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EFFECT OF ^{60}Co GAMMA RADIATION ON La_2CuO_4

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The effect of ^{60}Co γ-radiation on La_2CuO_4 solid catalyst prepared by the ceramic method has been studied. Gamma irradiation of La_2CuO_4 samples has been found to increase the Cu^+ content, electrical conductivities and decrease the magnetic susceptibilities of the catalyst. The results have been interpreted on the basis of the crystal field model of the structure of La_2CuO_4.

INTRODUCTION

Oxides crystallizing in perovskite and related structures have been increasingly used as catalysts[1] and fuel cell electrodes[2] in recent times. These compounds by virtue of their favourable crystal structure and oxygen lability participate readily in typical oxidation reactions. There are no detailed studies reported on the influence of ionizing radiations on these catalysts. With

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a view to study the effect of γ-radiation on these compounds, La_2CuO_4 a typical rare earth transition metal complex oxide belonging to the perovskite system has been chosen.

EXPERIMENTAL

Lanthanum oxide used supplied by Indian Rare Earths Ltd., was of 99.99% purity. All other reagents used in the present investigation were of A.R. grade. La_2CuO_4 was prepared by four different procedures employing the ceramic method[3]. Stiochiometric mixtures of component oxides and oxalates of La and Cu such as lanthanum oxide-copper oxide, lanthanum oxide-copper oxalate, lanthanum oxalate-copper oxalate and lanthanum oxalate-copper oxide were mixed well, ground and calcined in air for 20 h in the temperature range 900-1000 ^{o}C. The samples were analyzed by X-ray diffraction using a Phillips X-ray generator. The cell parameters were evaluated and found to be in close agreement with the literature values[4].

Irradiation of the samples with ^{60}Co γ-radiation was carried out in a 5000 Ci ^{60}Co gamma cell, having a dose rate of 0.4 Mrad h^{-1} supplied by BARC, Bombay. The samples were irradiated in Petri dishes in air. IR spectra of the samples were recorded on a PE 257 spectrophotometer in the region 650-4000 cm^{-1}. The Cu^{+} content in the catalyst samples was estimated by iodometric titration. About 0.2 g of La_2CuO_4 was dissolved in conc. nitric acid and the total Cu content determined iodometrically. The same procedure was repeated by dissolving the catalyst in sulphuric acid in a nitrogen atmosphere to prevent oxidation of Cu^{+} and the Cu^{2+} determined iodometrically. This titre value corresponds to Cu^{2+} alone. From the dif-

TABLE 1

Cu^+ content in La_2CuO_4 samples

Sample No.	Sample	Cu^+ content, %
1	La_2O_3 - CuO /OA/	0.3
2	Laoxal - Cuoxal /OB/	0.2
3	Laoxal - CuO /OC/	0.4
4	La_2O_3 - Cuoxal /OD/	0.5

ference in the titre values, the Cu^+ content was calculated. Electrical conductivity measurements were carried out on sintered pellets of the catalyst samples 11.5 mm in diameter and a thickness of 1.6 mm. The pellets of the samples were prepared by compressing the powders in a hydraulic press under a pressure of 4 tons cm^{-2}. The pellets of the samples were then sintered at a temperature of 600-800 ^oC for 6 h and the conductivity measured using a two probe d.c. cell.

The magnetic susceptibility of the catalyst samples in air at room temperature was determined with a Guoy magnetic balance. A magnetic field of the order of 5000 Gauss was used. The Guoy tube was calibrated using mercury tetrathiocyanato cobaltate as a standard.

RESULTS AND DISCUSSION

All the four samples of La_2CuO_4 were found to contain small amount of Cu^+ /Table 1/.

When the samples were spread in Petri dishes and irradiated in the γ-source at a dose rate of 0.4 Mrad h^{-1} for 30 days, a faint blue colour which became intense with

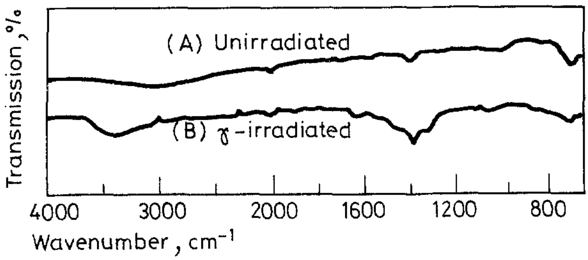

Fig. 1. Infrared spectra of unirradiated and γ-irradiated La_2CuO_4

progress of time was noticed after an irradiation period of 1 week. A distinct deep blue colour was noticed after an irradiation period of 30 days. The IR spectrum of the blue coloured portion of the γ-irradiated sample /Fig. 1./ showed peaks attributable to water /3000-3500 cm^{-1}/ and carbonate /1400 cm^{-1}/. The presence of carbonate in the blue coloured material of the irradiated sample was tested by treating the sample with acid and passing the evolved gas through a barium hydroxide solution.

On irradiation for a period of 30 days at a dose rate of 0.4 Mrad h^{-1} there has been an increase in the Cu^+ content in the case of all the preparations /Table 2/.

Pellets of the La_2CuO_4 samples were irradiated in the γ-source for 30 days in air with a dose rate of 0.4 Mrad h^{-1} and the electrical conductivities were measured before and after γ-irradiation /Table 3/.

