

Photoacoustic Determination of the Band Gaps of Ca_2MnO_4 and $\text{Ca}_3\text{Mn}_2\text{O}_7$ *

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Black powders of the magnetically layered semiconductors Ca_2MnO_4 and $\text{Ca}_3\text{Mn}_2\text{O}_7$ prepared by a carbonate-precursor technique have been investigated by photoacoustic spectroscopy (PAS) over the energy range 1.25–4 eV. The band-gap energies of these two compounds have been evaluated to be 1.6 and 1.4 (± 0.1) eV, respectively. It is concluded that PAS is a most useful method for determining the variation of the band gap with composition in large band-gap polycrystalline semiconductors.

Introduction

The interest in ternary layered metal oxides has grown continuously in recent years. One of the properties of central interest in semiconducting mixed-metal oxides is the band-gap energy E_g . Often E_g is not determined directly, but rather from the temperature dependence of the electrical resistivity, which yields the activation energy E_a . In this communication we report the direct measurement of the band-gap energies at ambient temperature of two magnetically layered oxides, Ca_2MnO_4 and $\text{Ca}_3\text{Mn}_2\text{O}_7$, whose structures are shown in Fig. 1 (1, 2), by using photoacoustic spectroscopy (PAS). These compounds are the first two members of the homologous series $\text{Ca}_{1+x}\text{Mn}_x\text{O}_{1+3x}$, where $x = 1, 2 \dots$ is the number of adjacent magnetic layers (see Fig. 1), which are important model systems for studying the transition from two-dimensional to three-dimensional magnetism (1).

Both compounds were shown experimentally to be semiconducting by MacChesney *et al.* (2). The conduction band e_g of Ca_2MnO_4 has been found by Mössbauer spectroscopy to be empty (3), as proposed by Goodenough (4). However, high-temperature (300–800 K) (5), intermediate-temperature (≈ 400 K) (6), and low-temperature (78–298 K) (2) resistivity measurements on Ca_2MnO_4 have resulted in activation energies of 0.80, 0.63, and 0.10 eV, respectively, whereas the latter measurements on $\text{Ca}_3\text{Mn}_2\text{O}_7$ yielded $E_a = 0.16$ eV (2). In view of the differences in activation energies determined from resistivity measurements, it is of interest to measure the band gap directly by PAS.

Experimental

The carbonate precursors of Ca_2MnO_4 and $\text{Ca}_3\text{Mn}_2\text{O}_7$ were prepared by coprecipitation. These materials were fired in flowing oxygen at 800 and 1400°C, respectively, for 24 hr in covered platinum crucibles. Elec-

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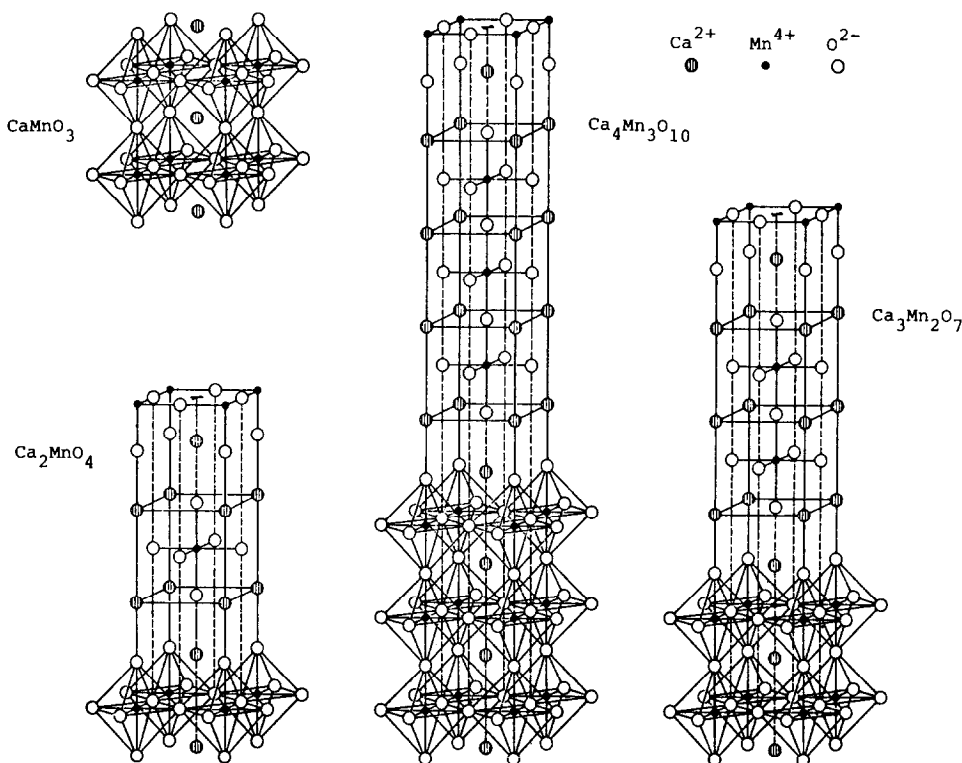


