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STRUCTURAL AND OPTICAL PROPERTIES OF SAMPLES $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Co}, \text{Ni}$) SYNTHESIZED BY SOL-GEL METHOD

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Abstract. *By sol-gel method, we synthesized $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Co}, \text{Ni}$; $x = 0.0; 0.1; 0.2; 0.3; 0.4; 0.5$) nano particles and investigated structure of Raman spectrum, absorption spectra, structural diagram of energy area and their density of states. The results showed that the average size of nanoparticles was about 10-30 nm. Absorption edge of each sample depended on the content of substitution of Co, Ni. Besides, the content of ion substitution also had influence on the structure, Raman spectrum, structural diagram of energy area and state density of samples. The results indicated that Co and Ni ions were substituted for position of Ti in the net cell, which changed structure of the material and reduced band gap of the synthesized materials and increases its conductivity.*

I. INTRODUCTION

In recent years, strontium titanate SrTiO_3 has been widely studied since the discovery of its ferroelectric properties. Due to the relatively high dielectric constant ($\epsilon = 300$) and low loss, this material is appropriated for applications in the high-frequency components, short wave devices, especially in the low temperature conditions [14]. The researches on SrTiO_3 often focused on doping and/or replacing Ti by transition metal ions that induced a distortion of cubic structure of the material and then led to the appearance of new physical phenomena.

The $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ (M is the transition metal ions) has attracted the world-wide researchers [11, 15, 16, 18, 26]. The researching results indicated that when Fe, Co, Ni substituted for the position of Ti, the materials demonstrated the electrical properties [17, 19]

and magnetic properties [7–9, 11], then materials could be changed into ones with multi-ferroic. Publication of optical properties was mainly reflected in the results of measuring the Raman scattering spectrum at the room temperature [24], and there was almost no research result in the absorption spectra, the Raman spectra of the sample in the range of low temperature. Particularly, the diagram of structure of the energy area and DOS has not been mentioned yet.

In this article, we present the synthesis of nanoparticles $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ by sol-gel method and study of the influences of Co, Ni substitution on structure and optical properties of the synthesized samples.

II. EXPERIMENTAL

$\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ samples were prepared by sol-gel method. The solution of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ with the appropriate volume was mixed in a solution with citric acid and ethylene-glycol in a volume ratio of 3:2. The solution was stirred and heated at the temperature of $150^\circ\text{--}200^\circ\text{C}$ for 2 hours to become transparent gel. We continued heating the mixture at 250°C for 4 hours, then reheated at 600°C for 5 hours. The crystalline phase was obtained by heating at 900°C for 9 hours.

X-ray diffraction measurements of the samples were performed on Siemens D5005 with Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$). Surface morphology of the samples was investigated by scanning electron microscope (FESEM) Hitachi S-4800. Absorption spectra of the samples was measured by using a Jasco system of 670 UV in the wavelength range from 190 nm to 2500 nm. Raman spectra measurements were recorded by a LABRAM-1B Jobin-Yvon using a laser light with the wavelength of 514.5 nm. The band structure and DOS were calculated by using the program CASTEP (Cambridge serial total energy package).

III. RESULTS AND DISCUSSION

As known the SrTiO_3 is a dielectric material having cubic perovskite structure with the crystallographic space group P_{m3m} and the lattice parameter of $a = 3.905 \text{ \AA}$ [5, 6]. By sol-gel method, we substituted transitional metals such as Co, Ni for Ti with concentration of $x = 0.1; 0.2; 0.3; 0.4; 0.5$. The X-ray diffraction results of the synthesized $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ samples are presented in Fig. 1 and Fig. 2 [2, 9, 20, 21, 23, 26].

Fig. 1a presents XRD patterns of the $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ samples. It is found that the synthesized samples are off the pure single SrTiO_3 phase. However all the X-ray peaks shifted even at the low substituted concentration of Co ($x = 0.1; 0.2$). The half-width of peaks have enlarged when the concentration of substitution Co was increased ($x = 0.3; 0.4; 0.5$). Especially, at the large 2θ angle, the diffraction peaks have an asymmetric form (see the inset in Fig. 2a). We believed that the asymmetric form of diffraction peaks is induced by a superposition of two different peaks. Therefore, we predicted that, a change in structure of the synthesized was occurred when concentration of substituted Co was increased. Lattice parameters (Fig. 2a) of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ were calculated and showed that the lattice parameter value in both structures reduced when concentration of the substitution concentration increased. This result is consistent with the reported by S.