It is clear from Table 3 that in the case of irradiated samples, before scraping the blue carbonate material formed on their surface during irradiation, there is a decrease in the electrical conductivity compared to that of unirradiated samples. However, after scraping the blue carbonate material on the surface of the pellets, the electrical conductivities of the samples are actually found to be more than that of unirradiated samples. The

TABLE 2

Determination of Cu^+ content in the La_2CuO_4. Samples before and after irradiation

Samples	Cu^+ content, %	
	Before irradiation	After irradiation
OA	0.3	1.5
OB	0.2	1.6
OC	0.4	1.7
OD	0.5	1.9

TABLE 3

Measurement of electrical conductivities of La_2CuO_4 samples

Electrical conductivity, σ, ohm^{-1} cm^{-1}		
Unirradiated, $x10^{-4}$	γ-irradiated	
	Before scraping blue carbonate material, $x10^{-5}$	After scraping blue coloured material, $x10^{-3}$
1.3	2.9	2.3
2.4	3.1	4.2
1.0	2.8	4.0
1.4	3.4	3.1

decrease in the conductivity noticed in the case of irradiated unscraped samples is evidently due to the blue carbonate material on the surface which seems to act as an insulator. The increase in the conductivity of the irradiated scraped samples clearly indicates an increased

TABLE 4

Measurement of electrical conductivities and Cu^+ content of sample OA irradiated in various atmospheres

Medium of irradiation	Electrical conductivity, σ, $ohm^{-1}\ cm^{-1}$	Cu^+ content, %
Unirradiated	1.3×10^{-4}	0.3
Irradiated in vacuum, dry nitrogen, dry oxygen, dry carbon-dioxide	1.3×10^{-4}	0.3
Irradiated in moisture free from carbon dioxide	2.0×10^{-3}	1.1

effect of components in air on the electrical conductivities and Cu^+ content of La_2CuO_4 samples during irradiation pellets of sample OA were irradiated in vacuum, dry nitrogen, dry oxygen, dry carbon dioxide, and in presence of traces of moisture free from carbon dioxide /Table 4/ for 30 days in the γ-source at a dose rate of 0.4 Mrad h^{-1}. The results are given in Table 4.

The above results indicate that moisture present in air plays a significant role during irradiation in the enhancement of electrical conductivity and Cu^+ content. It can be inferred that moisture facilitates the formation of charge carriers during the reaction of the radiolyzed products of moisture with the surface of the catalyst.

TABLE 5

Magnetic susceptibilities of La_2CuO_4 samples before and after γ-irradiation

Sample	Magnetic susceptibilities			
	Before irradiation		After irradiation	
	χ/CGS Units/	μ	χ/CGS Units/	μ
OA	0.54×10^{-6}	0.73	0.29×10^{-6}	0.52
OB	0.52×10^{-6}	0.72	0.18×10^{-6}	0.42
OC	0.38×10^{-6}	0.62	0.20×10^{-6}	0.44
OD	0.40×10^{-6}	0.63	0.10×10^{-6}	0.55

Magnetic susceptibilities

The magnetic susceptibilities of all the four La_2CuO_4 samples were measured before and after γ-irradiation /Table 5/.

It is clear from Table 5 that the magnetic susceptibilities of all the samples decrease after γ-irradiation.

Various models have been proposed[5-8] to explain the electrical conductivity and magnetic behaviour of La_2CuO_4. One of them is the crystal field model which is adopted here for explaining the mode of formation of Cu^+, the observed increase in the electrical conductivities and decrease in the magnetic susceptibilities in the γ-irradiated samples. On the basis of the crystal field theory, the electronic configuration of La_2CuO_4 can be written as in Fig. 2.

Air which contains traces of moisture is radiolyzed by the high intensity γ-rays to give various radicals as

$$H_2O \rightsquigarrow OH,\ H,\ H_2O_2,\ HO_2,\ \ldots\ e^-_{eq}.$$

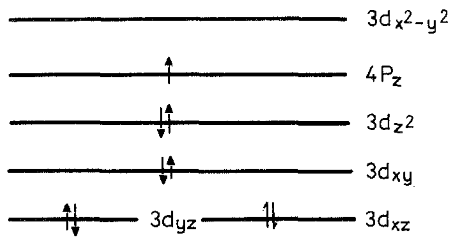

Fig. 2. Energy-level diagram of Cu^{2+} in La_2CuO_4, assuming that the equatorial Cu-O distances are sufficiently small for the $3d_{x^2-y^2}$ level to lie above the $4p_z$ level. The x, y, and z axes are along the Cu-O bonds, with the z axis lying the direction of crystallographic C axis

The electron from the γ-radiolysis of moisture reduces the Cu^{2+} to form Cu^{+}. It is clear from the energy level diagram of La_2CuO_4 that $4p_z$ level of Cu^{2+} is half filled. So, the electron obtained by the radiolysis of H_2O can enter the $4p_z$ level of Cu^{2+} which forms a π-bond with the $2p_z$ level of oxygen. Since there is an increase in the concentration of electrons in the π-bond, which is the conduction band, there is an increase in the electrical conductivity of La_2CuO_4 samples on γ-irradiation.

It is seen from the above discussions that the $4p_z$ level is considerably filled by the electrons produced during irradiation in air. This situation leads to the decrease in the number of unpaired electrons in the sample. Consequently the magnetic susceptibility is decreased.

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