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A study on selected properties of $La_{1-x}Sr_xCoO_3$ and its application in sealed CO_2 lasers

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Samples in the composition series $La_{1-x}Sr_xCoO_3$ with $x = 0$–0.8 were synthesized, and their crystal structures, conductivities and catalytic activities were studied. When $x < 0.6$, they have a rhombohedrally distorted perovskite structure. When $x = 0.3$–0.5, their conductivities at room temperature are of the order of 10^3 S m^{-1}. When the temperature is higher than 250 °C, the catalytic activities of $La_{1-x}Sr_xCoO_3$ were very high which reaches a maximum for the sample at $x = 0.3$. Cylindrical samples were made from $La_{1-x}Sr_xCoO_3$ $x = 0.3$ and used as a cathode in sealed CO_2 lasers. Compared to the traditional Ag–Cu alloy cathode, the performance of $La_{0.7}Sr_{0.3}CoO_3$ is better. The maximum output of a 1.0 m length laser tube using the new cathode is 53.1 W m^{-1}.

1. Introduction

Due to its structural simplicity and ease of use, sealed CO_2 lasers have found application in many areas. Unfortunately their output power and operational life remain insufficiently high. One of the main factors that affects the output and operational life is the performance of the cathode. The usual cathode materials are metals or alloys that have the disadvantages of (i) being easily oxidized and (ii) high sputtering rates. These problems result in oxygen being absorbed from the gas mixture in the laser tube, which in turn reduces the output power and operational life.

The rare earth oxide compounds $La_{1-x}Sr_xCoO_3$ have many promising characteristics such as high conductivities, high heat and chemical stabilities, high catalytic activities and also a low sputtering rate. These properties make $La_{1-x}Sr_xCoO_3$ a promising cathode material.

Iehisa *et al.* [1] have used $La_{1-x}Sr_xCoO_3$ as a cathode in a sealed CO_2 laser. A considerable amount of work has been expanded on understanding the properties of $La_{1-x}Sr_xCoO_3$ [2], but no systematic study on the properties of use to application in CO_2 lasers exists in the literature. However a detailed understanding of the material properties would be of considerable use in the preparation of the cathode materials.

The preparation technology plays an important role in making an $La_{1-x}Sr_xCoO_3$ cathode. We have prepared a cylindrical cathode for use in a sealed CO_2 laser. The cathodes not only have a strong mechanical strength and a high conductivity, but also a suitable porosity to ensure a high catalytic activity.

2. Experimental procedures

The $La_{1-x}Sr_xCoO_3$ samples were synthesized using conventional ceramic techniques. The starting materials are La_2O_3, $SrCO_3$, and Co_3O_4 with a purity of 99.9%. Stoichiometric amounts of the starting materials were weighed to produce samples of composition $La_{1-x}Sr_xCoO_3$ at $x = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6$ and 0.8. Then each sample was mixed, ground into a powder of particle size < 325 mesh, pressed into a cylindrical shape and fired at 1150 °C for 5 h.

The X-ray diffraction spectra of these samples were determined with a Rigaku D/max r-A X-ray diffractometer. The conductivities were measured using the four-probe method. The samples were made into the form of a bar with dimensions of $3 \times 6 \times 12$ mm.

For the catalytic activity measurements, samples with a 18–60 mesh particle size were placed into a quartz glass reactor. The temperature was controlled by use of a furnace. In the mixed atmosphere of CO_2 and air, the content of CO_2 was 3–5 vol % and the air flow rate was 5 l h^{-1}. The gas composition was analysed using a gas chromatograph produced by Beijing Analysis Device Plant.

The sealed CO_2 laser cathodes were made from $La_{0.7}Sr_{0.3}CoO_3$ powders with organic binders being added to ensure high sample density and strength. A specific mould was used to enable the production of

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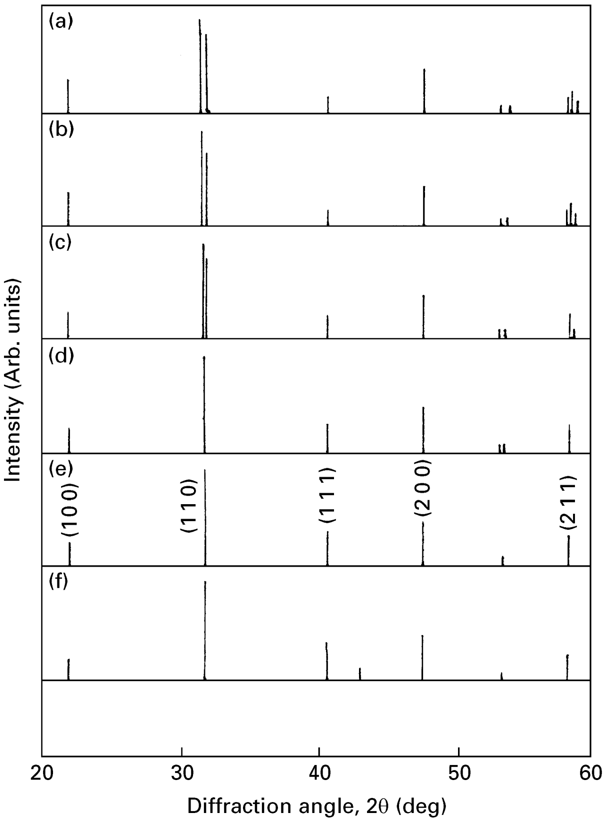

