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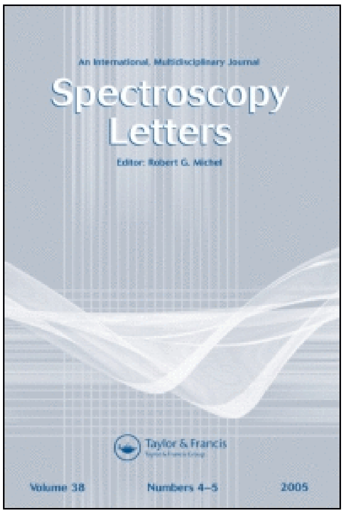

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Rodica M. Candea[a]
[a] Institute of Isotopic and Molecular Technology, ROMANIA

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PHOTOPYROELECTRIC SURFACE REFLECTANCE SPECTRA OF $Pr_{2-x}Ce_xCuO_4$ SINGLE CRYSTALS

Key words: photopyroelectric spectroscopy, reflectivity of $Pr_{2-x}Ce_xCuO_4$ (x:0;0.025;0.075).

Rodica M.Candea
Institute of Isotopic and Molecular Technology, POB 700
Cluj-Napoca 5, 3400 ROMANIA

ABSTRACT

Surface reflectance spectra of $Pr_{2-x}Ce_xCuO_4$ (x:0;0.025;0.075) single crystals in the photon energy range 0.5-3 eV were determined by the photopyroelectric (PPE) technique from direct measurements of absorptance. PPE reflectance spectroscopy allows a better resolution of the structural shape of the spectra. The main spectral features of the Pr_2CuO_4 reflectance are a peak around 1.45 eV and two shoulders (around 1.1 eV and 1.85 eV). The reflectivity peak is strongly reduced even for low level of Ce doping (x:0.025) although it can still be seen as a sharp peak with the maximum around 1.5 eV. The metallic Drude-like behavior, which appears already for x:0.025, becomes evident at x=0.075, with a clear reflectivity edge around 1.05 eV.

INTRODUCTION

Recently, a simple photopyroelectric (PPE) method suitable for determining the absolute spectra of surface reflectance $R_s(E)$ of opaque materials was suggested, based on the proportionality of the amplitude of the PPE signal (V_{PPE}) on the surface absorptance A_s[1,2]. This PPE technique has the advantage of measuring directly, with a pyroelectric (PE) sensor placed in thermal contact with the back of the sample, the absorbed optical energy deposited in the sample (through direct and indirect thermal de-excitations) as thermal energy (heat). Generally, the thermal de-excitation channels are in competition with other energy conversion channels (non-thermal) such as photochemical reactions, photoelectric processes and luminescence. In what follows we will assume that only thermal energy conversion channels are possible for the samples analyzed.

Measuring only the absorbed energy, the PPE signal is implicitly sensitive also to the reflected energy through a factor $A_s=1-R_s$. Therefore, the dependence of the surface reflectance on the energy E of the incident radiation may influence significantly the PPE spectra and determine absorption-like features, even in cases when the PPE signal is saturated in terms of optical absorption coefficient. In fact, a more detailed analysis reveals that it is the surface absorption modulated by the radiation to heat conversion efficiency, that is being measured by the PPE signal, thus the PPE technique constituting also a method of determining this characteristic of the material[1].

Based on these aspects the PPE reflectance spectroscopy can offer a simple, sensitive and versatile alternative to the conventional optical spectroscopies with better performances especially in the case of scattering samples. The surface reflectance being determined from $R_s=1-A_s$ and A_s being measured directly, problems related to scattering losses which depend on the surface optical quality are avoided by this method.

Using the PPE reflectance spectroscopy the features of the reflectivity of $Nd_{2-x}Ce_xCuO_4$ single crystals (x:0;0.03) were already determined[2], in good agreement with the data obtained in the literature by optical conventional spectroscopy[3-6].

In this letter we apply the same procedure for determining the surface reflectance spectra of $Pr_{2-x}Ce_xCuO_4$ (x:0;0.025;0.075) as grown crystals.

