

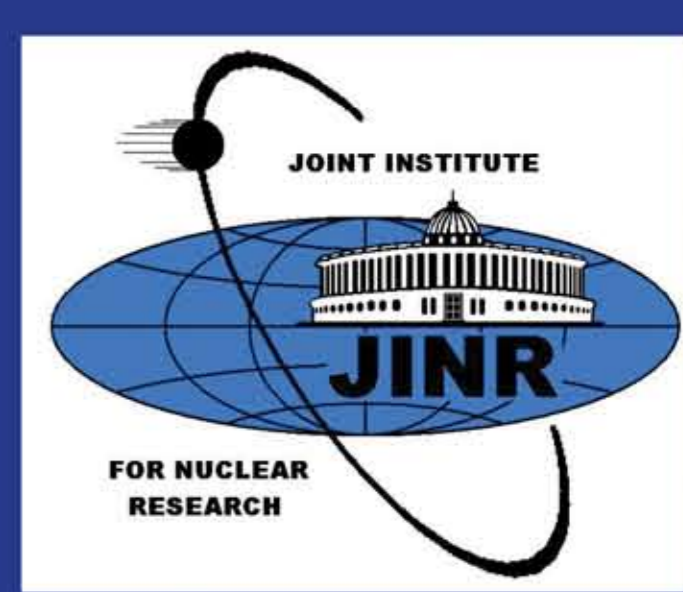


Preparation and characterization of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ perovskite oxides for energy materials

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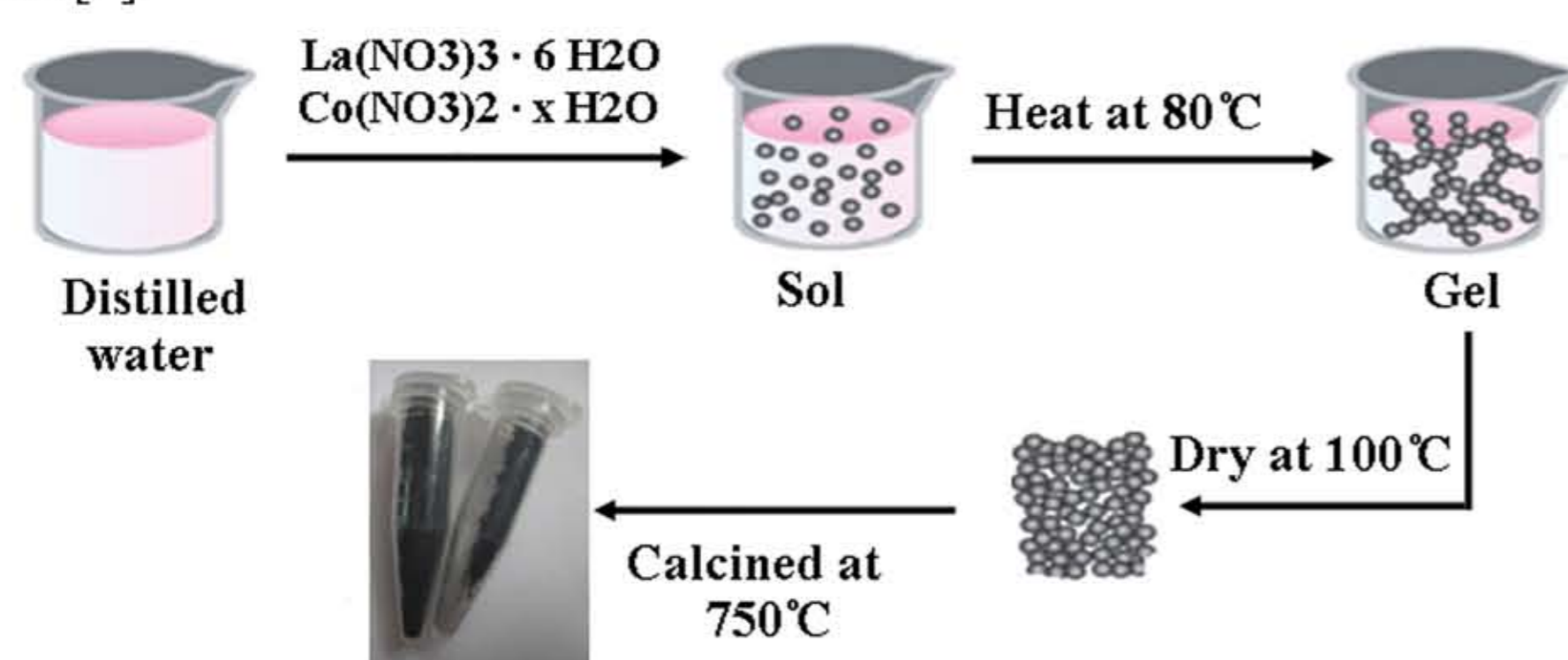