Figure 1 X-ray diffraction spectra of $La_{1-x}Sr_xCoO_3$ for x values of (a) 0.0, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.6 and (f) 0.8.

the cathode and the simultaneous fixing of the lead wire.

The sealed CO_2 laser discharge tube is made from No 11 glass and has a diameter of $\varphi = 10$ mm and a length of 1 m. The anode material is tungsten. The radius of curvature $R = 3$ m. The gas composition ratio of $Xe:CO_2:N_2:Ne = 1:3:5:15$ was used at a total pressure of 2000 Pa.

The new cathode and the conventional Ag–Cu alloy cathode were installed into the same tube under the same conditions. Their output power performance was then measured.

3. Results and discussion

The X-ray spectra presented in Fig. 1 show that when $x < 0.6$, $La_{1-x}Sr_xCoO_3$ has a rhombohedrally distorted perovskite structure and that when $x = 0.6$, the structure becomes cubic. Compared to the X-ray pattern for a cubic perovskite structure, the X-ray pattern for a rhombohedral distortion contains more reflections, and this is especially noticable for the (1 1 0) reflection which splits into two inequivalent reflections when the rhombohedral distortion appears. $LaCoO_3$ has a perovskite structure with a significant rhombohedral distortion. As Sr^{2+} is substituted onto the lanthanium site in increasing quantities the two lines become continuously closer hinting that the distortion is continuously decreasing, until at $x = 0.6$, the compound regains its cubic perovskite structure. At $x = 0.8$, impurity phases are present in the sample. The above results are in agreement with those reported by Ohbayashi *et al.* [3].

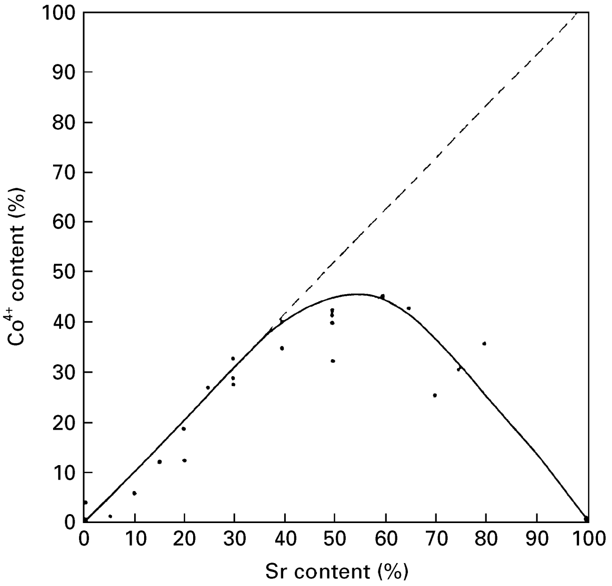

Figure 2 Co^{4+} content (% of total amount of Co) of (La, Sr) cobaltites. —— experimental curve, – – – theoretical curve (see [4]).

In $La_{1-x}Sr_xCoO_3$, all the Co ions have a 3 + oxidation state, Co^{3+}. When the La^{3+} in $La_{1-x}Sr_xCoO_3$ is partially substituted by Sr^{2+}, charge compensation can be accomplished by either of the following two mechanisms; the oxidation of the Co^{3+} ion to Co^{4+} or the formation of an O^{2-} vancancy

$$La^{3+}_{1-x}Sr^{2+}_{x}Co^{3+}_{1-x}Co^{4+}_{x}O_3 \qquad (1)$$

$$La^{3+}_{1-x}Sr^{2+}_{x}Co^{3+}O_{3-x/2}V_{Ox/2} \qquad (2)$$

where V_O is the crystal oxygen vacancy. The results of an investigation into the Co^{4+} content in $La_{1-x}Sr_xCoO_3$ by Jonker and van Santen [4] are shown in Fig. 2. A maximum of 45% Co^{4+} was obtained in the compound at 60%Sr ($x = 0.6$). When $x < 0.6$, the Co^{4+} content increases as the Sr^{2+} content increases. When $x > 0.6$, the Co^{4+} content decreases as the Sr^{2+} increases. A comparison with Equations 1 and 2 suggests that when $x > 0.6$, the latter mechanism is dominant. As x increases, the crystal vacancy concentration eventually becomes too large to allow the perovskite phase to exist, and this results in the appearence of a phase with a lower coordination number for the cobalt. This is probably the cause of the impurity phase that was observed when $x = 0.8$.