FIG. 1. Idealized structures of the first three ($x = 1, 2, 3$) and last ($x = \infty$) members of the $\text{Ca}_{1+x}\text{Mn}_x\text{O}_{1+3x}$ series. The formula can also be written $(\text{CaMnO}_3)_x \text{CaO}$, and the structures can be visualized as being built up of x perovskite (CaMnO_3) blocks interleaved by a CaO layer.

tron microprobe analysis yielded Ca/Mn ratios of 2.06 and 1.46 (± 0.04), respectively. The lattice parameters for Ca_2MnO_4 determined by powder neutron diffraction at ambient temperature are $a = 3.6696(4)$ and $c = 12.0642(9)$ Å. X-ray powder diffraction yielded $a = 3.678(4)$ and $c = 19.41(3)$ Å for the lattice parameters for $\text{Ca}_3\text{Mn}_2\text{O}_7$.

The basic photoacoustic instrument used has been described previously by Moore (7). Briefly, the method consists of irradiating a sample with chopped radiation, which, upon absorption, produces a temperature fluctuation at the chopping frequency and hence causes a modulation of the gas pressure within the sample chamber. This pressure modulation is detected by a microphone to yield a qualitative indi-

cation of the power absorbed by the sample. The PAS spectrum is derived by monitoring the microphonic signal as a function of the wavelength or energy of the incident radiation. A 500-W xenon lamp was used as the light source. A servo controlled Jobin Yvon M 25 grating monochromator was used to scan the energy range 1.25–4.00 eV at the rate of 1 nm/sec. The spectral slit width was 12 nm, and the chopping frequency was 25 Hz. The acoustic output was monitored by a microphone, preamplified, and then fed into an Ithaco lock-in amplifier. The output data were digitized, entered onto tape in a Tektronix 4051 computer, and reduced by division by the lamp output, obtained by previously running a sample of carbon black.

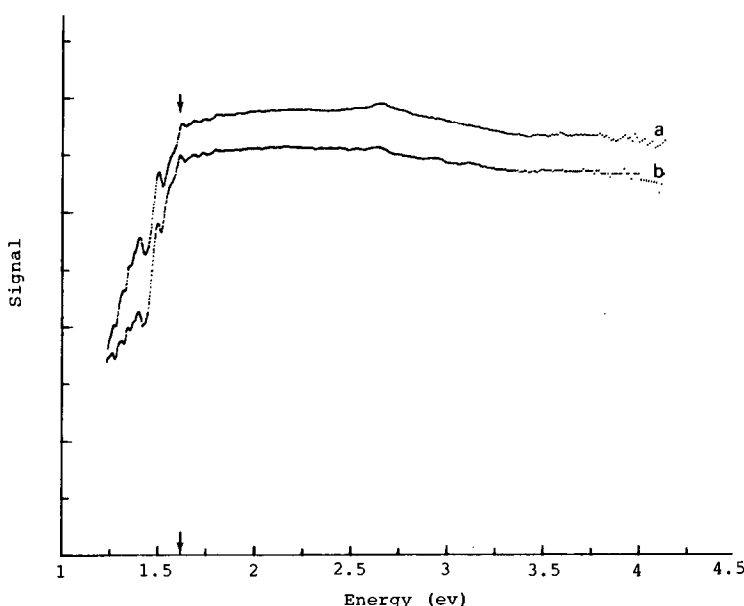


FIG. 2. Photoacoustic spectra of Ca_2MnO_4 . Sample a was prepared in this work and sample b was prepared independently at Exxon Company. The arrow indicates the absorption edge.