Introduction

Perovskite type oxides with general formula ABO_3 may potentially replace noble metal catalysts due to their high activity, thermal stability and low costs [1]. The catalytic properties of ABO_3 basically depends on the nature of A and B ions. Therefore the electronic properties and catalytic activity of the perovskite-type oxides can be modified by substitution of other heterovalent ions into the A or B sites [2]. Nanostructured perovskites with a high specific surface area and small crystallite size offer the potential for a substantial increase in the performance of catalyst [3, 4]. In this work, nanostructured Ce doped perovskite type oxides, with x ranging from 0 to 0.4, were synthesized by sol-gel method. The main objective of this work was to study the effect of Ce doping on the structure, surface and absorption properties of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$.

Experimental

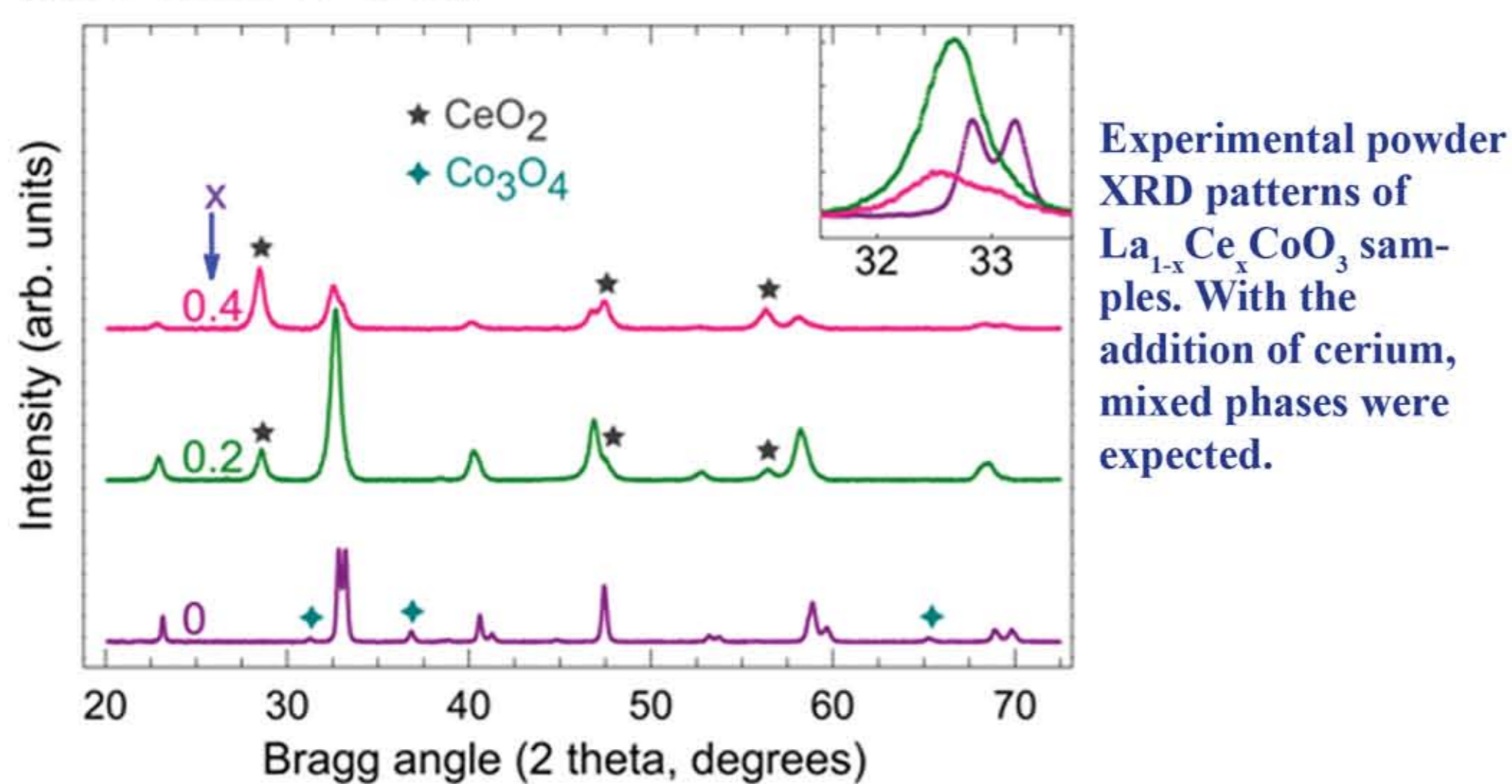
$\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x=0, 0.2, 0.4$) perovskites were prepared by the sol-gel method [5].