The conductivities of the $La_{1-x}Sr_xCoO_3$ samples are listed in Table 1. The conductivity of $LaCoO_3$ is not high enough for practical applications. However La^{3+} is partially substituted by Sr^{2+} then the conductivity of $La_{1-x}Sr_xCoO_3$ rapidly increases so that when the Sr^{2+} content is 0.2, the conductivity has increased by two orders of magnitude and when $x = 0.3$, it increased by another order of magnitude. At this point the conductivity appears to saturate and when $x = 0.4$, 0.5, the conductivity is effectively constant until at $x > 0.6$, the conductivity begins to decrease.

At room temperature, $LaCoO_3$ is a semiconductor [3]. As the La^{3+} is partially substituted by Sr^{2+}, the

TABLE I The conductivities of $La_{1-x}Sr_xCoO_3$ ($\times 10^3$ S m^{-1})

Composition, x	0	0.2	0.3	0.4	0.5	0.6	0.8
Conductivity	6.37×10^{-3}	3.94×10^{-1}	2.70	2.21	2.99	4.48×10^{-1}	9.14×10^{-1}

electronic properties begin to change, and at $x > 0.125$, the $La_{1-x}Sr_xCoO_3$ system becomes ferromagnetic due to the Co^{4+}–O–Co^{3+} exchange interaction [5]. Ferromagnetism is closely related to the existence of itinetant electrons (i.e., electrons contributing to metallic type conductivity). As the Sr^{2+} content increases, the Co^{4+} content also increases, and thus the number of itinerant electrons also increases which is reflected in an increase in the conductivity. When x is 0.5–0.6, the Co^{4+} content reaches its maximum and if the Sr^{2+} content is increased any further, the structural phase transition occurs and impurity phases are produced. These effects are reflected in a decrease in the conductivity.

The conductivity–temperature behaviour of the sample at $x = 0.3$ is shown in Fig. 3. The conductivity increases with an increase in the temperature, which is promising for the application of this material as a cathode.

The catalytic activity of $La_{1-x}Sr_xCoO_3$ for the oxidation of CO is listed in Table II. It can be seen from the table that at lower temperatures, $La_{1-x}Sr_xCoO_3$ compounds are poor catalysts for CO oxidation. However as the temperature increases, the activity rapidly increases, with $La_{0.7}Sr_{0.3}CoO_3$ showing the highest values. When $x < 0.3$, the activity decreases as x decreases whilst for samples with $x > 0.3$, the activity decreases as x increases.

Voorhoeve [2] has reported that at low temperatures ($< 350\,^{\circ}$C), the oxidation of CO by O_2 over a perovskite is a "superficial" process. During the oxidation of CO on $La_{1-x}Sr_xCoO_3$, the CO is bonded to the Co as a carbonyl group by the donation of the carbon lone pair into an empty d_z^2 orbital of the metal to form a σ bond, and back donation of t_{2g} electrons of the metal into the CO π^* bond [6, 7]. It is therefore advantageous if the e_g levels are empty but the t_{2g} levels are full.

In the perovskite structure, the electron configuration of Co^{3+} using crystal field splitting arguments can be considered to be $t_{2g}{}^6 e_g^0$, thus the d_z^2 orbital is empty and the t_{2g} orbital is full and thus Co^{3+} is expected to show catalytic activity. However the t_{2g} orbital of a Co^{4+} ion is not full, and therefore it shows poorer catalytic properties. In summary the experimental results on the catalytic activity of $La_{1-x}Sr_xCoO_3$ for the oxidation of CO can be explained as: when $x < 0.3$, the Co^{4+} content increases as x increases, but in addition the oxygen vacancies also simultaneously increase. This oxygen vacancy formation is advantageous for catalysis and in fact it overides the negative influence of the Co^{4+} production. So when $x < 0.3$, the catalytic activity increases as x increases whereas between $0.3 < x < 0.6$, where the Co^{4+} concentration continuously increases its negative effect on the oxidation catalytic activity is dominant, which results in a decrease in the catalytic activity as x increases. At the highest substitution contents investigated in this work impurity phases were observed to exist and these phases tend to decrease the catalytic activity.

