

## **In<sub>2</sub>O<sub>3</sub> STRUCTURE ANALYSIS BY RAMAN SPECTROSCOPY**

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### **Summary**

The analysis of Raman scattering of doped In<sub>2</sub>O<sub>3</sub> ceramics was carried out and the mechanism of doping influence on In<sub>2</sub>O<sub>3</sub> grain structure was suggested.

### **1. INTRODUCTION**

Analyzing the doping influence on parameters of In<sub>2</sub>O<sub>3</sub>-based ceramics we have found out that even low concentration of additives could strongly affect both electrophysical and gas sensing characteristics of metal oxides [1,2]. We have assumed that such effect was connected with structure modification, taking place during In<sub>2</sub>O<sub>3</sub> ceramics doping. It was carried out the Raman spectroscopy of In<sub>2</sub>O<sub>3</sub>-doped ceramics for establishment a mechanism of this influence.

### **2. EXPERIMENTAL DETAILS**

In<sub>2</sub>O<sub>3</sub>-based ceramics was prepared using the sol-gel technology. During metal oxide synthesis it was carried out doping by Ga, P, Mn, Cu and B. The concentration of doping impurities varied between 1 and 10 wt %. Samples of In<sub>2</sub>O<sub>3</sub>-based one-electrode gas sensors used for declared research have been fabricated in INNOVATSENSOR [3]. For Raman spectroscopy we have used a Jobin Yvon spectrometer with a 514 nm line of argon laser with a power among the sample of 2mW. We have registered a silicon Raman spectrum before each In<sub>2</sub>O<sub>3</sub> + additive spectrum. Comparing this spectrum with the known band of silicon at 520 cm<sup>-1</sup> we were able to correct instrumental errors of our spectrums. We have used 240 s as acquisition time. All measurements of Raman spectra (50-700 cm<sup>-1</sup>) have been carried out at room temperatures.

### 3. RESULTS AND DISCUSSION

Results of research are shown in Figs. 1-5. Figs 1,2 and 5 reflect doping influence on the shape of Raman scattering spectra, and Fig. 4 on the shift of main peaks' position.