EXPERIMENTAL

The PPE signal was measured in a typical experimental set up containing the PPE system sample//sensor with the back of the sample placed in intimate thermal contact with the front of the pyroelectric sensor (3x4x0.2mm ceramic PZT provided with gold electrodes) supported by a porous plastic fiber material for thermal insulation. The experimental set up also contained the modulated radiation source (formed of Oriel QTH filament lamp, ISA H-20 grating monochromator, and mechanical modulator) and the PPE signal acquisition and processing system (formed of two EG&G type 3210 and 5301A lock in amplifiers) as already described in reference 2. The experiment was controlled by a work station and the data were collected via an IEEE bus.

The monochromatic light in the photonic energy range (0.5-3 eV), mechanically modulated at f_c = 5.7 Hz, impinged on the front surface of the optically opaque sample.

The samples were as grown single crystals of thicknesses d ◘ 0.4-0.6 mm and of large enough area to cover completely the surface of the PE sensor. The natural faces of the crystals were used, after a 15 min chemical etch in 2% HI solution in methanol.

In order to obtain the absolute value of the absorptance A_s, the PPE signal was normalized to the signal obtained for the blackened sample. A thin layer of China ink (R_s^b=0.05) was painted on the sample, without removing it from the sensor. All the other experimental conditions were maintained the same.

RESULTS AND DISCUSSION

It was shown that for the case of opaque samples of thickness d, absorption coefficient β, and complex thermal diffusion coefficient σ, under ideal conditions of good thermal contact between the sensor and the sample, negligible thermal capacity of the sample and PPE system thermally insulated from the ambient, the amplitude of the PPE signal is given by[1,2]

$$V_{PPE} = K(1-R_s) \qquad (1)$$

if the sample is thermally thin, and by

$$V_{PPE} \;◘\; K(1-R_s)\exp(-\sigma d) \qquad (2)$$

if the sample is thermally thick. This means that if the thermal properties of the sample corroborated with the chopping frequency allows for the thermal diffusion length μ to satisfy the condition $\beta^{-1}<d<\mu$, the PPE signal reaches the sensor as an unattenuated thermal wave, and if the condition $\beta^{-1}<\mu<d$ is satisfied, the signal reaches the sensor as an exponentially attenuated thermal transmission wave. K is a constant characteristic of the experimental set up. As it can be seen, in both cases, the PPE signal does not depend on the optical absorption

coefficient and the only dependence on the energy of the incident radiation arises from the $R_s(E)$ dependence. Thus R_s can be easily determined from (1) or (2) if K and exp($-\sigma d$) can be eliminated. One simple and accurate enough way of doing this is by normalizing to the signal obtained in the same experimental conditions, for the same sample having deposited on the surface a thin black absorbing layer provided that the black layer is of negligible thermal capacity.

It is generally agreed, based on data obtained for cuprate superconductors by conventional optical spectroscopy procedures (Kramers-Kronig analysis of reflectivity spectra for single crystals[4-9] and transmission spectroscopy for thin films[3]), that the reflectivity and absorption spectra in the photon energy range below 3 eV can be attributed to charge transfer (CT) excitations between Cu and O electronic states and to Drude free carriers absorption.

The CT peak is seen at 2 eV in La_2CuO_4 and in the range 1.4-1.6 eV in the Nd_2CuO_4[2-5] and Pr_2CuO_4[7,8]. A structural shape of the reflectivity curve for the undoped samples is noticed in some of the references[2,3,4,6,8,9] which could not be easily interpreted but found to be dependent on oxygen doping level[3,4,9]. As it is suggested in reference 3 the reducing treatment of Nd_2CuO_4 films produces the disappearance of the 1.5 eV reflectivity peak because of the electron doping effect due to the formation of oxygen vacancies.

Doping Ce ions in Nd_2CuO_4 also produces the decreasing effect on the 1.5 eV reflectivity peak, thus suggesting that the electron carriers come from the same origin[3]. The reflectivity edge is positioned in the range 1-1.1 eV.

