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# Synthesis and Properties of the Layered Oxycarbonates $Sr_{2-x}Ba_xCuO_2(CO_3)$

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

We report here the synthesis and infrared characteristics of the solid solution of the layered oxycarbonates $Sr_{2-x}Ba_xCuO_2(CO_3)$ ($0 \leq x \leq 2$). Synthesis, under partially enclosed conditions, from $(Sr,Ba)CO_3$ and CuO is observed to give enhanced stability of the oxycarbonate as the partial pressure of $CO_2$ over the sample appears to retard both the reaction and the subsequent decomposition of the oxycarbonates. Compounds with higher barium content are more stable, in keeping with the considerable stability of $BaCO_3$ with respect to decomposition. The **a** lattice constant shows an anomalously large increase at high barium content, accompanied by an anomaly in the Cu–O inplane vibration occurring at around 500 $cm^{-1}$ and an accompanying loss of antiferromagnetic order. Both effects are attributed to the presence of additional oxygen in the structure of compounds at these stoichiometries, analogous to that found earlier for $(Ba,Sr)_2CuO_{3+\delta}$ materials. © 1993 Academic Press, Inc.

## Introduction

The family of layered oxycarbonates having the general formula $A_2CuO_2(CO_3)$, where $A$ = Sr, Ba, has a tetragonal structure (*1–3*) consisting of alternating layers of carbonate and strontium ions and of corner-sharing $CuO_4$ units, as shown in Fig. 1. These corner-sharing $CuO_4$ units are analogous to those found in all high $T_c$ cuprate superconductors. $Sr_2CuO_2(CO_3)$ was discovered independently by a number of groups being observed as an intermediate in the reaction of $SrCO_3$ and CuO to form $Sr_2CuO_3$ (*1–5*). Under typical synthetic conditions adopted for this phase (1000°C firing in air) $Sr_2CuO_2(CO_3)$ forms and decomposes again very rapidly. Indeed it has been reported by Babu *et al.* that single phase $Sr_2CuO_2(CO_3)$ cannot be prepared in air in an open tube furnace as a result of convection currents (*2*). We have recently shown that the incorporation of small amounts of Ba in the solid solution phase $Sr_{2-x}Ba_xCu$

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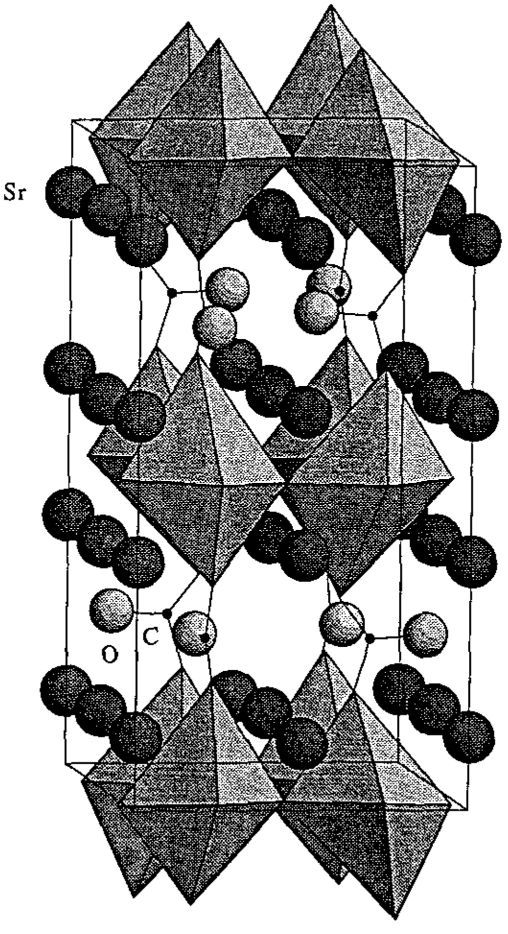

FIG. 1. Schematic representation of the structure of $Sr_2CuO_2(CO_3)$.