The prepared powder samples were characterized by X-ray Diffraction (XRD), X-ray absorption spectroscopy (XAS), Energy dispersive X-ray spectroscopy (EDS) and BET surface area analysis.

Results and discussion

For $x=0$, the structures were the rhombohedral LaCoO_3 -type (JCPD-ICDD 25-1060); when $x=0.2$ and 0.4 , the samples exhibited the pattern of cubic LaCoO_3 (JCPD-ICDD 75-0279).



The whole patterns shift to lower 2θ angles for doped samples accordingly with increasing x as shown in the inset graphs. The decrease of the reflection angle is attributed to larger lattice parameters due to lattice relaxation (Table 2). The dose $x=0.4$, whose peak in the inset is not as sharp as for the case $x=0.2$, might have reached or exceeded the threshold of Ce insertion. More CeO_2 aggregates (observed at $2\theta=28.6^\circ, 47.4^\circ$ and 56.5°) may cause the particles to be disordered or to have smaller coherent length.

Table 1. The EDS analysis show the composition is almost the same (within experimental error) as the nominal composition of the samples.

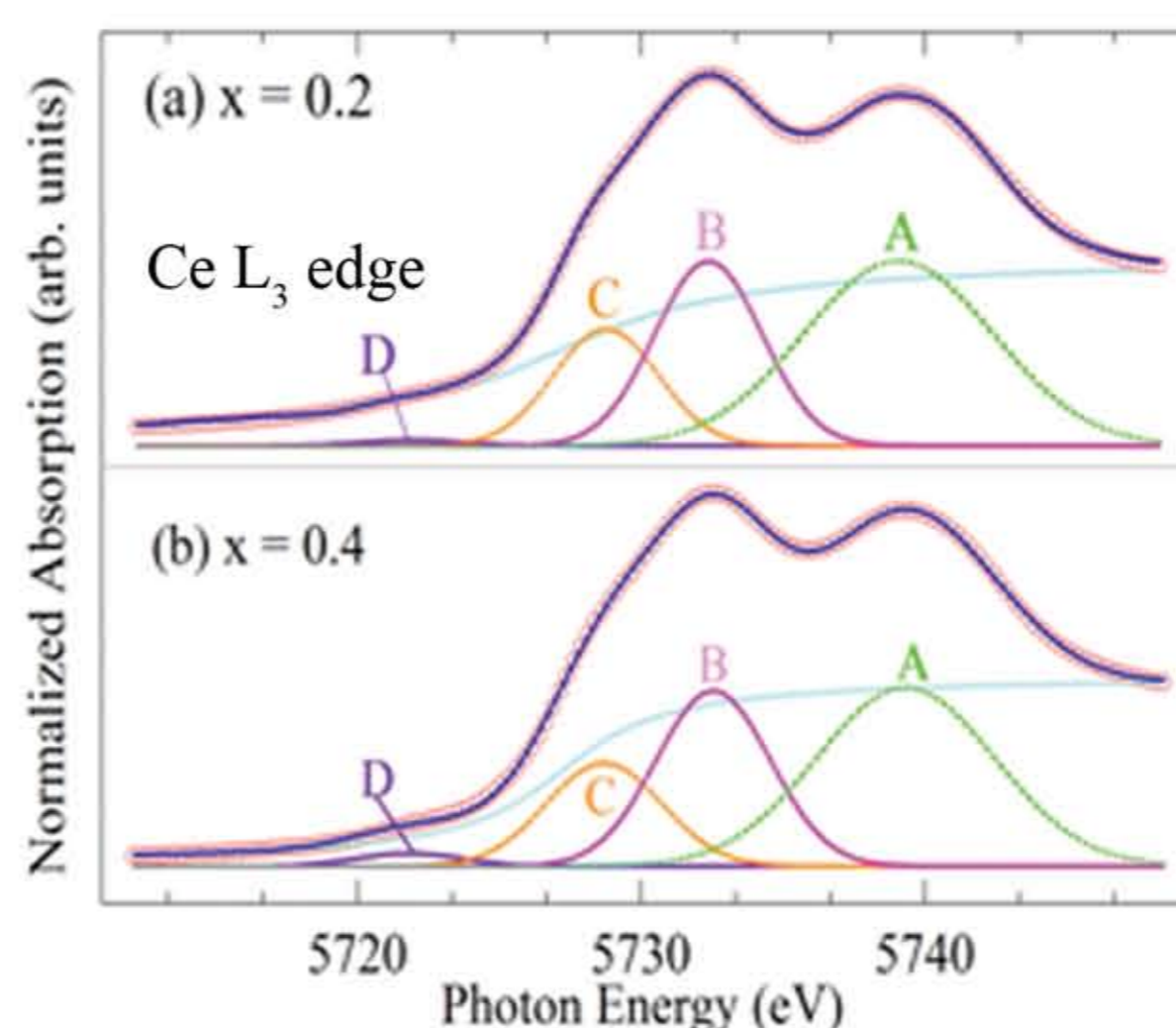
| Element | LaCoO_3 | | $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x=0.2$) | |
|---------|------------------|---------|--|---------|
| | N (wt%) | M (wt%) | N (wt%) | M (wt%) |
| La | 56.50 | 51.58 | 45.15 | 54.79 |
| Co | 23.97 | 33.29 | 23.94 | 20.38 |
| O | 19.52 | 15.13 | 19.5 | 19.45 |
| Ce | | | 11.38 | 5.38 |

