Trap state spectroscopy in CMR manganites and spinel manganates using opto-impedance

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Abstract

The photo-induced AC-impedance method is used as a versatile instrumentation to study the trap state densities and the carrier relaxation times in magneto-resistive manganites and magneto-conductive manganates and thus as a probe to check the crystal quality, which is important for the performance of any device material. A comparative study using compounds of different defect densities is presented. High defect concentrations in the compounds are identified through the photoresistivity and/or the photo-induced capacitive build up.

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1. Introduction

Semiconductor physics normally employs transient methods such as time resolved thermo-electric effects (TTE) [1], deep level trap state spectroscopy (DLTS), thermally stimulated depolarization (TSD) [2], electron paramagnetic resonance (EPR), etc. in order to determine trap state densities, carrier relaxation times and diffusion coefficients.

The TTE method in particular makes use of the photogenerated charge carriers brought about by shining a light pulse on one sample end and measuring the internal voltages created. Besides voltages due to the Dember and Seebeck effects, voltages due to trap state related space charges of both signs can be detected as transients [3].

In this context, a photogenerated TTE voltage transient has been reported recently in the semiconducting region of neodymium strontium manganite, and was analyzed using ambipolar space charges [4]. Furthermore, ambipolar space charge transients based on the existence of trap states have been observed in hydrogenated amorphous silicon samples [5], and so this type of space charge capacitance might be observable in other compounds of standard quality, too.

Similarly, though in a continuous wave mode, the photoimpedance method can detect space charges, but now both in the dark and UV-light shined conditions. In such an experiment, the AC-impedance of a sample is measured and it usually contains both a resistive and a capacitive component. While the resistive component R can be used for the detection of defects through the residual resistance (Matthiessen's rule), the capacitive component C is in general indicative of space charges or electrical dipoles in the sample.

In order to show the potential of the photoimpedance method [6] in respect to the detection of defects, in this paper we study the trap state densities and the carrier relaxation times in two magneto-conductive manganates and in two magneto-resistive manganites using the photo-induced AC-impedance method; it uses a more versatile and simpler instrumentation as the more specific and involved methods described in the introduction, but may deliver comparable amounts of information.

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2. Experimental

Stoichiometric bulk samples $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ were prepared by a solid state reaction method, annealed at $900\,°C$ in air and cooled at a rate of $50\,°C\,h^{-1}$. It is worth mentioning that while the oxygen deficiency was introduced here to control the trap state density, the samples always contain unintentional defects and hence even for the sample with $\delta c0$ it is better to talk in terms of two solids with different defect densities rather than of a solid with defects ($\delta\sim0.12$) and without defects ($\delta\sim0$).

The phase purity of the samples was confirmed using a DRON-3M X-ray diffractometer in Cu Kα radiation. Other phase pure samples $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ ($\delta\sim0$ and $\delta\sim0.12$) were laser ablated in order to obtain thin films of neodymium strontium manganate on a glass substrate which are suitable for opto-impedance studies. The oxygen deficiency of the manganite layers was controlled by changing the oxygen partial pressure in a laser ablation chamber and determined by comparing physical properties like the magnetization and the resistivity curves with those of the equivalent bulk series [3,4,7].

On the other hand, spinel type $LiMn_2O_4$ samples were prepared by a fuel assisted combustion method at $500\,°C$ in air. Phase purity was confirmed using a PANalytical XRD machine in Cu Kα radiation. Pellets of the samples (diameter $= 18\,mm$; thickness $= 2\,mm$) were prepared under 600 MPa and sintered at $500\,C$ for 1 h. Silver electrodes were attached to the two opposite pellet corners using liquid silver paste. Then, the pellets were dried at room temperature for a day. AC-impedance measurements were performed using an EIS-Princeton Applied Research–AC-impedance analyzer in the frequency range 100 kHz–10 Hz. A short wave-length UV lamp (central wavelength $= 254\,nm$) was used for illumination purposes.

In order to study the effect of sintering on the trap state density, experiments were also carried out on an un-sintered pellet (as-grown state) having the same geometry as that of the sintered pellet.