Malo and A. Maignan [9]. We know that the Co ions can exist in multiple oxidation states such as Co^{2+} , Co^{3+} , Co^{4+} [13]. Where Co^{2+} has the radius of 0.745 Å, and 0.65 Å in the high (HS) and low spin (LS) states, respectively, similarly ion Co^{3+} has the radius of 0.61 Å, and 0.545 Å for the HS and LS states. Co^{4+} ion existed in the HS and LS with the radius smaller than 0.53 Å. Thus, it was likely that Co^{4+} or Co^{3+} (LS) had replaced Ti^{4+} in the crystal lattice, have cause a decreasing the unit cell size as well as lattice parameter.

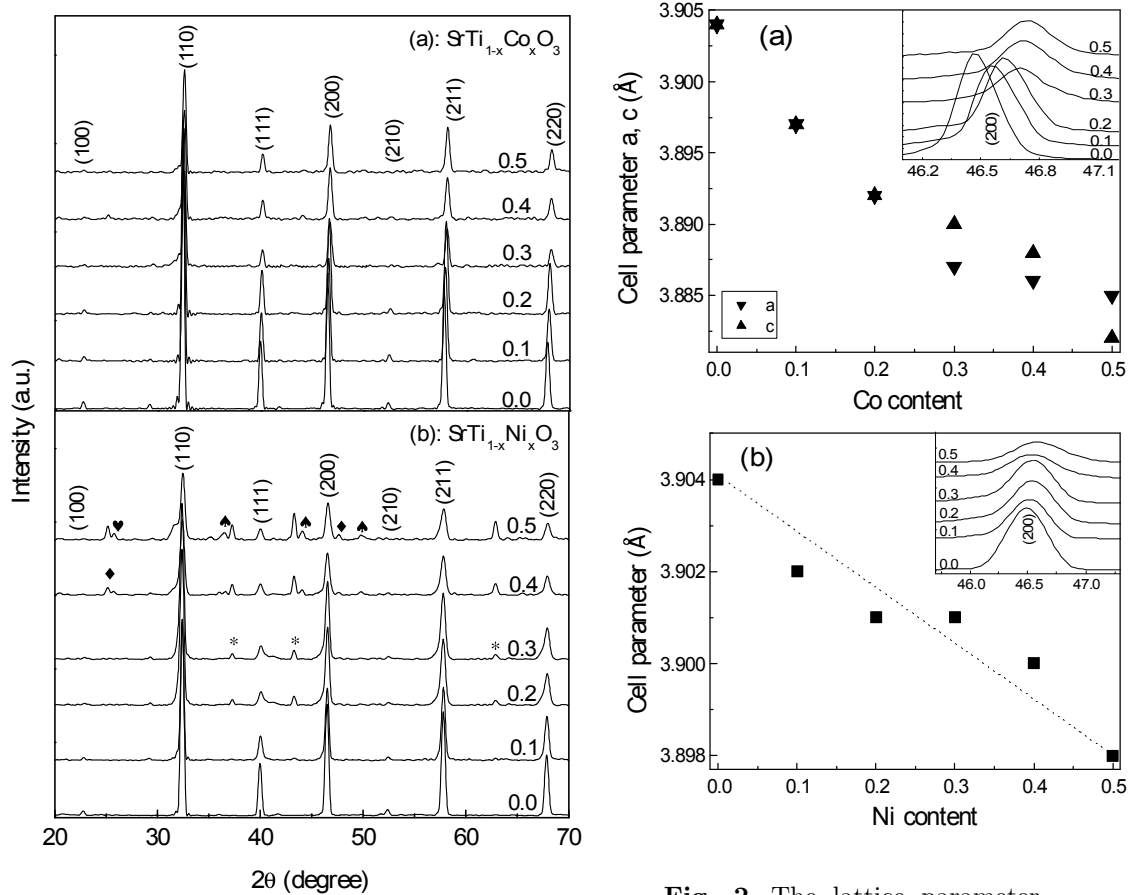


Fig. 1. XRD patterns of samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Co}, \text{Ni}$). Phase signals: TiO_2 (*), TiO (\heartsuit), Ti_3O_5 (\spadesuit), Ni (\clubsuit).