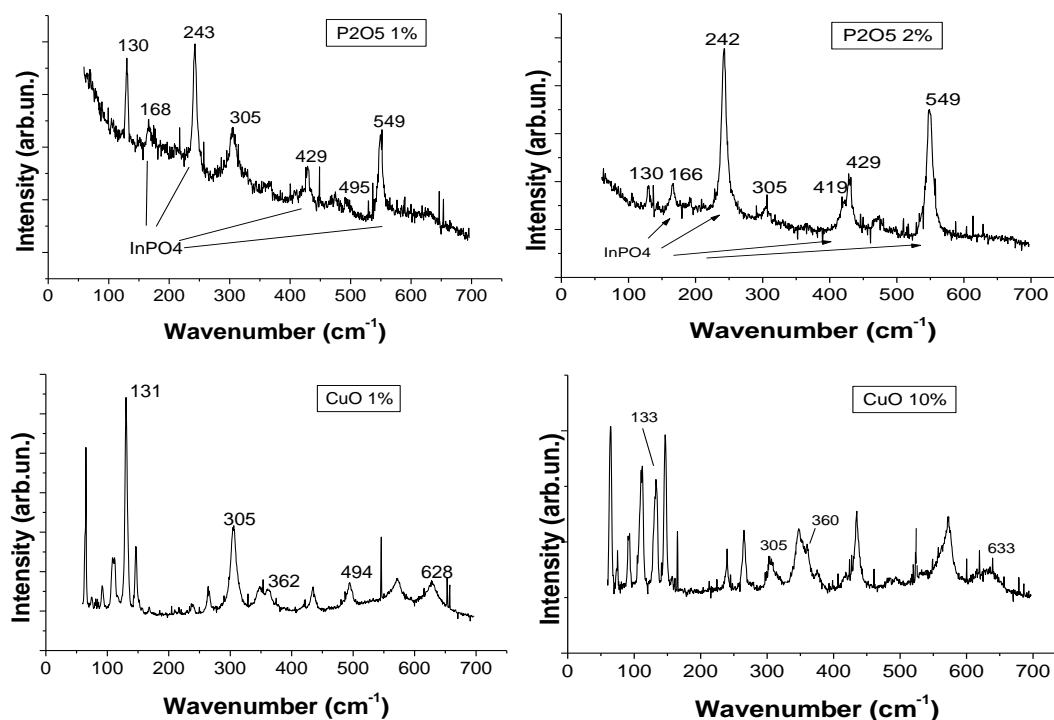


Fig.1 Raman spectra of  $\text{In}_2\text{O}_3\text{:P}$  and  $\text{In}_2\text{O}_3\text{:Cu}$

Analyzing the results of Raman spectroscopy of metal oxide nanocomposites [4-9] one can establish that there are four main causes of Raman spectra change. They are the following: (1) The appearance of second phase in base oxide (appearance additional peaks in Raman spectra); (2) The change of chemical and crystallographic structure (the change of the shape of Raman spectra); (3) The change of grain size (peak spreading and the shift of their position); and (4) The change of lattice constant (the shift of Raman peak position).

Examining obtained results one can make a conclusion that all above mentioned processes may take place during bulk doping of  $\text{In}_2\text{O}_3$  ceramics. At that both phosphorus and copper are the strongest modifiers of  $\text{In}_2\text{O}_3$  Raman spectra (see Fig.1). After doping by phosphorus, it was found the appearance of new peaks, peculiar to  $\text{InPO}_4$  ( $175\text{ cm}^{-1}$ ,  $243\text{ cm}^{-1}$ ,  $418\text{ cm}^{-1}$ , and  $548\text{ cm}^{-1}$  [10,11]) and the decrease of the intensities of the peaks peculiar to  $\text{In}_2\text{O}_3$  ( $130\text{ cm}^{-1}$ ,  $308\text{ cm}^{-1}$ ,  $365\text{ cm}^{-1}$ ,  $490\text{ cm}^{-1}$ , and  $637\text{ cm}^{-1}$  [10,11]). We should note that our values for main Raman lines within  $4\text{-}8\text{ cm}^{-1}$  differ from indicated ones. However this difference could be easily explained by structural difference of studied objects. In case of  $\text{In}_2\text{O}_3$  doping by copper the situation was more complicated. We could not connect new peaks with any binary copper oxide ( $\text{CuO}$ ,  $\text{CuO}_2$ ) [12,13]. We suppose

that the forming ternary compound such as  $\text{In}_x\text{Cu}_y\text{O}_z$  is the cause of observed change of Raman spectra.