$O_2(CO_3)$ ($0 \leq x \leq 2$) is an effective method for enhancing the stability of these oxycarbonates (*1*). Furthermore, we proposed the possibility of chemically inducing superconductivity via judicious control of the substitutional chemistry of the more stable members of the solid solution series. Recently Kinoshita and Yamada have reported the occurrence of superconductivity, with transition temperatures of up to 40 K, in $(Ba_xSr_{1-x})_2Cu_{1+y}O_{2+2y+\delta}(CO_3)_{1-y}$ ($0.4 \leq x \leq 0.65$, $y \sim 0.1$) (*6*). Preparation of this material employed a two stage process involving prefiring in air at 800–850°C to produce a mixture of $Ba_{2-x}Sr_xCuO_2(CO_3)$, $BaCuO_2$, and $Sr_2CuO_3$ followed by annealing at 1000°C under 250 atm pressure (20% $O_2$, 80% Ar). This gave single phase superconducting samples for $0.4 \leq x \leq 0.65$ with a maximum $T_c$ of 40 K for $x = 0.55$. The structure is tetragonal, space group $P42_12$ or $P\bar{4}2_1m$, and has about 11% of the carbon atoms replaced by copper. It has been proposed that this defect introduces the holes that give rise to superconductivity (*7*). We have synthesized a range of materials in the $Sr_{2-x}Ba_xCuO_2(CO_3)$ solid solution, using a variety of preparative methods. For small values of the compositional parameter $x$ the samples were fired in partially enclosed containers which ensured the slow escape of the carbon dioxide produced in the decomposition of the alkaline-earth carbonate. For samples with high barium content ($x \geq 1.2$) both this method and synthesis in an open boat were employed.

Infrared measurements have been used both to confirm the presence of carbonate ions in the structure and also to probe the electronic structure of the Cu–O sheets. In the layered oxycarbonates we can confirm the empirical relationship between Cu–O bond length and IR stretching frequency recently reported by Ganguly *et al.* (*8*) for cuprate materials. Materials with $x \leq 1.35$ exhibit antiferromagnetic order with a Néel temperature in the region of 250 K, while no long range order has been observed at higher barium content (*9, 10*). The absence of an ESR signal at high barium content indicates that short range order persists at compositions with $x > 1.35$.

## Experimental

Starting materials used in the synthesis of the $Sr_{2-x}Ba_xCuO_2(CO_3)$ compounds were $SrCO_3$, $BaCO_3$, $BaO_2$, and CuO. For compositions with $x \leq 0.8$, $SrCO_3$ was used as the only source of carbonate ions, with the source of barium being $BaO_2$. A typical sample enclosure was an alumina crucible with a lid. Samples were generally fired at temperatures ranging between 900 and 935°C with reaction times dictated by the sample volume (larger samples requiring longer times). Several firings were necessary with intermediate grindings to ensure sample homogeneity and phase purity; the latter was monitored between firings by powder X-ray diffraction. Firing times were decreased progressively as the reaction neared completion. For $x \geq 0.8$, $BaCO_3$ was used as a starting material along with a variable quantity of $BaO_2$. For $x \geq 1.1$ a variety of routes were tested, including enclosed conditions, an open alumina boat, and combinations of the two. Attempts to prepare the barium end-member centered on firing under a moderate flow of nitrogen with one end of the furnace tube open to the air, thus allowing the diffusion of atmospheric $CO_2$ over the sample. Barium peroxide was used as a starting material in this case due to the great stability of $BaCO_3$. Lattice parameters were obtained by Rietveld refinement of powder X-ray, and in some cases powder neutron, diffraction data.

For the infrared measurements the samples were ground in a Spex electrical mill, mixed with dry CsI (or polyethylene for the far infrared measurements), and pressed at 10 tonne $cm^{-2}$ into disc-shaped pellets of diameter 13 mm. Each pellet contained 2 mg of sample, and identical pellets of the diluent were used as reference material. All pellets were stored in dry, cool conditions and measured within 24 hr of creation. The absorption measurements were made under vacuum at room temperature in the far–mid infrared region (150–5000 $cm^{-1}$) using a Bruker 113V FTIR spectrometer. An Aspect 3000 computer was used for data collection and least-squares band profile analysis using Voight profiles. The absolute frequency of each phonon band was obtained directly from the spectrum with a random error in measurement of $\pm 0.3$ $cm^{-1}$.