Fig. 2. The lattice parameter depends on concentration of substitutes Co, Ni. (a) samples $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$, (b) samples $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$. The inset shows the shift and splitting peaks around $2\theta = 46^\circ$.

XRD patterns of the samples $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$ are presented in Fig. 1b. It can be seen that when concentration of replaced Ni is small ($x = 0.1$), the sample contains a single phase of pure SrTiO_3 . When the concentration of substituted Ni increased to the value $x = 0.2$ and $x = 0.3$, a strange phase TiO (\heartsuit) appeared, and other seconde phases

Ti_3O_5 (\blacklozenge), TiO_2 ($*$), Ni (\blackspade) co-appeared in samples doped with $x = 0.4$ and 0.5 . The intensity of the diffraction lines decreased and the position of diffraction peaks shifted to large angle 2θ (inset of Fig. 2b). Therefore lattice parameter as well as the cell unit size reduced (Fig. 2b). This reduce of the unit cell and lattice parameters of the $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ (M=Ni and Co) is supposed to be related with the substitution of Ti^{4+} by Ni and Co ions appearing in spin state (HS, LS) with radius which is smaller than ionic radius of Ti^{4+} .

In order to evaluate the influence of the concentration of Co, Ni on the changes in form and size of particles in the samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$, we carried out SEM images for all the samples.

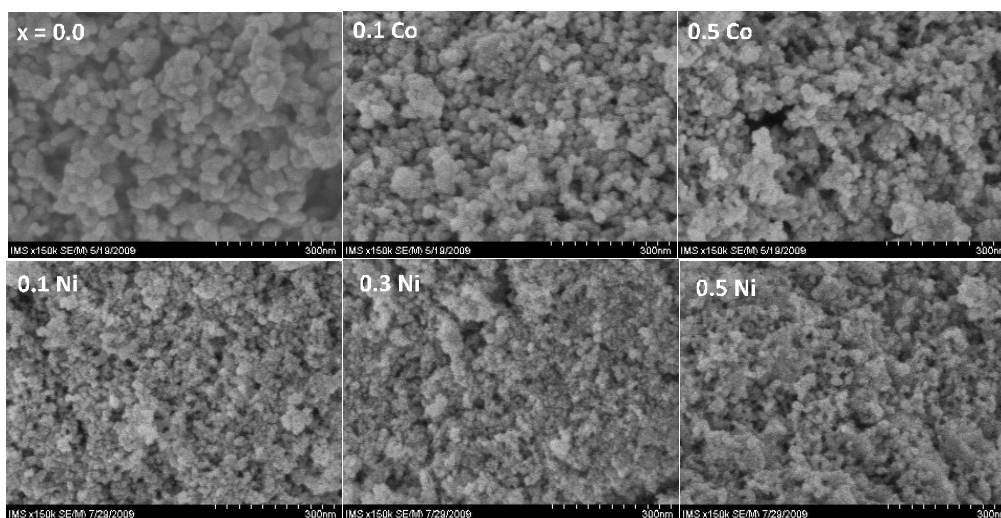


Fig. 3. SEM images of $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ nanopowers (M = Co, Ni).

Fig. 3 presents the SEM images of a powder $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ calcined at 600°C . Based on the SEM images the average particle size has been evaluated about 10 - 30 nm for all the $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ samples.

Raman spectra of the $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ samples at room temperature are presented in Fig. 4 (this result is similar to the recorded for $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$). In comparison with the Raman spectra of pure SrTiO_3 [1], which contains a strong peak at 170 cm^{-1} of $\text{TO}_2\text{-LO}_1$ mode, a weak peak at 234 cm^{-1} corresponding to the B_{2g} mode, a broad peak at 270 cm^{-1} belong to $\text{TO}_3\text{-LO}_2$ mode, a peak at 545 cm^{-1} corresponding to the TO_4 mode, and asymmetric peaks at 791 cm^{-1} of the $\text{LO}_4\text{-A}_{2g}$ modes.

