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Electrooptical Memory Effect in $Zn_xIn_yS_z$ Compounds.

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Recently[1] we have reported that monocrystals of $ZnIn_2S_4$, present a charge storage effect which can be described in the following way: if these crystals are illuminated with gap-energy light at temperatures inferior to a fixed temperature, the resistance decreases several orders of magnitude and this conducting state remains also if the crystals are reported in the dark. The crystals can be reported at their original state in three different ways: a) by heating them to room temperature; b) by applying an electric field; c) by illuminating them with light of wavelength between 7000 and 8000 Å. On the basis of the other results that we have previously published[2] we have been able to interpret such a phenomenon with the existence of a double acceptor level that exists in a double negative charged state and in a single negative charged state that presents a repulsive potential barrier for the recombination of the free electrons. In this work we report that another compound of the series $Zn_xIn_yS_z$ that is $Zn_3In_2S_6$ presents the same effect. The study of new compounds of this series is justified by the fact that some of these would be able to present a critical temperature of passage from the charge storage state to the original insulating state, higher than that which we have observed in $ZnIn_2S_4$ and which is about 200°K. This would be important for practical applications. The forbidden gap of $Zn_3In_2S_6$ is 2,9 eV whereas the forbidden gap of $ZnIn_2S_4$ is 2,7 eV. The resistivity, at R.T., is $10^{10}\Omega\cdot cm$ and 10^{12}-10^{13} $\Omega\cdot cm$, respectively, for $ZnIn_2S_4$ and $Zn_3In_2S_6$. As said before, these compounds present the charge storage effect as described in (1) for $ZnIn_2S_4$. In fig. 1 we report the current versus temperature behaviour for crystals of $Zn_3In_2S_6$ together with $ZnIn_2S_4$ warming the samples from LNT to RT after the preillumination of the samples by the gap energy light at LNT. The critical value of temperature where storage begins disappearing is different for the two samples. The highest temperature is about 220°K for $Zn_3In_2S_6$. The storage quenching may be obtained by illuminating the crystals by light energy much lower than gap energy. For both the compounds, we observed that quenching is much more effective if we use a light-wawelength of 7000-8000 Å. For both $Zn_3In_2S_6$ and $ZnIn_2S_4$, the total quenching has been obtained in less than one second by an intensity of about 10^{-4} w/cm^2. Supposing, like in (1), that such phenomenon is due to the existence of a double acceptor level which presents a repulsive potential barrier for the recombination of free electrons, we measured the mean life-time of photoelectron-decay as a function of the temperature in the zone where the current rapidly varies in function of the temperature. We observed that the mean life-time varies exponentially with temperature. In this way, we calculated the barrier energy offered by the levels to the electron recombination. We obtained 0.15 eV for $Zn_3In_2S_6$ whereas for $ZnIn_2S_4$ we have 0.13 eV. Because of the existence of such a double acceptor level in the forbidden gap of these materials, in certain conditions of temperature or illumination, we may have "N" type and "S" type negative resistance phenomena or the both phenomena together as reported in (1).

Since there are possibilities of practical application for these materials as electrooptical memories, we think that a chemical-physical study would be very use ful. This can clarify the nature of these double-acceptor levels that we think can be attributed to stechiometric defects. However untill now we have not detailed information about the nature of these levels.

References

1) N.Romeo, A.Dallaturca, R.Braglia and G.Sberveglieri, Appl.Phys.Lett. 22, 21 (1973).

2) N.Romeo and O.Vigil, Phys.Stat.Sol.(a) 10, 447 (1972).

Figure captions

Fig. 1 - Current versus temperature in $ZnIn_2S_4$ and $Zn_3In_2S_6$ monocrystals, previously illuminated by gap energy light at liquid nitrogen temperature and, then, kept in the dark. The contacts on the crystals are made by indium evaporated under high vacuum. The applied voltage is 1 volt for both the crystals. The distance from the electrodes is 1 mm.

• $ZnIn_2S_4$, ■ $Zn_3In_2S_6$.