N – nominal, M – measured

Results and discussion

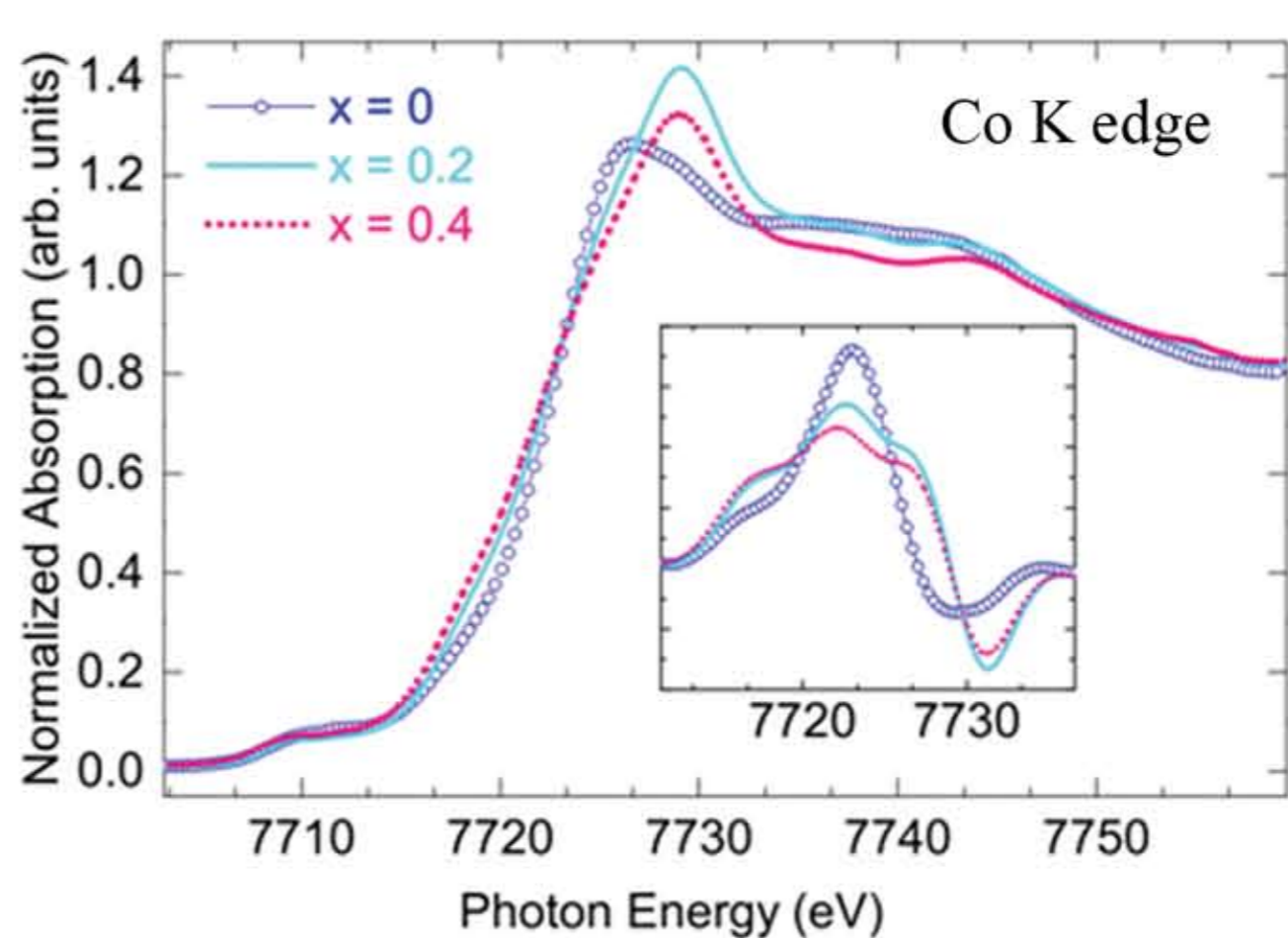
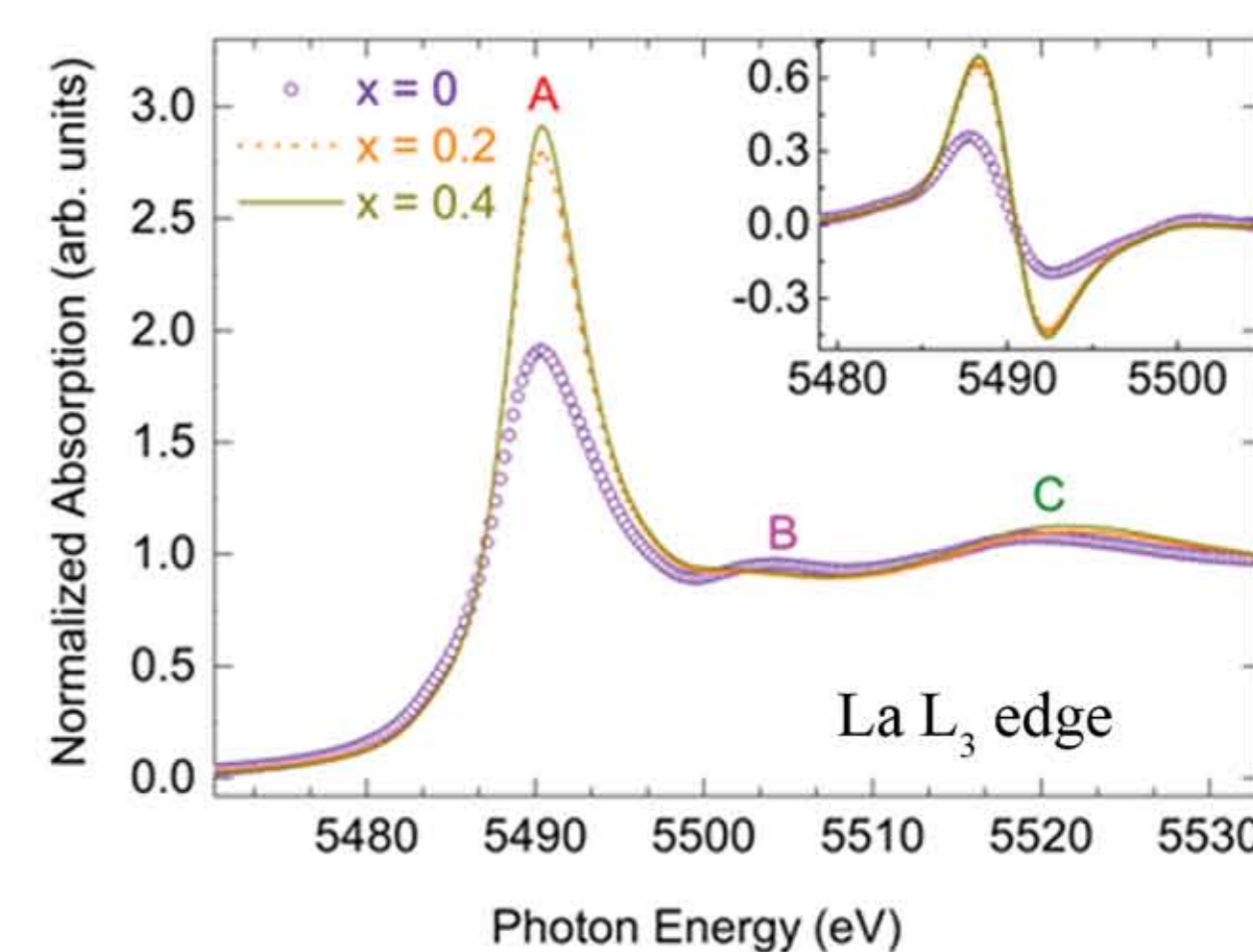
Table 2. XRD and BET analysis results of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x=0, 0.2, 0.4$). Lattice parameters enlarged due to lattice relaxation and the crystallite size decreased with the increase of doping concentration.