Fig. 5 presents Raman spectra of some $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ samples in a temperature range of 77 - 230 K. It is clearly seen (Fig. 5b) oscillations modes at 500, 720, 800, 1600 cm^{-1} for the samples with the low Co concentration. With the high Co concentration ($x = 0.5$, Fig. 5c), the typical first order Raman scattering TO_4 (545 cm^{-1}) was not observed, but oscillation modes of the second order Raman scattering at 710 cm^{-1} and 1600 cm^{-1} appeared. In addition, a broad asymmetric mode at about 1400 cm^{-1} was also

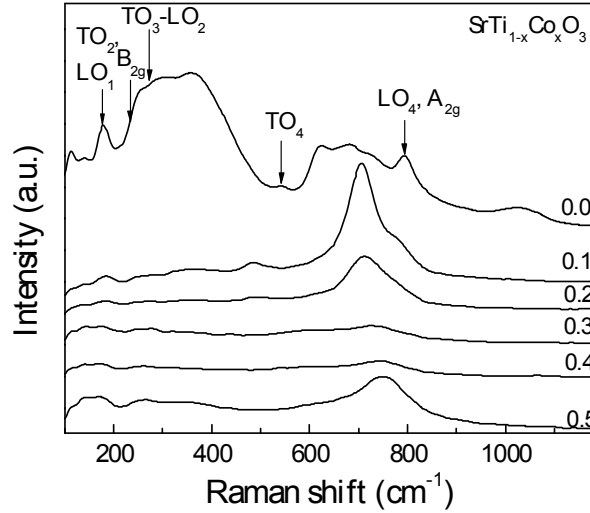


Fig. 4. Raman spectra of samples $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ at room temperature with $x = 0.0 - 0.5$.

observed. The appearance of these oscillation modes may be because of the contribution of the frequency resonant effect and/or the harmonics of these oscillation modes.

So, it can be seen that when content of Co increased up to $x \geq 0.3$ (Fig. 5c) the peak intensity in the region of $500\text{-}750\text{ cm}^{-1}$ decreased, whereas peak intensity in the region of $1300\text{-}1700\text{ cm}^{-1}$ increased. This unusual phenomenon may be related to the change in structure of materials as observed in the results of XRD (Fig. 2a). This means that when $x \geq 0.3$ in $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$, the second phases and/or crystalline disorder may appear in the $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ sample. In addition, a unusual change in the area ratio of 710 and 780 cm^{-1} in the temperature dependence have to suggest an existence of phase transition in the temperature range of $110\text{-}130\text{ K}$. Therefore, Co doped in the $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ caused an increase of phase transition from 105 K to 130 K . This result is consistent with report [12] for $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ doped with Ca.

Raman spectra of $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$ samples indicated that the typical oscillation modes appeared at $550, 700, 800\text{ cm}^{-1}$ and their peak intensity increased with decreasing temperature. When the Ni concentration reached value $x = 0.5$, the expansion of peak at 800 cm^{-1} was observed. it is supposed to be related with a superposition of two spectral peaks. This peak expansion may be attributed to the contribution of impurities, causing deformation in material and or an appearance of a random distribution of Ti and Ni cations in unit cell SrTiO_3 . From graph, it was found that the phase transition of the $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$ samples occurred at around 150 K .

The cause of change in the oscillation mode and the appearance of new peaks in $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ samples doped with transition metals M (Co, Ni) can be related to the distortion of the octahedral TiO_6 . The transition metal ion M substituted for Ti site in the unit cell, causes a change in the binding energy, binding length and angle because of the

