X-ray photoelectron spectroscopy studies of PrAlO$_3$ crystals before and after thermal treatment

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The as-grown PrAlO$_3$ single crystals grown by the Czochralski method are brown colored and after annealing in the reducing atmosphere (20%) H$_2$/N$_2$ they change the color to green. The X-ray photoelectron spectroscopy was used to study the chemical composition and electronic structure of PrAlO$_3$ single crystals before and after the thermal treatment. The core electron lines of praseodymium, aluminum and oxygen were measured and deconvoluted into the synthetic peaks to determine the chemical shifts. The mixed ionic and covalent character of bonds was found. The praseodymium valency may influence the coloration of the PrAlO$_3$ crystal. In the as-grown sample an additional Pr $3d_{5/2}$ peak at about 965 eV has higher intensity than that in the annealed one and is attributed to the presence of Pr$^{4+}$ ions. The measurements showed the reduction of oxygen during thermal treatment and that interstitial oxygen was not removed in this process.

Keywords: characterization, praseodymium compounds, perovskites, oxides.

1. Introduction

The aim of this work was a high resolution X-ray photoelectron spectroscopy (XPS) study of PrAlO$_3$ single crystals grown by the Czochralski method [1]. PrAlO$_3$ crystal is interesting and also very difficult to grow because it undergoes three phase transitions: C2/m $\rightarrow$ Imma $\rightarrow$ R3c $\rightarrow$ Pm3m [2–7]. The as-grown crystals are dark brown in color. Annealing in the reducing atmosphere, (20%) H$_2$/N$_2$, temp. 1150°C, causes a change of the color to light green, characteristic of crystals with Pr$^{3+}$ ions. From the absorption measurements it occurs that in the samples from the as-grown crystal the Pr$^{3+}$ peaks have smaller intensity than in the samples annealed in the reducing atmosphere (green). It is probable that the brown coloration of the as-grown crystals comes from the Pr$^{4+}$ ions. From the absorption measurements PAWLAK et al. [1] concluded that the concentration of Pr$^{4+}$ ions in the as-grown samples was ca. 1/4 of all praseodymium ions.
The change of coloration was connected with the change of praseodymium valency also in other materials. Liu et al. [8] found for the PrGaO₃ crystals doped with Mg²⁺ that color of the sample changed from black to light green after its being treated in H₂ atmosphere. The change of the coloration was explained to be the result of reduction of Pr⁴⁺ ions to Pr³⁺. In the case of PrGaO₃ doped with Mg²⁺, Pr⁴⁺ ions were created besides oxygen vacancies, which caused black coloring of the sample. The change of the coloration was reversible, when the green sample was annealed in air, its color changed to black again. The change of the color was caused by the Pr valency change because the crystal structure did not alter.

In order to show whether the change of coloration could be connected with the change of praseodymium ion valency in PrAlO₃ crystals, the XPS measurements were carried on the as-grown and annealed in the reducing atmosphere samples.

2. Experimental procedure

Crystals with stoichiometric composition, PrAlO₃, were obtained using the Czochralski method [9]. The melts were prepared from high purity Al₂O₃ and Pr₆O₁₁ oxides (99.995%). A conventional Czochralski apparatus, Oxypuller 05-03 (Cyberstar), and RF heating were used. Single crystals were grown from an iridium crucible, 25 mm in diameter, in nitrogen atmosphere with the partial pressure of oxygen ca. 20–30 ppm. The pulling rate was 1 mm/h and the rotation rate was 12 rpm. The crystals were seed-grown on the iridium plate. The as-grown crystals exhibited dark brown coloration. To remove the color they were annealed in a 20% H₂/N₂ atmosphere at 1150°C for 15 hours.

The XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al Kα X-ray radiation (1486.6 eV). A hemispherical mirror analyzer analyzed the energy of the electrons with an energy resolution of about 0.3 eV. X-ray emission from a surface area of 800×2000 µm was measured. All measurements were performed under UHV of the order of 10⁻¹⁰ torr. In every case a neutralizer was used to eliminate the charge effect which occurs for non-conducting samples. The binding energy was determined with reference to the C 1s line at 284.8 eV of adventitious carbon. The angle between the X-ray source and the sample surface was 45°. The azimuth was at random.

The Multipak Physical Electronics program enables quantification of the XPS spectra utilizing peak area and peak height sensitivity factor. Standard atomic concentration calculation provides the ratio of each component to the sum of other elements considered in the data. Only those elements for which the specific line is clearly visible in the spectrum were considered. For these specific lines the background was subtracted, the limit of the region of the line was individually selected and after that integration was done [10, 11]. The accuracy of this method is less than ±10%. The peaks were deconvoluted after background subtraction, using a Gaussian–Lorenzian function.
3. Results and discussion

In Figure 1 the as-grown and annealed in the reducing atmosphere samples of PrAlO$_3$ crystal are shown. The XPS spectrum of the as-grown PrAlO$_3$ crystal measured in a wide energy range is shown in Fig. 2. The spectrum reveals dominant peaks from Pr, Al, O ions with a C 1s peak coming from carbon contamination. Besides carbon, excess of oxygen in relation to the nominal value was found in the spectrum, indicating the existence of oxygen contaminations as well. In perovskites, in general, the amount of oxygen is expected to be rather higher than nominal due to the oxygen vacancies [12], though some authors observe interstitial oxygen ions [13].

Using the Multipak program chemical composition of the samples fractured under UHV in several regions of the as-grown and annealed crystals was calculated (Tab. 1). The XPS chemical analysis was made over the area of 800×2000 µm. The results showed that oxygen concentration was changing from place to place. The average chemical compositions obtained were: Pr$_{0.90}$Al$_{0.92}$O$_{3.30}$ for the as-grown crystal, and

![Fig. 1. PrAlO$_3$ cubicoids: as-grown (a) and annealed in (20%) H$_2$/N$_2$ (b), T = 1150°C.](image1)

![Fig. 2. XPS spectrum in the wide energy range of the as-grown PrAlO$_3$ crystal.](image2)
Table 1. Chemical composition of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pr</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>0.90</td>
<td>0.92</td>
<td>3.30</td>
</tr>
<tr>
<td>Annealed in (20%) H$_2$/N$_2$</td>
<td>0.90</td>
<td>0.90</td>
<td>3.09</td>
</tr>
</tbody>
</table>

Table 2. Binding energies of the Pr 3d$_{5/2}$, Al 2p, O 1s in PrAlO$_3$ crystal; $M$ – main line, $S_1$, $S_2$, $S_3$ – satellite lines, $E_{BM}$ – binding energy of the main line (experiment), $E_{BC}$ – binding energy (catalogue position [8]).

| Pr$_{0.90}$Al$_{0.90}$O$_{3.09}$ for the crystal annealed in reducing atmosphere. The amount of praseodymium and aluminum is similar in both samples but oxygen concentration was smaller in the annealed one.

The Pr 3d, Al 2p and O 1s lines were deconvoluted after background subtraction. A comparison of the binding energies of the main lines of elements existing in the compound with the values given in literature is shown in Tab. 2. The chemical shifts obtained indicate the mixed bonds. The bond between oxygen and praseodymium and between oxygen and aluminum has an ionic character, while the bond between praseodymium and aluminum has a covalent one. The chemical shifts of the praseodymium, aluminum and oxygen for as-grown crystal are similar to that in annealed crystal.

A comparison of the core electron spectra of the Al 2p, O 1s and Pr 3d of the as-grown and annealed in 20% H$_2$/N$_2$ crystals is shown in Figs. 3–5. All core electron lines of the annealed samples of PrAlO$_3$ are broader and more complex compared to those of the as-grown ones.