## Results and Discussion

The strontium end-member of the solid solution was found to decompose as soon as the reaction reached completion, making preparation of monophasic $Sr_2CuO_2(CO_3)$ extremely difficult. However, the substitution of only a small quantity of barium for strontium was found to exert a considerable stabilizing influence which appreciably retarded both the rate of formation and the subsequent decomposition of the oxycarbonate phase. For barium content up to $x = 0.8$ no problems with sample homogeneity were encountered arising from the use of barium peroxide as a starting material. During the course of the reaction, barium peroxide was observed to form $(Sr,Ba)CO_3$, and as the reaction neared completion the barium concentration of this unreacted carbonate increased (as gauged by the change in lattice parameters). This increased barium concentration in the unreacted $(Sr,Ba)CO_3$ was found to reduce its reactivity and appeared to suppress the decomposition of $Sr_{2-x}Ba_xCuO_2(CO_3)$.

The use of $BaO_2$ at barium content above $x = 0.8$ gave inhomogeneous products, and better results were obtained if $BaCO_3$ was used. At high barium content the samples fired exclusively under enclosed conditions reacted exceedingly slowly, and hence all subsequent preparations were at least prefired in air, with later firings either in air or in an enclosed vessel. Some problems with sample inhomogeneity were encountered with preparations fired only in air. Single phase $Ba_2CuO_2(CO_3)$ could not be prepared, though it was the dominant phase in a number of samples. Its formation was discovered to be critically dependent on experimental factors such as nitrogen flow rate, size of furnace tube, and reaction temperature. Further investigation will be necessary to optimize the synthetic conditions required to prepare this compound as a single phase.

The refined lattice constants for a range of compositions are shown in Table I, and plots of the lattice parameters as a function of ionic radius, assuming eight-fold coordination of the alkaline earth (*11*), are shown in Fig. 2. Especially noteworthy is a clear

TABLE I

UNIT CELL DIMENSIONS FOR $Sr_{2-x}Ba_xCuO_2(CO_3)$

| $x$ in $Sr_{2-x}Ba_xCuO_2(CO_3)$ | $a$/Å | $c$/Å |
|---|---|---|
| 0.0 | 3.9033(2) | 7.4925(4) |
| 0.5 | 3.9281(1) | 7.6045(2) |
| 0.8 | 3.9389(3) | 7.6615(6) |
| 1.1 | 3.9586(4) | 7.761(1) |
| 1.35 | 3.9685(1) | 7.8051(3) |
| 1.5 | 3.9915(3) | 7.860(1) |
| 1.6 | 3.9917(1) | 7.8781(2) |
| 1.6[a] | 4.035(2) | 7.903(3) |
| 1.7 | 4.022(2) | 7.916(2) |
| 2.0 | 4.002(1) | 7.974(3) |

[a] Data from Ref. (*12*).

deviation from linearity in the **a** parameter for large values of $x$ (but not $x = 2.0$). We have found that the magnitude of this deviation is dependent on the experimental conditions employed during synthesis. For $x = 1.5$ and 1.7 the sample was fired in air only, whereas our sample with $x = 1.6$ was prefired in air with several subsequent heat treatments under enclosed conditions. The sample for $x = 1.6$, with a very large anomaly, reported by Greaves and Slater (*12*), was prepared in air and oxygen. This, combined with the relatively small **a** parameter observed for $x = 2.0$, strongly suggests a correlation with the oxygen content of the material. The enclosed conditions used for the synthesis of our $x = 1.6$ sample would clearly be less oxidizing than those used in the preparation of the samples with $x = 1.5$ and 1.7 as a result of the relatively high concentration of carbon dioxide (and hence low $O_2$ concentration) in the atmosphere around the sample. Likewise, the nitrogen flow used in the synthesis of $Ba_2CuO_2(CO_3)$ would inhibit oxygen uptake. It is thus not surprising that the sample prepared by Greaves and Slater in air and oxygen has an unusually large **a** lattice constant. Neutron diffraction studies of a sample with a small lattice constant anomaly have not provided an unambiguous answer for the precise location (and amount) of the additional oxygen, presumably as a result of the low concentration. However, Chaillout *et al.* (*13*) have recently reported the structure of $BaSrCuO_{2.22}(CO_3)$, in which extra oxygen was located around carbon. Since this is the most open region of the structure this seems entirely reasonable.