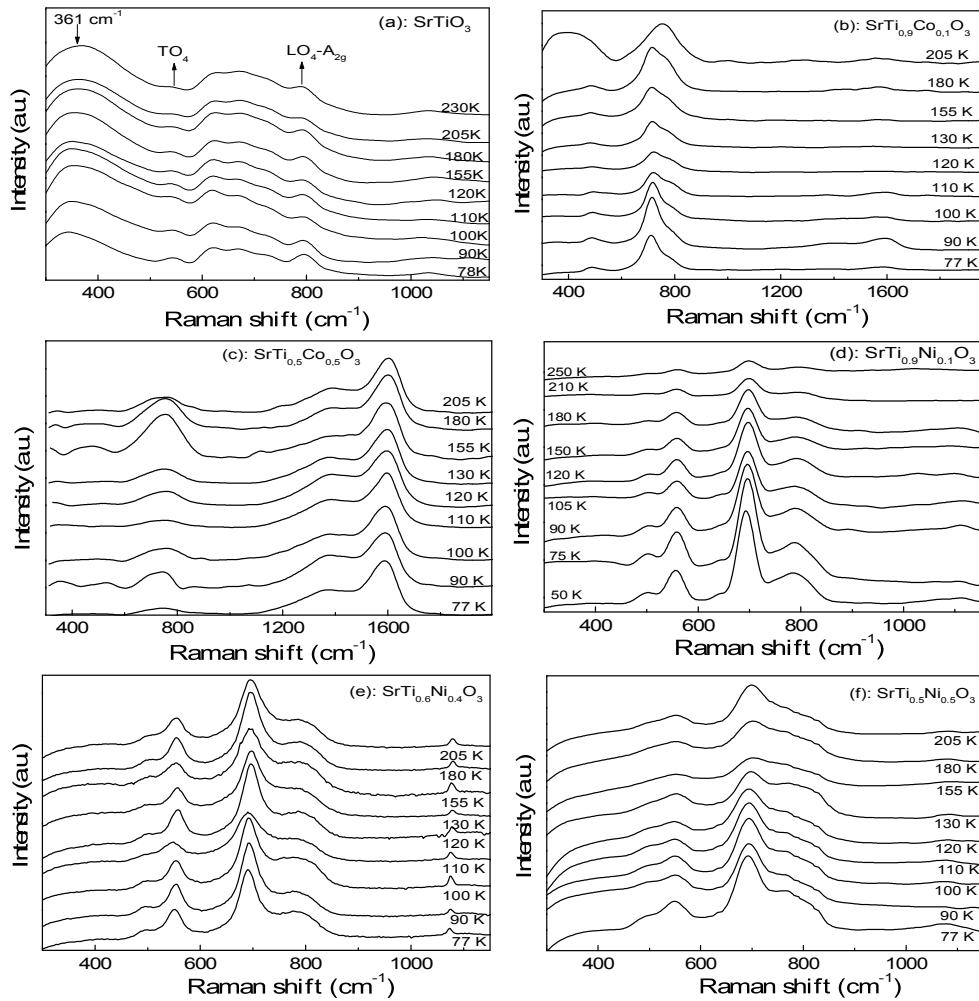


Fig. 5. Raman spectra samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ (M = Co, Ni) measured in range of temperature at 77-230 K

difference in ion radius of M and Ti ions. These changes induces a change in the molecular oscillation frequency that was reflected on the Raman spectra of samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$. These results are consistent with the results obtained from XRD, which have shown the change in the lattice parameter of samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$.

Raman spectra of samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ at low temperatures were recorded, It has shown that the phase transition temperature of this samples increased from 105 to 160 K. It may be caused by the defect or oxygen vacancy or impurities [12].

SrTiO_3 is a material having large dielectric constant ($\epsilon = 300$ at room temperature). The theoretical and experimental reported values of the width of the band gap for this material are very confused. L. Soledade *et al* [22], by theoretical calculations, reported a

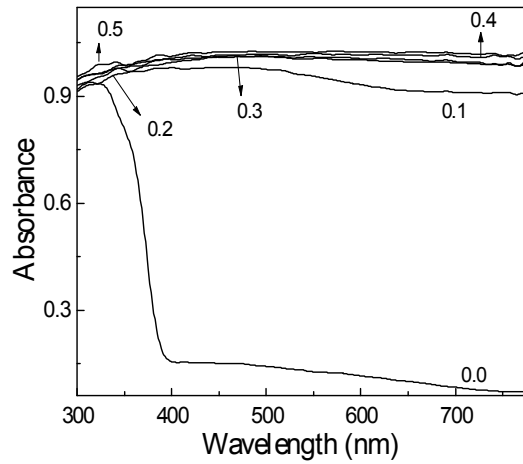


Fig. 6. Absorption spectra of samples $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.0 \div 0.5$).