Deconvolution of the O 1s peak showed the existence of two components in the spectrum of the as-grown sample and more components for the annealed one. The main line was ascribed to the constitutional oxygen. The O 1s satellite line at higher binding energy can be attributed to the external oxygen contamination and/or
Fig. 3. XPS O 1s lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.

Fig. 4. XPS Al 2p lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.

Fig. 5. XPS Pr 3d lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.
the presence of interstitial oxygen ions due to an increased amount of this element. Pajączkowska et al. [14] showed that existence of interstitial oxygen ions in the SrPrGaO₄ crystal lattice influenced the coloration of the crystal. The SrPrGaO₄ as-grown crystals were dark green with some red stripes and after annealing in H₂-N₂ atmosphere they changed to green. The authors ascribed the line at lower binding energy from the main peak to the interstitial oxygen. During the annealing process this line disappeared due to removal of the interstitial oxygen.

The shape of Pr 3d peak for the PrAlO₃ as-grown sample is similar to that of the Pr₂O₃. The complex peak shape originates from the simultaneous effect of covalency hybridization and intraatomic electrostatic coupling between 3d hole and the outer unpaired 4f electrons [15, 16]. The Pr 3d₃/₂ and 3d₅/₂ lines are split due to final-state configurations of 4f³L (where L denotes the hole on the O 2p valence band) on the low binding energy side (marked as S) and of 4f² on high binding energy side (marked as M) [15, 16]. The Pr 3d₃/₂ line has an additional peak on the tail of the main line at the high binding energy side (marked as T), which is also attributed to shake-up process [16, 17].

The Pr 3d spectra in both PrAlO₃ samples are similar except one feature. The Pr 3d₃/₂ line at about 965 eV for the as-grown PrAlO₃ sample (marked as F) has higher intensity than for the annealed sample. This peak may be attributed to 4f³L² final state which indicates the presence of Pr⁴⁺ ions [15, 18]. The weak 4f³L² satellite predicts mainly trivalent Pr and only a small amount of Pr⁴⁺.

In Figure 6, a comparison of the valence band of the as-grown and annealed in reducing atmosphere PrAlO₃ samples is shown. The XPS valence band consists of the oxygen 2p states hybridized with the praseodymium 4f states. The Pr hybridized and localized states are in the same energy region and cannot be separated [19]. Moreover,
the valence band of PrAlO$_3$ shows the Pr 4$f$ band maximum at ca. 2 eV below the Fermi energy level and the O 2$p$ band at ca. 2 eV above. The Pr 4$f$ is at the same energy as the top of the valence band and is located in the band gap of the crystal. This is in agreement with PrAlO$_3$ powder valence band measurements [20]. There exists a similar separation of the $f$ and $p$ bands in PrAlO$_3$ as in Pr$_2$O$_3$ [18]. The existence of satellite peak at about 9 eV indicates some amount of chemisorbed oxygen on the surface [19]. The XPS spectrum of the valence band of annealed sample is broadened and smeared in comparison with the as-grown sample but both crystals show features of valence band characteristic of Pr$^{3+}$ [18, 20].

4. Conclusions

The praseodymium valency may influence the coloration of the PrAlO$_3$ crystal. In the XPS spectrum of the as-grown crystal suspected for containing a mixture of Pr$^{3+}$ and Pr$^{4+}$ ions, the additional Pr 3$d_{3/2}$ peak at ca. 965 eV was found to have higher intensity than that of the annealed sample. This peak was attributed to the presence of Pr$^{4+}$ ions in the sample.

The color of the PrAlO$_3$ changes from brown to green after annealing the sample in the reducing atmosphere, which may show that Pr$^{4+}$ ions are reduced to Pr$^{3+}$ due to oxygen reduction and valency balance conservation.

The annealing process resulted in the broadening of oxygen lines and appearance of an extra line connected with new migrations of ions in the lattice structure.

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References


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