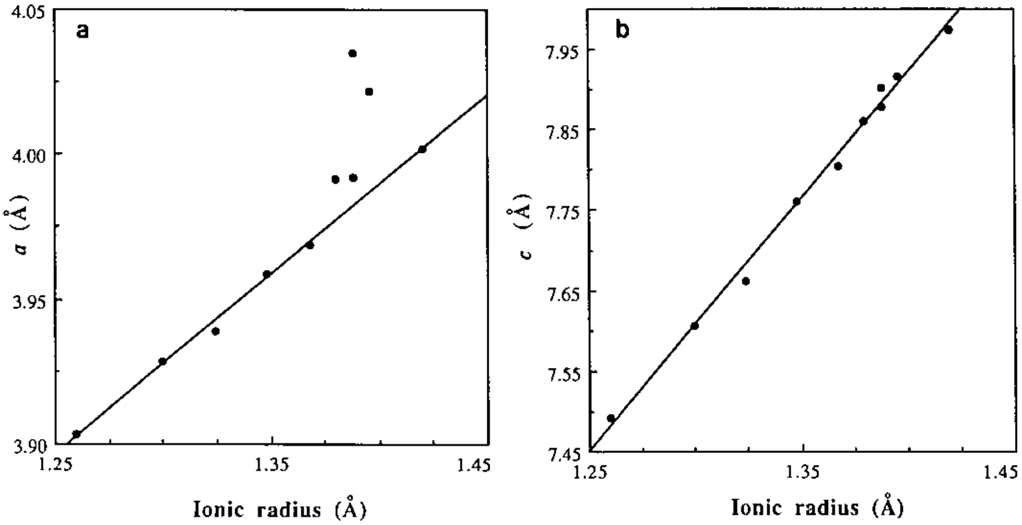

FIG. 2. Variation of (a) **a** lattice parameter and (b) **c** lattice parameter for the series $Sr_{2-x}Ba_xCuO_2(CO_3)$ as a function of the effective ionic radius of the alkaline-earth cation.

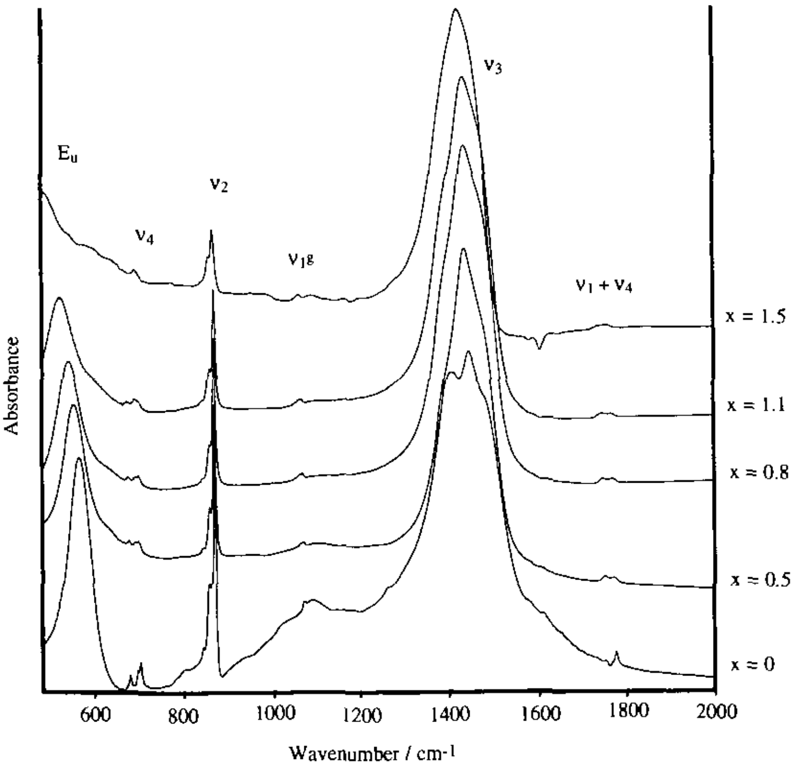

FIG. 3. Infrared absorption spectra for $Sr_{2-x}Ba_xCuO_2(CO_3)$ from 500 to 2000 $cm^{-1}$ for samples with $x = 0$, 0.5, 0.8, 1.1, and 1.5. The band assignment is also given in Table II.