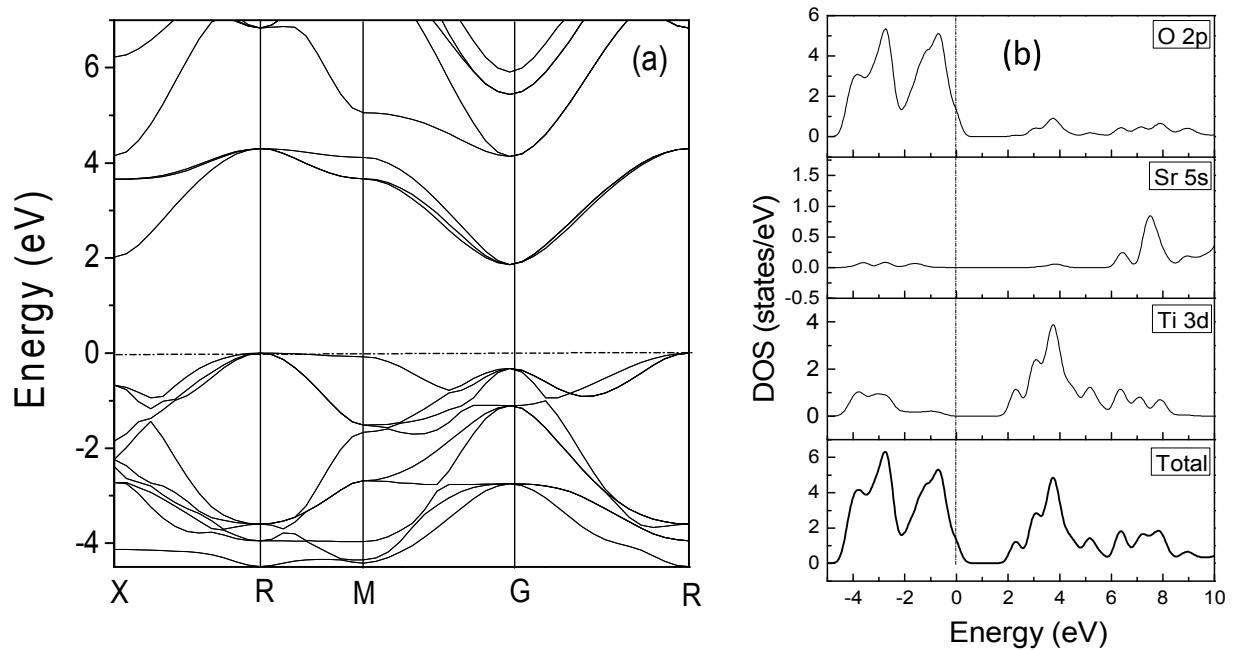


Fig. 7. Undoped SrTiO_3 : (a) band structure and (b) total DOS and PDOS.

band gap of 3.73 eV. Whereas a different experimental value of 3.22 eV was reported by other authors [4].

The measuring results of absorption spectrum of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ in wavelength range from 200 to 800 nm are shown in Fig. 6. When Co concentration increased to $x \geq 0.2$

samples showed complete absorption to light in the visible and infrared area. This result is similar to that of sample $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$.

We know that, in pure SrTiO_3 materials, the absorption edge of the material is corresponding to the transition between the O 2p and Sr 4p to Ti 3d states [25]. Thus, when we replaced Co, Ni ions, in samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$, the 3d states overlapped on the O 2p, which caused decrease band gap.

Or perhaps, when replacing a part of the ion transition metals Co^{2+} , Ni^{2+} for the site ion Ti^{4+} in the samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$, these ions became the impurity acceptors and formed impurity energy band in restricted areas. When the concentration of Co, Ni increased, the impurity energy band caused a narrowing band gap.

Our prediction on the formation of the impurity energy band in the band gap when replacing the transition metal ions Co, Ni for Ti in $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ were checked by density-functional theory (DFT). In this report, we used local density approximation (LDA) to calculate the energy band structure, density states of $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ with replaced Co Ni in the program CASTEP (Cambridge Serial Total Energy Package). Crystal structure of SrTiO_3 material was taken from the Materials Studio software library.