3. Results and discussion

3.1. General remarks

Photogeneration of carriers is observable only in the semiconducting state of a sample and when the carrier lifetimes are large. If there is extensive carrier recombination at point defects, surfaces or grain boundaries, the photoconductance is quenched. Thus, we expect a reduction of the resistive component R under UV-light exposure rather with the sintered and the stoichiometric samples, where the defect densities are supposed to be lower (rule 1). With the capacitive component C, the situation is more complex. As C is expected to relate to space charges, i.e. to the number of filled trap states, at first sight it should be larger in the un-sintered or O-deficient samples, because those are expected to have the larger trap state densities,

both in the dark and UV-shined conditions. However, for the UV-shined and dark conditions a different trap state filling scenario has to be assumed. In the dark state, there could be a low or zero capacitance even if there exist filled trap states, i.e. if equal numbers of trap states of both signs are distributed at random. With the UV-light shining on one sample surface, there will be an ambipolar carrier diffusion or drift (ACD) into the sample, with the two carrier types having unequal mobilities. In the presence of trap states, there will be a refilling of those states, such that the centers of gravity of both trap state densities differ in their distance from the surface [3]. This would always yield a larger sample capacitance in the UV-shined case as compared to the dark situation (rule 2). Besides, the overall modification of the impedance spectrum of a sample upon exposure to light might have to do with the creation of electron–hole pairs at the surface from where they diffuse into the bulk of the solid, with the electrons diffusing faster than the holes. However, significant carrier motion into the bulk is only possible in a sample of high quality in which case the electron–hole pair has ample time to diffuse into the bulk before it can recombine and vanish. Furthermore, in any experiment connected with the measurement of electrical conductivity, generation of charge carriers will show its signature with an enhanced conductivity. However, if the number of trap states is that large, that the carrier recombination at the surface and in the bulk is very fast resulting in both a quenching of the photoconductivity and filling the shallow trap states, that could lead to an enhanced scattering and thus even to a rise in resistance under illumination (violation of rule 1).

Thus, if (small) violations of rules 1 and 2 occur, we expect them to occur in high trap density situations. In comparing the R and C parameters in the dark and under illumination, we face another problem. While the as grown samples may have a frozen-in (non-equilibrium) trap occupancy situation, reflecting historical details, under illumination there is at least a defined refilling mechanism, which might bring the trap state occupancy closer to equilibrium. Nevertheless, rule 3 would be that samples with the higher overall defect density would have the higher resistive component R.

In Sections 3.2 and 3.3, we discuss the AC-response patterns of two neodymium strontium manganite and lithium manganate samples both in the dark and under UV-illumination.

3.2. Manganites

Fig. 1 shows the AC-impedance spectrum of $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ ($\delta\sim0$ and $\delta\sim0.12$) samples under UV-illuminated and dark conditions, and the fitted data are displayed in Table 1. An RC-parallel circuit is used to fit the impedance curves of the manganites and the equivalent circuit is shown in Fig. 3a.

The resistance values noticed in the O-deficient sample are always higher as those of the O-defect free sample. This is
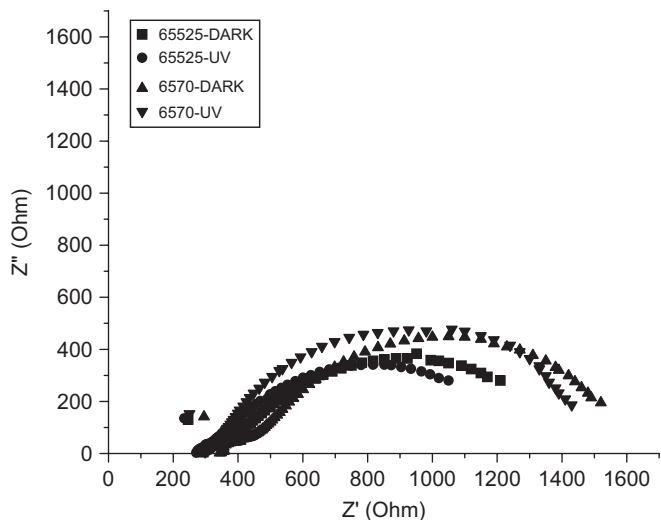
Fig. 1. Opto-impedance pattern of $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$. The sample 65525 corresponds to $\delta \sim 0$. The sample 6570 corresponds to $\delta \sim 0.12$.