It is expected that the features of the reflectivity spectra for $Pr_{2-x}Ce_xCuO_4$ will be similar with those for

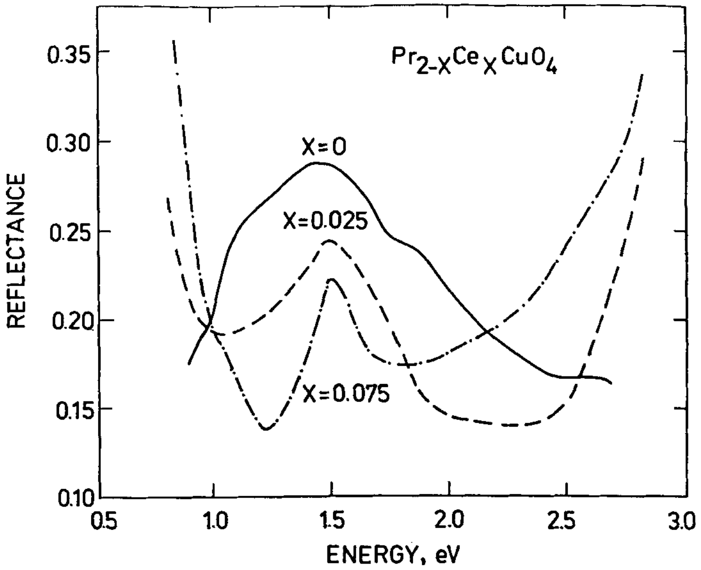

Fig.1 - Room temperature photopyroelectric reflectance spectra of $Pr_{2-x}Ce_xCuO_4$ single crystals.

$Nd_{2-x}Ce_xCuO_4$[7]. Indeed, the main reflectivity peak is found around 1.4 eV (optical conductivity peak around 1.6 eV)[7,8].

Concerning the spectral change of $Pr_{2-x}Ce_xCuO_4$ reflectivity below 3 eV with Ce doping it was until now reported that for x=0.12 the spectral weight of 1.5 eV excitation was completely transferred to the lower energy region[8].

The PPE reflectance spectra of our $Pr_{2-x}Ce_xCuO_4$ (x:0;0.025;0.075) samples are presented in Fig.1 and several features can be noticed: the peak around 1.45 eV, a shoulder around 1.1 eV and another shoulder at 1.85 eV. While the position of the peak agrees well with the data in the literature[7,8], differences in the structural shape are noticed. The shoulder in the high energy region does not appear in reference 7 but it is clear in reference 8; no shoulder is found in the low energy region[7,8].

At energies higher than 2.5 eV another shoulder seems to be present in Fig.1.

Doping caused the reducing of the reflectance peak, more abruptly in the low energy region, giving the impression of the peak shifting to 1.5 eV. The peak is still present for x=0.075. The plasma reflectivity edge which already appeared for x=0.025, is clearly set in at around 1.05 eV. The reflectivity below edge and in the high energy region increases as the doping level increases.

The fact that the reflectance spectra for the undoped Pr_2CuO_4 has a structural shape which includes, besides the main peak, also shoulders, as in the case of of Nd_2CuO_4[2] and, particularly evident, in the case of $La_{2-x}Sr_xCuO_4$[6], suggests that a more systematic study of the effect of oxygen and Ce doping, and, at the same time, of the temperature dependence of the reflectivity, is necessary before a complete picture of the origin of the features of the optical spectra and the evolution of the electronic structure on doping is established.

CONCLUSION

The photopyroelectric spectroscopy, due to the fact that it is sensitive only to the absorbed (and thermallized) energy, offers the possibility of a direct and sensitive measurement of the reflectivity of opaque samples.

The photopyroelectric reflectance spectra of Pr_2CuO_4 obtained by this method indicated clearly a structural shape with a main peak (around 1.45 eV) and at least two clear shoulders (around 1.1 eV and 1.85 eV).

Doping the samples up to x:0.075, although determined the appearance of the reflectivity edge, thus indicating the presence of the free carriers generated by Ce doping, did not replace yet completely the charge transfer mechanism.

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