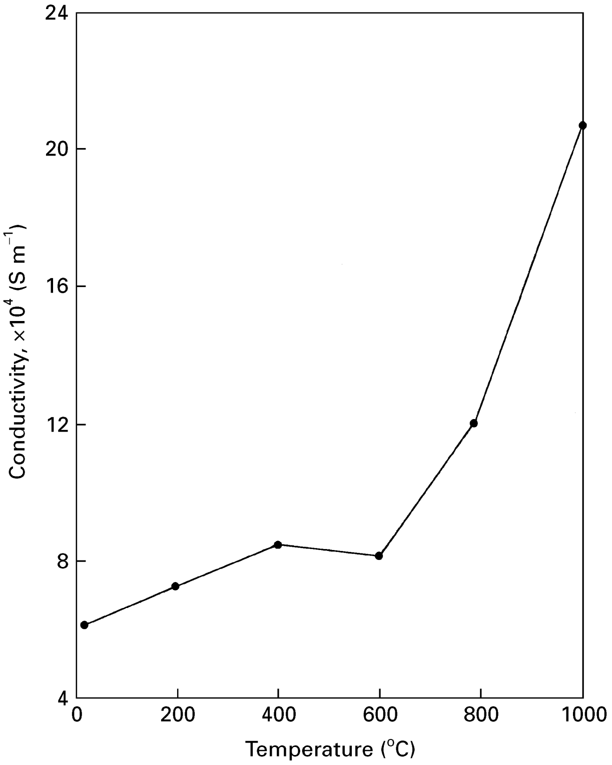

Figure 3 Conductivity as a function of temperature for $La_{0.7}Sr_{0.3}CoO_3$.

During CO_2 laser operation, some of the CO_2 in the tube can decompose into CO and thus the performance of the laser will decrease due to the deviation from the optimal gas composition ratio. It is clear from the previous discussion that $La_{1-x}Sr_xCoO_3$ materials have high catalytic activities for the oxidation of CO with a maximum being observed for the $La_{0.7}Sr_{0.3}CoO_3$ sample. Thus this composition was chosen for study application as a cathode in a sealed CO_2 laser.

A cylindrical cathode was prepared from $La_{0.7}Sr_{0.3}CoO_3$ powders combined with an organic binder to ensure a high sample density and the optimum conductivity value and catalytic activity required for use as a cathode [8] in a sealed CO_2 laser.

The output power curves of the $La_{0.7}Sr_{0.3}CoO_3$ and the Ag–Cu alloy cathodes in the same sealed CO_2 laser are shown in Fig. 4. The potential of the new cathode is quite obvious. The 1.0 m long CO_2 laser containing the $La_{0.7}Sr_{0.3}CoO_3$ cathode can reach a maximum output power of 53.1 W m^{-1}. The operational life of such a CO_2 laser using the new cathode is over 4800 h when used for medical purposes. The

TABLE II The catalytic activities (in terms of percentage conversion) of the oxidation of CO using $La_{1-x}Sr_xCoO_3$

Temperature (°C)	Composition, x 0	0.2	0.3	0.4	0.6	0.9
100	0.4569	3.2388	3.3124	0.4170	1.3038	0.0929
150		18.1198	95.4686	22.9197	14.7634	4.3511
200	39.4054	71.9436	98.4469	40.5122	60.9748	83.9866
250	92.0437	94.4565	98.5586	96.7165	96.8876	97.2611
300	96.0826	98.0682	98.6214	96.7165	96.8876	97.2611
350	97.0483	99.1824		98.6380	98.8022	97.8235
400	97.1736				88.8947	97.7581

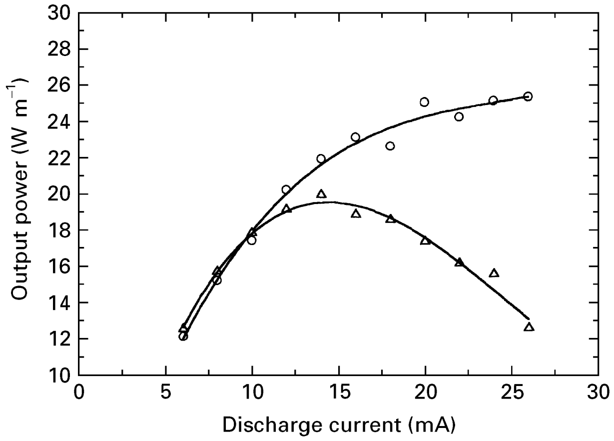

Figure 4 The comparison curves of the new cathode and the traditional one. (△) The traditional Ag–Cu alloy, (○) $La_{1-x}Sr_xCoO_3$, $x = 0.3$.

number of pulses is over 20 000. The sputtering rate of the $La_{0.7}Sr_{0.3}CoO_3$ cathode is very low.

4. Conclusions

The rhombohedrally distorted perovskite structured compound $La_{1-x}Sr_xCoO_3$ has a high conductivity and catalytic activity for the oxidation of CO. It is a promising cathode material for use in sealed-CO_2 lasers and has excellent performance characteristics.

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