Absorption spectra for $Sr_{2-x}Ba_xCuO_2(CO_3)$ covering the ranges 500–2000 and 150–550 $cm^{-1}$ are shown in Fig. 3 and 4 respectively. The carbonate ion internal vibrational modes are clearly visible and are tabulated for $x = 0$ and $x = 1.5$ in Table II (*14*). Mode frequencies for the samples with intermediate Ba content are found to decrease with increasing $x$ and generally lie within the values for strontianite ($SrCO_3$) and witherite ($BaCO_3$). A splitting of the $\nu_3$ mode is evident with decreasing Ba content and is attributed to changes in the vibrational selection rules due to the influence of the crystal field environment around the carbonate ion. Similarities between $Sr_{2-x}Ba_xCuO_2(CO_3)$ and other compounds with a square planar $Cu^{2+}$ coordination (*15*) suggest that the far infrared modes are at around 180, 205, and 380 $cm^{-1}$ can be ascribed to vibrations of the heavy ions Ba/Sr–Cu along the $c$ axis and in the $ab$ plane. Note that except for the mode near 483 $cm^{-1}$ in the $x = 1.5$ sample, all phonon lines remain relatively sharp. The lack of drastic heteroge-

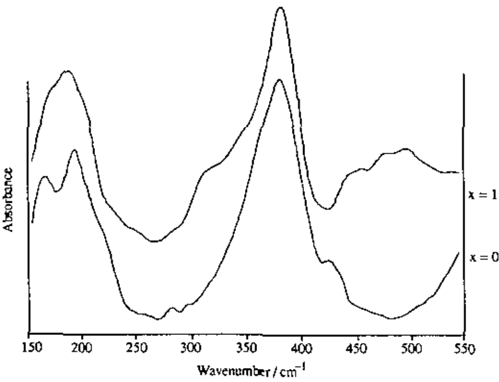

FIG. 4. Infrared absorption spectra for $Sr_{2-x}Ba_xCuO_2(CO_3)$ from 150 to 500 $cm^{-1}$ for samples with $x = 0$ and 1.5.

TABLE II

CARBONATE ION INTERNAL VIBRATIONAL MODES ($cm^{-1}$) IN $Sr_{2-x}Ba_xCuO_2(CO_3)$ FOR COMPOSITIONS $x = 0.0, 1.5$

| | Ba content ($x$) | |
|---|---|---|
| Mode | 0.0 | 1.5 |
| $\nu_1^g$ | 1072 | 1062 |
| $\nu_2$ | 858 | 858 |
| | 870 | 867 |
| | 844 | |
| $\nu_3$ | 1412 | 1427 |
| | 1449 | |
| $\nu_4$ | 681 | 694 |
| | 699 | |
| | 704 | |
| $(\nu_1 + \nu_4)$ | 1756 | 1756 |
| | 1778 | |

neous line broadening suggests incorporation of Ba into the structure in a fairly homogeneous manner without production of Ba-rich clusters or segregation of Ba on lattice imperfections, etc. It is evident that this may not be the case for the sample with $x = 1.5$.

There is a marked effect of Ba content on the Cu–O in-plane vibration occurring at around 570 $cm^{-1}$ ($x = 0$). This mode is probably of $E_u$ symmetry (*15*) and a large decrease in the mode frequency with increasing $x$ is observed; these data are summarized in Table III. The observed mode softening of the Cu–O phonon with Ba content can be formally described in the treatment of the weakly anharmonic crystal by the Grüneisen relationship,

$$\gamma_i = -\frac{\partial(\ln \omega_i)}{\partial(\ln V)}$$

for the $i$th mode, with $V$ the molar volume. Assuming complete carbonate ion occupancy it is found that the Cu–O phonon frequency decreases with increasing molar volume and can be accurately modeled by a quadratic function (least-squares refinement). This results in a mode Grüneisen parameter that increases from $\gamma = 0.56 \pm 0.03$ for $x = 0$ to $\gamma = 3.30 \pm 0.05$, as shown in Fig. 5. These values are typical for other structures with corner-sharing polyhedral units (*16, 17*) and also for compounds incorporating Cu–O planes (e.g., high $T_c$ superconductors) (*18*). This kind of volume-strain behavior is reminiscent of the sort often observed in the region of a criticality, for example structural phase transitions in $As_2O_5$ and leucite (*19*). In the case of the layered oxycarbonates examined here the critically is associated with the departure from linearity observed in the **a** lattice parameter, and we propose that this occurs as a result of the incorporation of extra oxygen in the structure. Furthermore we have observed a loss of long-range antiferromagnetic order in this region of the solid solution (*9, 10*). This is in keeping with oxidation of the copper–oxygen sheets comparable with that found in cuprate high $T_c$ superconductors.