Fig. 7 shows the band structure and density of states (DOS) of pure SrTiO_3 materials. We see that the characteristics of the band structure and DOS of materials were similar to the previous announcements [10, 20] We observed clearly that the top of the valence band and the bottom of the conduction band was located at point G and Z in the Brillouin zone (Fig. 7a). So, pure crystal SrTiO_3 is a dielectric material with oblique prohibited zone. Width of the band gap of the material determined from point G to point Z was 1.84 eV. This value was consistent with a number of other theoretical calculations, but it was much smaller than the experimental results obtained of 3.2 eV. There is a difference between the experimental results and the theoretical results obtained from the LDA approximation method. It may be caused by an approximation that there was no interaction between electrons in the homogeneous electron gas [27].

Diagram of the partial density of state PDOS (Fig. 7b) shows that the valence band is the result of a contribution of O 2p, Sr 5s, Ti 3d states, but O 2p was near the Fermi level and had more electronic contribution. The hybridization between O 2p states and Ti 3d states appeared in the energy range from -4.0 to -2.0 eV below the Fermi energy. This result demonstrated that the chemical bond in the crystal SrTiO_3 is mainly covalent links between the Ti-O. In the conduction band, the states of Ti 3d dominated. Besides, there were also small contributions from Sr 5s states. Thus, when doped or replaced electronic in materials SrTiO_3 , the impurity band energy can be formed, or the Fermi level can be shifted towards the conduction zone which cause decrease in width band gap.

Calculation results of the energy structure and DOS of materials $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ with replaced Co with $x = 0.125$ is shown in Fig. 8. On the band structure (Figure 1.8a), it can be seen that the impurity energy ranged above the Fermi level, decreasing band gap of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ about 0.35 eV. In accordance DOS (Fig. 8b), the impurity energy band was formed by the Co 3d states. This result is consistent with report on the conductive natures of materials $\text{SrTi}_{1-x}\text{Cr}_x\text{O}_3$ [3] and $\text{CaTi}_{1-x}\text{Cu}_x\text{O}_3$ [28]. Thus, the electrons would shift from the top of an impurity energy to the bottom of the conduction band, causing

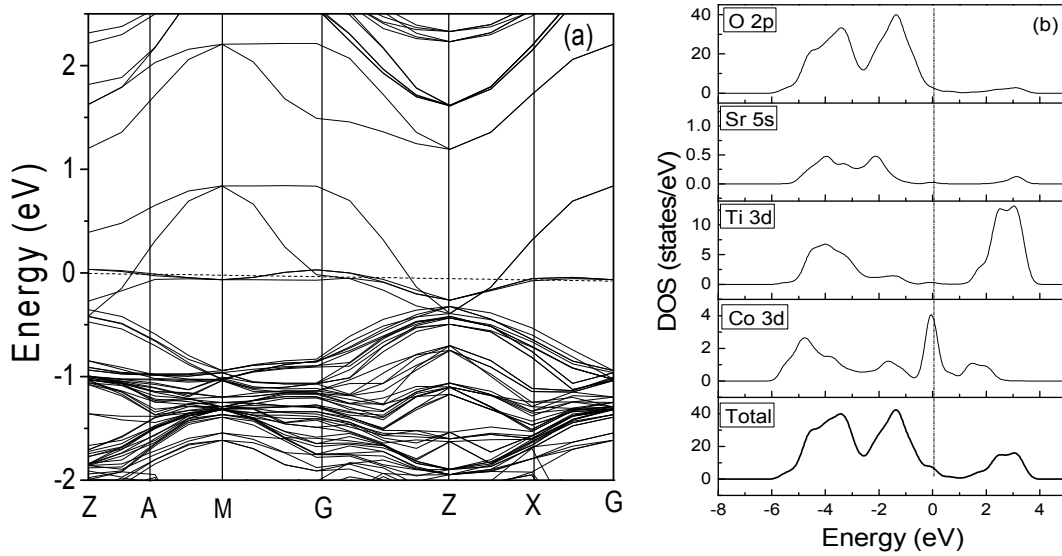


Fig. 8. Co 12.5% - doped SrTiO_3 (a) band structure (b) total DOS, PDOS of Co impurity and its nearest atoms.