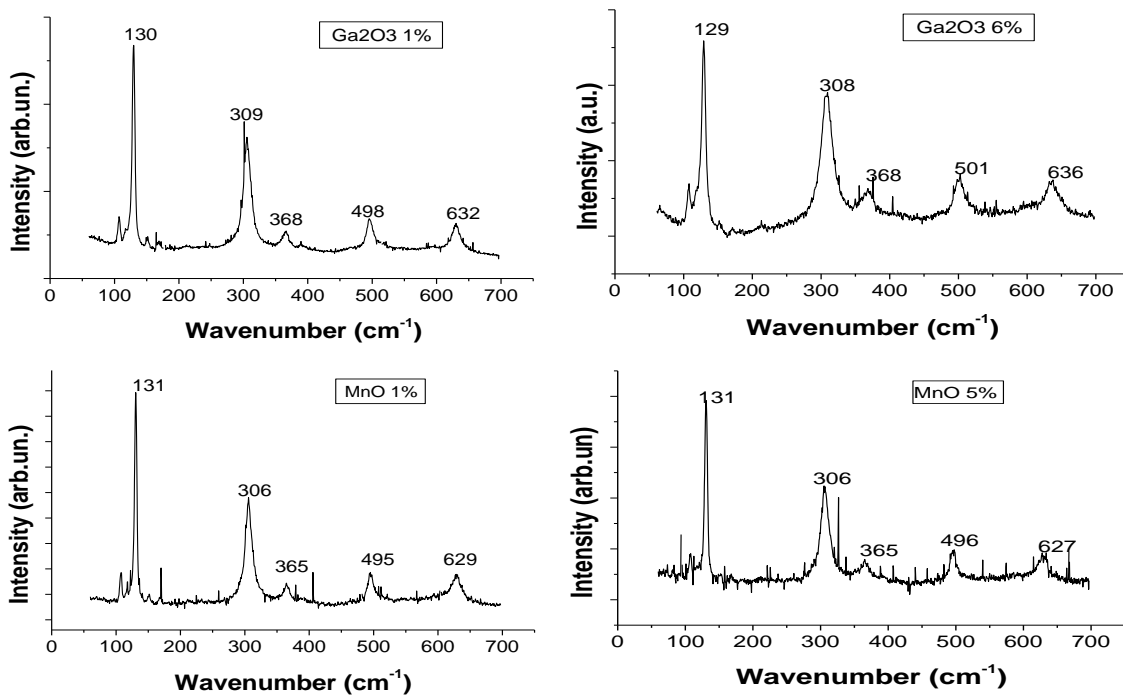


Fig.2. Raman spectra of  $\text{In}_2\text{O}_3:\text{Ga}$  and  $\text{In}_2\text{O}_3:\text{Mn}$

In case of  $\text{In}_2\text{O}_3$  doping by Mn and Ga, the structure of the Raman spectra did not change (see Fig.2). It indicates that the  $\text{In}_2\text{O}_3$  crystallites remain dominant phase in oxide matrix. Only some peak broadening, indicating that  $\text{In}_2\text{O}_3$  grain size decreases while Ga concentration in  $\text{In}_2\text{O}_3$  increases, takes place. However the absence of the peaks peculiar to Ga and Mn oxides is not the evidence of these phases absence. X-ray analysis indicates that Ga and Mn oxide phases present in  $\text{In}_2\text{O}_3:\text{Ga}$  and  $\text{In}_2\text{O}_3:\text{Mn}$  in sufficient quantity. On the base of above mentioned we have supposed that these phases in  $\text{In}_2\text{O}_3$  matrix were in the fine dispersed state. According [5,7] one can assume that the grain size of these phases does not exceed 1-2 nm. Results presented in [5,7] have shown that the Raman spectra of metal oxides with indicated grain size do not have any clear structure; and the intensity of these peaks is very low. This conclusion finds confirmation in [14,15]. Research of two-phase systems, where the concentration of the second phase is much less than the concentration of based oxide, have shown that the second oxide phase, as a rule, is a fine disperse one, and it is being formed at the surface of the based oxide's grains.

It is necessary to note that indicated behavior of the second oxide phase during bulk doping

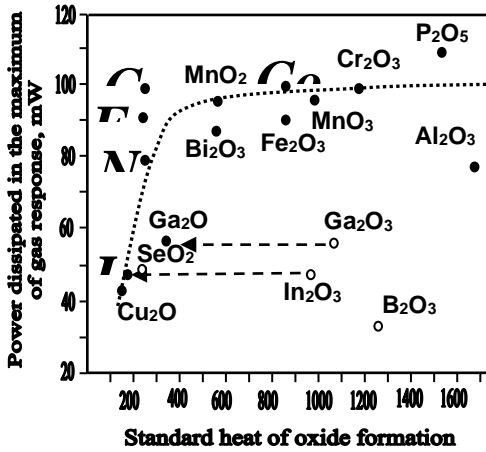


Fig.3. Doping influence on  $P_{max}$  ( $T_{max}$ ) of  $In_2O_3$  gas response to ozone

is good explanation for observed effect of doping influence on the temperature position of  $In_2O_3$  gas response maximum ( $T_{max}$ ) (see Fig. 3). It was established that  $In_2O_3$  doping is accompanied by increase of the dissipated electrical power of the heater in the maximum of gas response ( $P_{max}$ ). This increase occurs according to growth of standard heat of oxide formation of doping element.