Table 1
CMR-manganite with (a) lower defect density (sample 65525) and (b) higher defect density (sample 6570)

	High frequency region
(a) Lower defect density ($\delta \sim 0$)	
Dark	$R = 90.26 \, \Omega$
	$C = 1.05 \times 10^{-7} \, F$
UV-shined	$R = 67.39 \, \Omega$
	$C = 1.27 \times 10^{-7} \, F$
(b) Higher defect density ($\delta \sim 0.12$)	
Dark	$R = 110.66 \, \Omega$
	$C = 7.82 \times 10^{-8} \, F$
UV-shined	$R = 73.44 \, \Omega$
	$C = 1.61 \times 10^{-7} \, F$

Estimated parameters errors; 3%.

expected as all defects generate scattering centers (rule 3). While UV shining causes a fall in resistance, the capacitance value increases both in the defect sample and in the defect-free sample, probably due to photoconductivity and the space charge repositioning effects (rules 1 and 2).

We now turn to the comparison of the response of the $\delta \sim 0$ and $\delta \sim 0.12$ samples with due caution. From Table 1a we find that under UV-shined conditions the capacitance value is higher in the O-deficient sample than in the O-defect-free sample. This is generally to be expected as an O-defect constitutes a trap state and/or an electrical dipole [8].

However, under the dark condition we find that the reverse happens. This anomaly in the as-grown state suggests that concerning the trap state occupancy we might have non-equilibrium situations in the dark condition which by the UV-light exposure is softened to a different extent. This means that under light exposure, the traps are being reoccupied according to their energetic level, resulting in a corresponding space charge, while in

the dark case, many of the energetically low lying trap states are eventually not filled, resulting in a too low relative capacitance value.

Alternatively, there also exists a possibility of a sharpening of the level distribution of the defects under O-deficiency doping. In that case one has to assume that some trap states are shifted from a deep to a shallow level, or vice versa, thus increasing (decreasing) the overall space charge capability.

From Fig. 1 we also observe an opposite response of the two CMR samples. We notice curve crossings between the UV/dark conditions. However from the fit parameters of Table 1, we find the same type of response: in both cases photoconductivity occurs and the space charge increases under UV-light. This is interesting and requires extracting R and C distributions from the data. Both the deviations from an exact circular behavior as well as the double (triple) features of the impedance plots suggest that this might be possible.

3.3. Double manganates

Fig. 2(a) shows the AC-impedance spectrum of an un-sintered $LiMn_2O_4$ sample under UV-illuminated and dark conditions. The corresponding spectrum for sintered $LiMn_2O_4$ is shown in Fig. 2(b), and the fitted data are displayed in Table 2. A combination of two RC-parallel circuits, connected in series is used to fit the AC-impedance curve for the double manganates. The equivalent circuit is shown in Fig. 3b. In the as-grown case, there is very little change in resistance ($\sim 3.5\%$) between the dark and UV shined cases, suggesting a high trap density. The sintered case always yields a lower resistance (rule 3) and higher capacitance values than the un-sintered one. Also within the sintered case, UV shining causes a significant decrease in resistance as well as an increase in capacitance (rules 1 and 2).

In the sintered case we notice $-\Delta R$ (fall in resistance) and $+\Delta C$ (raise in capacitance). In the un-sintered case, while we notice $-\Delta R$ and $+\Delta C$ in the high frequency part, too, we notice an anomaly in the low frequency region with $+\Delta R$ and $-\Delta C$. Although these small changes are eventually insignificant, the anomaly $+\Delta R$ and $-\Delta C$ observed in the low frequency region of the un-sintered sample can be explained as due to a large number of trap states that quenches any photoconductivity but allows a refilling of shallow trap states.