TABLE III

FREQUENCY OF $E_u$ Cu–O MODE ($cm^{-1}$) FOR INCREASING $x$ IN $Sr_{2-x}Ba_xCuO_2(CO_3)$

| Ba content ($x$) | Frequency ($cm^{-1}$) |
|---|---|
| 0.0 | 569.8 |
| 0.5 | 559.4 |
| 0.8 | 544.8 |
| 1.1 | 524.8 |
| 1.5 | 483.3 |

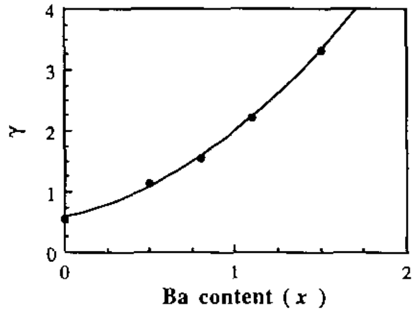

FIG. 5. Plot of the mode Grüneisen parameter, γ, against Ba content ($x$) in $Sr_{2-x}Ba_xCuO_2(CO_3)$. The line is a quadratic least squares fit to the data.

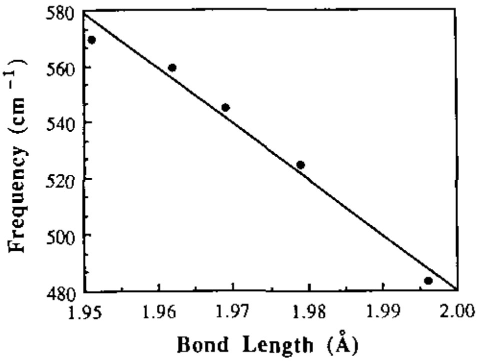

FIG. 6. Graph showing the linear correlation between the $E_u$ Cu–O mode frequency (cm$^{-1}$) and the observed Cu–O bond length in $Sr_{2-x}Ba_xCuO_2(CO_3)$.

Also evident from our data is a linear dependence of the $E_u$ Cu–O mode frequency on the bond length, as illustrated in Fig. 6. Similar observations have been previously reported by Ganguly *et al.* (*8*) who considered a range of copper (II) oxides with square planar coordination and deduced a so-called "titration curve"—a remarkably good empirical correlation between the Cu–O bond length and $E_u$ mode frequency. Our results are in excellent agreement with those of Ganguly *et al.* (*8*) and thus confirm the importance of such an empirical approach. It is advantageous to reiterate the wealth of structural information that can be gained from a detailed band profile analysis of the Cu–O phonon mode. Its shape yields information on phase purity/homogeneity, while its frequency characterizes quantitatively the Cu–O bond length, molar volume, and volume expansivity in $Sr_{2-x}Ba_xCu O_2(CO_3)$. In view of the work of Ganguly *et al.* (*8*), it is probable that this approach extends to many other square planar coordinated copper (II) oxides.

In conclusion we have synthesized and investigated a range of layered oxycarbonates of the general formula $Sr_{2-x}Ba_xCu O_2(CO_3)$ ($0 \leq x \leq 2$). Detailed information on the nature of the constituent $CO_3^{2-}$ ion has been obtained by infrared spectroscopy. Changes in the compositional parameter ($x$) lead to detectable variation in the C–O vibrational characteristics. In addition, in samples with high Ba content our data suggest the incorporation of excess oxygen in the structure. Variable temperature studies of the related superconducting oxycarbonates $(Ba, Sr)_2Cu_{1+y}O_{2+2y+\delta}(CO_3)_{1-y}$ ($y \sim 0.1$) may provide important information as to the role of the carbonate anion in this electronic transition.

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