Due to segregation at the surface of based oxide, the additives even with low concentration may control the properties of inter-grain contacts.

However it is necessary to highlight that in spite of analogous of the Raman spectra of  $In_2O_3:Ga$  and  $In_2O_3:Mn$  there are considerable differences in the influence of both Ga and Mn additives on the position of main Raman peaks. If the doping by Ga led to the strong shift of  $In_2O_3$  Raman peaks, especially at high Ga concentration in  $In_2O_3$  (see Fig. 4), the doping by Mn almost does not change the position of these peaks. The position of main Raman peaks for studied  $In_2O_3$  samples is shown in Fig. 4 by dotted line. It is known that  $Ga_2O_3$  and  $In_2O_3$  have high mutual dissolubility and they can form solid solutions [8]. Taking into account that ionic radiuses of Ga and Mn are very similar, indicated difference could be explained in the frame of assumption that Mn dissolubility in  $In_2O_3$  is very low in comparison with Ga dissolubility. It means that the formation of Mn oxide layer at the surface of  $In_2O_3$  grains, which may limit the film conductivity, is possible already at very low concentrations of additives.

In [5] it was shown that the highest frequency band in Raman spectra of oxides with C-type rare earth oxide structure ( $\sim 630\text{ cm}^{-1}$  for  $In_2O_3$ ) is related to the M(1)-O cation-oxygen distance in M(1) octahedron.

According [5] the decrease of metal-oxygen distance is accompanied by shifting of this band in the region of higher frequency. In the frame of this model, the results, shown in Fig.4, testify that

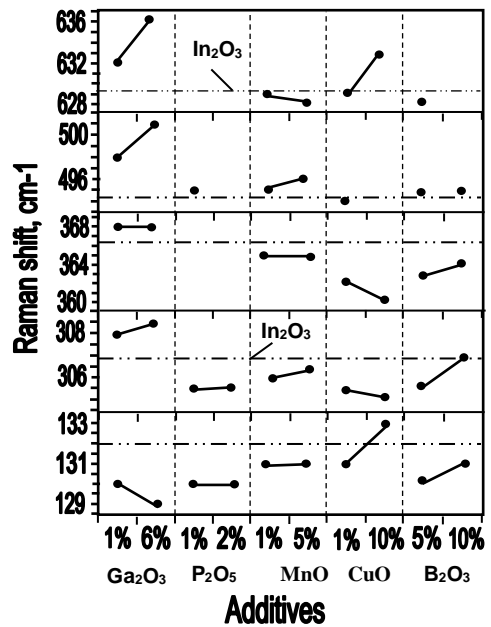


Fig.4. Doping influence on the position of main Raman peaks

doping by Ga and Cu decreases the M(1)-oxygen distance in  $\text{In}_2\text{O}_3$  lattice. Such influence is anticipated, because Ga and Cu have smaller ionic radiuses than In.

During  $\text{In}_2\text{O}_3$  doping by B (see Fig.5) we have some intermediate case. The structure of  $\text{In}_2\text{O}_3$  Raman spectra remains the same. However the ratio of the intensities of individual