| Samples | Lattice parameter (Å) | Crystallite size (nm) | SSA (m^2g^{-1}) |
|--|-----------------------|-----------------------|-----------------------------------|
| LaCoO_3 | $a=b=5.401, c=13.312$ | 13.2 | 2.18 |
| $\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ | $a=b=c=5.379$ | 12.8 | 5.68 |
| $\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$ | $a=b=c=5.384$ | 8.3 | 3.32 |



Therefore, some Ce^{3+} are present in $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ at La vacant sites to compensate the lattice charge. If we view the picture that the insertions of cerium ions take place at and reduce the number of La^{3+} vacancies, the increased lattice parameters found in XRD results are comprehensive.

The white line (A) with a sharp single peak reflects holes in 5d-band while the two post-edge structures B and C denote the contribution of O 2p states hybridizing with La 5d states. La 5d-band of the pristine cobaltite is not empty as expected, but instead, partially filled and becomes less occupied with the effect of Ce doping.



The pre-edge peak structure is attributed to $1s \rightarrow 3d$ quadrupole transitions. The coordination number of CoO_6 octahedron was not affected by Ce doping. The Ce induced blue shift of the Co K edge may demonstrate the fact that Co ions gain electrons and their oxidation states likewise get reduced.

Conclusions

- Nanostructured $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ with a crystallite size of 8–13 nm and a specific surface area of 2–5 m^2g^{-1} were prepared by sol-gel method.
- The XRD pattern of LaCoO_3 confirms the sample to be in rhombohedral phase. When cerium is doped the samples are found to be in cubic phase. The results are in agreement with the increased lattice parameters and the evolution of the symmetry group into pseudo-cubic demonstrated by the XRD.
- XAS investigations have proved the actual incorporation of Ce ions, possibly in forms of Ce^{3+} , into the perovskite.
- An integration of all these results obtained in the best performance of the sample when $x=0.2$.

References

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