Results and Discussion

The PAS spectra obtained are presented in Figs. 2 and 3. The apparent fine structure superimposed on the absorption spectra is due to slight errors in matching the lamp and sample data, causing inexact cancellation of the spikes in lamp intensity present at lower energies. As shown in Fig. 2, PAS measurements performed on different preparations of Ca_2MnO_4 yield nearly identical results. However, on low-surface-area samples, such as melt-grown Ca_2MnO_4 , no PAS spectrum was detected above the instrumental background, presumably due to the large particle size resulting from these high-temperature preparations. The values $E_g = 1.6 \pm 0.1$ eV for Ca_2MnO_4 and $E_g = 1.4 \pm 0.1$ eV for $\text{Ca}_3\text{Mn}_2\text{O}_7$ are readily obtained from Fig. 1 by the method of Rosencwaig (8), in which the position of the knee is taken as the gap value. For Ca_2MnO_4 , it is possible to compare this value with that derived from high-

temperature resistivity measurements using the equality $E_g = 2 E_a$, which is valid when the mobility is not activated (9). Since $2 E_a = 1.60$ eV (5), values of E_g determined by both methods are in excellent agreement. Although a value of E_a for $\text{Ca}_3\text{Mn}_2\text{O}_7$ is not available for a similar comparison, the observed decrease in E_g of the comparatively Mn-rich $\text{Ca}_3\text{Mn}_2\text{O}_7$ phase relative to that of Ca_2MnO_4 corresponds to a similar decrease in E_a observed when the Mn content of CaMnO_3 is increased (10). This behavior is also consistent with our inability to detect an absorption edge above the background in CaMnO_3 prepared by the carbonate-precursor technique, which probably results because the band gap in CaMnO_3 is well below the energy range studied.

It is noteworthy that the above results disagree with the values $E_a = 0.10$ and 0.16 eV for Ca_2MnO_4 and $\text{Ca}_3\text{Mn}_2\text{O}_7$, respectively, which we obtained from the low-temperature resistivities of these materials (2) as well as with the value $E_a = 0.63$ eV

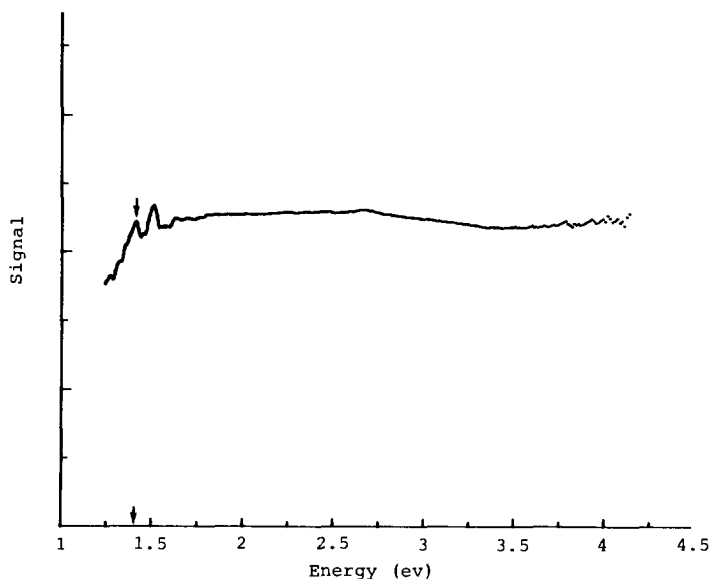


FIG. 3. Photoacoustic spectrum of $\text{Ca}_3\text{Mn}_2\text{O}_7$. The arrow indicates the absorption edge.

for Ca_2MnO_4 obtained from resistivity measurements near 400 K. The smaller band gaps in these compounds, estimated from low-temperature resistivity measurements, undoubtedly originates from impurities which have lower excitation energies into the conduction band. The impurity contribution to the resistivity is most noticeable in materials having a large band gap, and this impurity problem in the determination of reliable band gaps in such materials can be circumvented by using the PAS technique. Moreover, since PAS can be performed at ambient temperature, it has the added advantage that it can be applied to thermally sensitive materials. Hence PAS is a most useful method for determining the variation of the band gap with composition in large band-gap polycrystalline semiconductors.

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