From these observations, we can infer that generally the AC-photoconductance method might develop into a valuable supplementary tool in studying defects in solids. Specifically, photoillumination indeed lowers the resistance and enhances the capacitance, as expected. The RC values are generally smaller when the crystal quality is enhanced. In the case of the manganates this is probably due to the fact that sintering improves the crystal quality, thus increasing the lifetime of the electron–hole pairs. In the case of the manganites the lower RC value rests with the
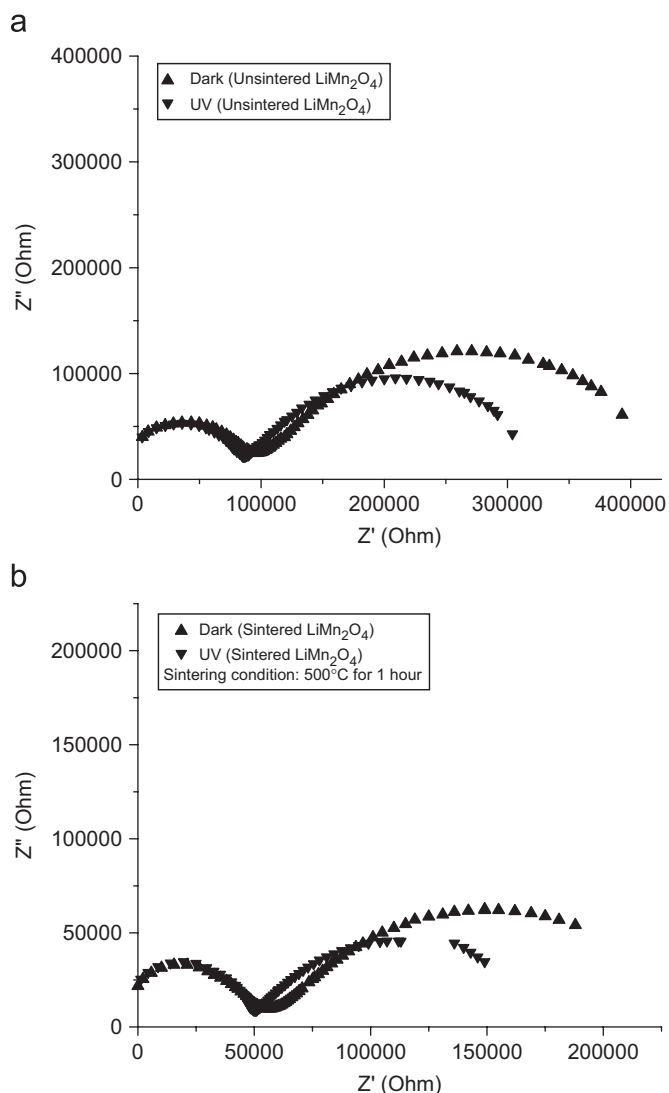
a

b

Fig. 2. Opto-impedance pattern of (a) unsintered $Li_xMn_2O_4$ and (b) sintered $Li_xMn_2O_4$.
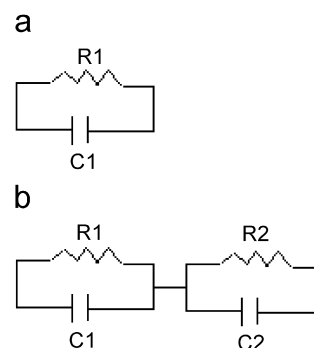
a

b

Fig. 3. (a) *RC* parallel circuit used to fit the AC-impedance curves of CMR-manganites. (b) Two *RC* parallel circuits, in series, used to fit the AC-impedance curves of spinel type double manganates.

stoichiometric sample. Note, however, that there are anomalies, but that they are small and thus would not be a bar to use the photoimpedance method as a defect detecting scheme.