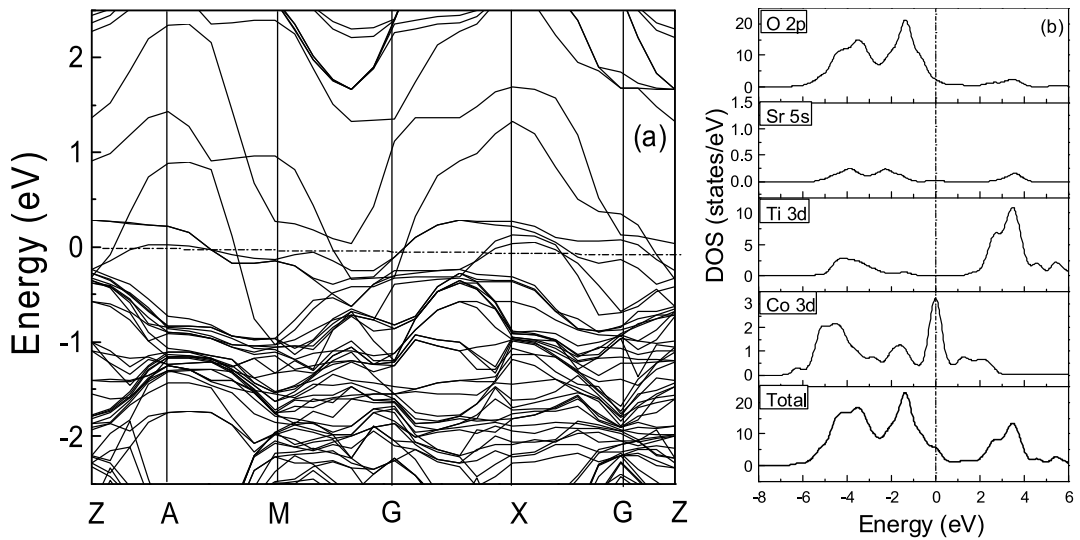


Fig. 9. Co 25% - doped SrTiO_3 (a) band structure (b) total DOS, PDOS of Co impurity and its nearest atoms.

decrease band gap. Density of states DOS diagram also shows that, at the vicinity of the Fermi level, the electronic O 2p states and Co 3d states dominated.

From the band structure of SrTiO_3 doped with 25% Co (Fig. 9a), we can see clearly that the overlap of impurity band to the top of the valence band. Therefore, when replacing Co 25% of the $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ material behaves as a metal material. In the density of states, energy levels are formed mainly by the hybridization between the O 2p, Ti 3d and Co 3d states. Unlike the case of the Co without replacement (Fig. 9b), the energy in the maximum valence band also had participation of Co 3d states. At the bottom of the conduction band, there was strong interaction between the Ti 3d and Co 3d states. It can be also noticed that there is no clear boundary between the impurity and the conduction band as shown in the DOS of SrTiO_3 pure sample.

Similarly for the samples $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$ (figure are not shown here), while replacing 12.5% of Ni, width of restricted band decreased to 0.14 eV. When replacing concentration increased to 25%, due to the overlap of impurity energy band, we could not distinguish between the boundaries of the restricted areas. Diagram of the density of states shows that, at the Fermi approximate level, there was mainly the contribution of Co 2p states (in the valence band), Ti 3d and 3d Ni states (in the conductive band).

Through the band structure and DOS of $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$, $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$ samples, we see that: The ions of Co, Ni are replaced in the samples $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ have become the impurity acceptor which appear in the band gap which lead to decrease the band gap. When the concentration of Co, Ni increase to about 25% the materials behaves metallic characteristics.

IV. CONCLUSION

We synthesized nanoparticles with size of 10-30 nm, then studied the effects of ions Co, Ni on the grain size, structure and optical properties of $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$. The change in lattice parameter proved that ions Co, Ni have substituted for Ti in crystal structure. Co and Ni substitution reduced the band gap and led to changes in Raman and absorption spectra. The research results on structure confirmed that the solubility of Co and Ni in $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ is limited at about 20%, and 10% for $\text{SrTi}_{1-x}\text{Ni}_x\text{O}_3$. Raman spectra at low-temperature showed that the phase transition was estimated around 105-160 K. The obtained experimental results have been predicted and examined through the band structure and density of states calculation.

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