at $x = 0.5$. As known the hole doping state established by the Sr substitution and oxygen excessive plays an important role in magnetic and transport properties of the nikelate. Therefore we have first to check oxygen concentration of the material. The oxygen concentration ($4 + \delta$) of all the samples was determined by using the dicromat method. As known in [3, 4, 9, 10] the replace of Sr^{2+} for La^{3+} induces a change of valence of the Ni from Ni^{2+} to Ni^{3+} , as a result of the charge neutralization in the material. Concentration of the Ni^{2+} and Ni^{3+} could be determined from the previously estimated values δ by using the principle of charge balance in the $La_{2-x}Sr_xNiO_{4+\delta}$ samples. The determined values of δ , Ni^{2+} and Ni^{3+} for all the $La_{2-x}Sr_xNiO_{4+\delta}$ samples have been plotted in dependence on x , as presented in figure 3.

Fig. 2: The lattice constant versus x (a), and the unit cell volume and the ratio c/a versus x (b) of $La_{2-x}Sr_xNiO_4$.

Fig. 3: Dependence of the oxygen, Ni^{2+} and Ni^{3+} on x in $La_{2-x}Sr_xNiO_{4+\delta}$ structure.

As known the ions radius of Sr^{2+} ($r_{\text{Sr}^{2+}} = 1.18 \text{ \AA}$) is larger than that of the La^{3+} ($r_{\text{La}^{3+}} = 1.032 \text{ \AA}$), otherwise the ion radius of Ni^{3+} ($r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$ and $0.6 \text{ \AA}$ with low spin and high spin, respectively) is smaller than that of the Ni^{2+} ($r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$) [12]. Therefore the Sr substitution has a tendency to increase the lattice parameters of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, otherwise as its result, it simultaneously decreases the lattice parameters due to increasing the content of Ni^{3+} , which has smaller ion radius. Consequently we received an non-monotonous dependence of the a , c and unit cell volume in the dependence on Sr concentration as presented in Fig. 2. The change of valence value of the Ni ion in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ and its ion radius in the dependence on Sr concentration are presented in Fig. 3. It is seen these dependences are linear and cross-cutting each other around the concentration value x of about 0.5, where the abnormal change was observed also in the dependence of the lattice parameters and unit cell of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ on the concentration of Sr as presented in Fig. 2. We know that the interaction forces between ions and distance between them have most important influences on the phonon modes of materials. In our case the influence of the substitution of Sr on crystalline structure, the valence of ion Ni, the La/Sr-O and Ni-O bond lengths is very complicated, and competitive. As known from group theory, the oxidized $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ with $I4/mmm$ (D_{4h}^{17}) symmetry has only 2 A_{1g} and 2 E_g Raman active normal modes at the Γ point, because of the $\Gamma^{\text{cry}} = 3A_{2u}(\text{IR}) + 4E_u(\text{IR}) + B_{2u} + 2A_{1g} + 2E_g$. The ions O(I) and Ni are in the site having center-symmetry, therefore their vibration modes are not Raman active. Only vibration modes of the La and oxygen O(II) could be Raman active.

Fig. 4 shows Raman spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ recorded at room temperature for $x = 0.0 - 1.0$. Two Raman lines at 220 cm^{-1} and 430 cm^{-1} are clearly observed for all the samples. According to the results reported by Maroni et al. [13] and Udagawa et al. [14], we identify the R_1 -Raman line at 220 cm^{-1} as an apical-oxygen vibration along the a axis with E_g symmetry and the R_2 -Raman line at 430 cm^{-1} as an apical-oxygen vibration along the c axis with A_{1g} symmetry. As is seen in Fig. 5, the Raman shift of R_1 and R_2 exhibits a non-monotonous dependence on Sr concentration. Both two modes R_1 and R_2 are quite unchanged at the low range of Sr concentration, subsequently have a clear change at around $x = 0.5$, R_1 slightly decreases, whereas the R_2 increases as presented in Fig. 5. The value of x , where the change in Raman shifts was observed is well coincided to the value

Fig. 4: Raman spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ recorded at 300K: From bottom to top: $x = 0.0 - 1.0$.

Fig. 5: Raman shift versus x of the A_{1g} and E_g modes, measured at room temperature.

recorded from X-ray diffraction. It reasonably confirms a strong correlation between crystalline structure and Raman scattering in this material. It was known that a change in the bond-length and so on consequently in the force constant, causes a change in the vibration energy of modes, which could be explicitly observed by means of the Raman spectra. Udagawa et al., [14] suggested that the force constant depends on the bond length by an empirical equation as following:

$$k' = k (r/r')^n$$

Here the k , and k' are force constants for bonds between the same type of atoms having bond length r and r' , respectively, n is a phenomenon parameter, depends on mass and valence of atoms and is about 5-7 in case of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$. Upon the results calculated by this equation Udagawa et al. [14] supported that the interaction force between Lanthanum and oxygen ions in LaO layers plays a strongest affect on the R_1 vibration mode. On the R_2 vibration mode both two interaction forces in the bonds of Nickel-Oxygen and Lanthanum-Oxygen in c direction are most important factors, which affects on Raman shift of this mode. By using the above principle we qualitatively evaluated the relation between the recorded Raman shift and the concentration of Sr. I was seen that the above principle could used to qualitatively explain Raman spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ in dependence of its hole-doping state, which could be induced by the substitution of Sr for La and/or by the excess of oxygen. Besides the two above modes we have also observed a weak line (marked as R_3) at $\sim 170 \text{ cm}^{-1}$ and a wide band around 700 cm^{-1} . We suppose the first one at $\sim 170 \text{ cm}^{-1}$ is a mode belonging to the A_{1g} symmetry mode, vibrating in c direction of La. This mode shifts up significantly (more than 10 cm^{-1}), and in addition its intensity remarkably increased with the increase of Sr. The wide band may be related with the excess of oxygen and/or Raman activation of the infrared modes of the samples.

4. CONCLUSION

By the solid state reaction method, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ samples ($0.0 \leq x \leq 1.0$) were successfully prepared. All the samples are of a single phase with K_2NiF_4 tetragonal structure. The Sr^{2+} substitution anomaly affects on a , c parameters and c/a ratio of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. The c/a ratio reaches a maximum value at x of about 0.5. Raman spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ were recorded at room temperature. An A_{1g} vibration mode of the energy of 220 cm^{-1} of the apical oxygen O(II) in the La-O layer, vibrating along the a axis, and an Eg mode of the energy of 430 cm^{-1} of the apical oxygen in the Ni-O-La chain, vibrating along c axis were recorded. A relation between the Sr substitution and Raman shift of the apical oxygen in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ was observed. It was shown that the Sr substitution complicatedly affects on the crystalline structure and Raman spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$, which could be qualitatively explained by using a relation between the bond length and the interaction force in the La-O layer and La-O-Ni chain in the crystalline structure of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. The Sr substitution with high concentrations could activate a wide band of Raman modes from the Infrared modes and also the a Raman line at $\sim 170 \text{ cm}^{-1}$, which was supposed to be identified as a A_{1g} vibration mode of La.

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