So far, however, no quantitative analysis of the relation of the trap state densities and the carrier relaxation times (τ_r) with the measured parameters has been offered. However, as a rule we can say, that: (1) the trap state density should be proportional to the residual resistance, $R-R_o$ (R_o is the thermal resistance). (2) Low *RC*-values or small half circle areas are a sign of high crystal quality, i.e. a low trap state density. (3) The observation of a large photoconductivity $-\Delta R$ is also a sign of high crystal quality. In commercial semiconductors $-\Delta R$ is commonly related to higher carrier lifetimes (τ_l) and thus a low deep level trap state density. Consequently, for a given sample and temperature, $-\Delta R/\tau_l = $ constant, would at least yield relative values of the involved lifetimes. (4) The increase of the capacitive term $+\Delta C$ with illumination awaits an analytical treatment, too, but might in the end give a clue to the difference in carrier mobilities.

We would like to conclude this section with the following statement. In the case of double manganates (such as $LiMn_2O_4$) there is practically only a change in resistance with sintering. That, of course is possible under strong recombination also. A large trap state density and with it a large scattering can exist while the apparent space charge is zero. It is necessary for the center of gravity of two (equal density) space charges $+$ and $-$ to separate before one gets a *C*-response in an outer circuit. Of course, a space charge compensation is never complete, but very small capacitance values are possible together with large resistance values, as observed here.

4. Conclusions

Manganese-based transition metal oxides (TMO) are interesting both in applied and fundamental physics [9,13]. They exhibit magnetic field induced modifications of the band structure which finds applications in devices that are based on the detection of a magnetic field [10].

Table 2
Unsintered (a) and sintered (b) $LiMn_2O_4$

	Low frequency semicircle (around 10 Hz)	High frequency semicircle (around 100 kHz)
(a) Unsintered $LiMn_2O_4$		
Dark	$R = 204.4\,k\Omega$	$R = 95.66\,k\Omega$
	$C = 1.508e{-}8\,F$	$C = 7.38 \times 10^{-11}\,F$
UV	$R = 206.2\,k\Omega$	$R = 92.35\,k\Omega$
	$C = 1.452e{-}8\,F$	$C = 7.42 \times 10^{-11}\,F$
(b) Sintered $LiMn_2O_4$		
Dark	$R = 132.58\,k\Omega$	$R = 66.45\,k\Omega$
	$C = 3.714e{-}8\,F$	$C = 7.52 \times 10^{-11}\,F$
UV	$R = 98.73\,k\Omega$	$R = 53.82\,k\Omega$
	$C = 5.692e{-}8\,F$	$C = 9.05 \times 10^{-11}\,F$

Estimated parameters errors; 3%.

Much research is in progress to exploit the simultaneous occurrence, in these materials, of ferromagnetism and semiconducting behavior, in the designing of super-fast computers [11]. Lithium insertion (de-insertion) into (from) $Li_xMn_2O_4$ finds application in high energy density lithium batteries for miniature electronics [12]. $Li_xMn_2O_4$ as a cheap and easy to prepare oxide is also highlighted as a prototype material in the general understanding of charge ordering in TMO [13].

The performance of these materials is highly sensitive to the microstructure details which depend upon the preparation conditions. Physical properties of TMO are extremely sensitive to preparative conditions which is due to the modification of the microstructure which includes parameters such as particle size, material compaction, morphology, percolation pathways, defect densities, etc. Besides affecting the device performance of these materials, the modification of the microstructure also poses problems to separate intrinsic phenomena from extrinsic phenomena which is crucial in fundamental research.

The defect density is an important microstructural property that is frequently encountered within semiconductor physics. So far, no quantitative analysis of the relation of the trap state densities and the carrier relaxation times (τ_r) has been offered. How defect densities in TMO get modified with respect to preparation conditions is illustrated in this paper, using the versatile photo-induced AC-impedance method on neodymium strontium manganite and lithium manganate, along with a qualitative analysis of the relation between trap state densities and carrier relaxation times.

Extracting R, C and τ (i.e. RC distributions) from the opto-impedance data as well as developing more detailed equations for the correlation of trap state densities and carrier relaxation times with the data is going on in our laboratory.

Acknowledgments

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