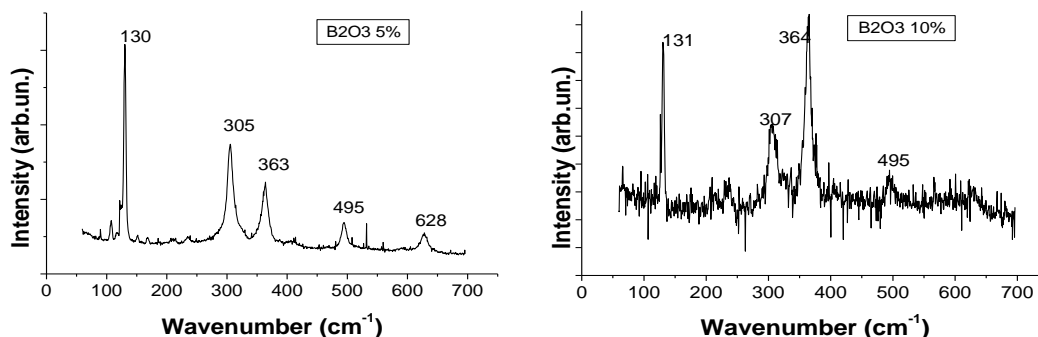


Fig.5. Raman spectra of  $\text{In}_2\text{O}_3\text{:B}$

peaks is being changed strongly. It testifies the doping by B modifies the crystallographic structure of  $\text{In}_2\text{O}_3$  grains. However those changes are taking place in the frame of the same initial space group of crystallographic structure [5]. The forming of borate could be the reason of observed changes. The appearance of weak bands at the wave numbers peculiar to borate [16] confirms our assumption.

#### 4. CONCLUSIONS

On the base of conducted research we have concluded that difference in the parameters of doped  $\text{In}_2\text{O}_3$  ceramics observed in [1,2] is the consequence of different structure forming during doping. Examples of such structures are shown in Fig. 6.

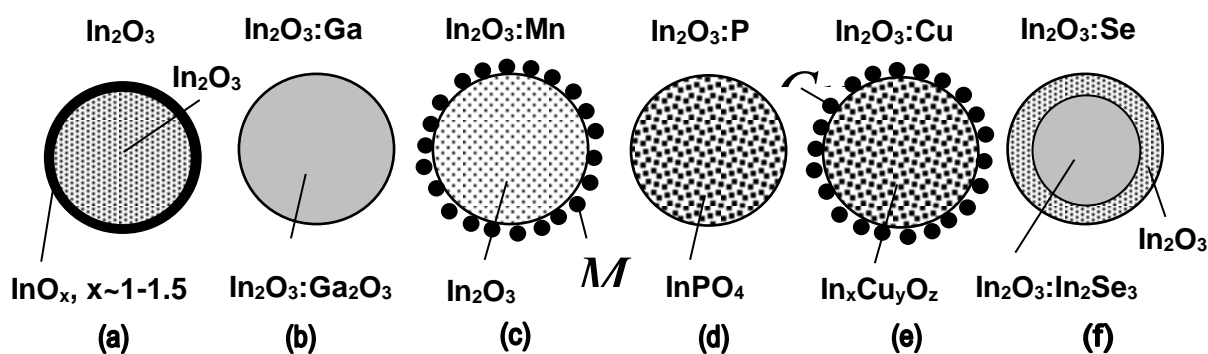


Fig. 6. Possible structures of doped  $\text{In}_2\text{O}_3$  grains

It is necessary to note that the appearance of thin unstoichiometric layer ( $\text{InO}_x$ ,  $x \sim 1-1.5$ ) at the  $\text{In}_2\text{O}_3$  surface was established experimentally by data of surface study using synchrotron radiation [17]. The presence of such layer brings the results, obtained for undoped  $\text{In}_2\text{O}_3$  sensors (see Fig.3), in correspondence with common regularity of standard heat of oxide formation influence of the temperature position of gas response maximum. Exception to the rule, found for  $\text{In}_2\text{O}_3\text{:B}$  (see Fig. 3), we have connected with peculiar properties of boron oxides, such as low

melting temperature and good water solubility. The forming of f-type structures (see Fig.6) we connect with low thermal stability of  $\text{In}_2\text{Se}_3$  compounds and high volatility of  $\text{SeO}_2$  oxides. As it is known, the process of ceramics production includes treatments at temperatures higher than temperature of  $\text{In}_2\text{Se}_3$  decomposition. Besides, during analysis of gas sensing characteristics of doped ceramics, we have to take into account that the increase of doping element concentration, especially in the range of limited solubility, may be accompanied by the change of grain structure. For example, at the increase of Ga concentration in  $\text{In}_2\text{O}_3$ , the transfer from b-type structure to e-type is possible.

## 5. ACKNOWLEDGEMENTS

Authors are thankful to CRDF (US) for financial support in the framework of Cooperative Grant Program (Grant MO-E2-2588-CH-04).

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