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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 $3d_{3/2}$ 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 $\xrightarrow{175\text{ K}}$ Imma $\xrightarrow{225\text{ K}}$ R$\overline{3}$c $\xrightarrow{1650\text{ K (1770 K)}}$ Pm$\overline{3}$m [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 $PrGaO_3$ crystals doped with Mg^{2+} that color of the sample changed from black to light green after its being treated in H_2 atmosphere. The change of the coloration was explained to be the result of reduction of Pr^{4+} ions to Pr^{3+}. In the case of $PrGaO_3$ doped with Mg^{2+}, Pr^{4+} 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 $PrAlO_3$ crystals, the XPS measurements were carried on the as-grown and annealed in the reducing atmosphere samples.

2. Experimental procedure

Crystals with stoichiometric composition, $PrAlO_3$, were obtained using the Czochralski method [9]. The melts were prepared from high purity Al_2O_3 and Pr_6O_{11} 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% H_2/N_2 atmosphere at 1150°C for 15 hours.

The XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al K_α 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 1*s* 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
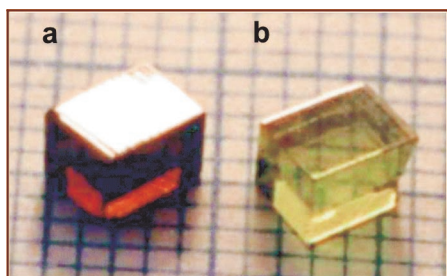

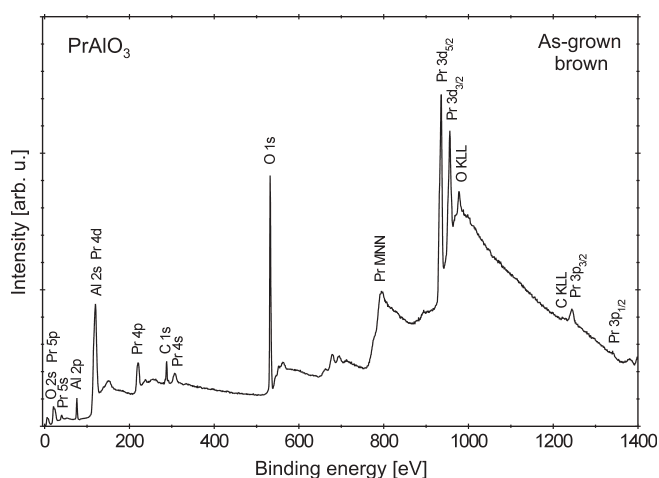Fig. 1. PrAlO$_3$ cubicoids: as-grown (**a**) and annealed in (20%) H$_2$/N$_2$ (**b**), T = 1150°C.

Fig. 2. XPS spectrum in the wide energy range of the as-grown PrAlO$_3$ crystal.

T a b l e 1. Chemical composition of as-grown and annealed in the reducing atmosphere $PrAlO_3$ crystal.

Sample	Chemical composition		
	Pr	Al	O
As-grown	0.90	0.92	3.30
Annealed in (20%) H_2/N_2	0.90	0.90	3.09

T a b l e 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, EB_M – binding energy of the main line (experiment), EB_C – binding energy (catalogue position [8]).

		Pr $3d_{5/2}$		Al $2p$		O $1s$			
$PrAlO_3$ as-grown	Binding energy (catalogue value)	$EB_C = 931.9$ eV		72.9 eV		531 eV			
	EB [eV] (compound)	M 932.5	S 928.2	M 72.9		M 529.1	S_2 530.9		
	Chemical shift Δ [eV] ($\Delta = EB_M - EB_C$)	+0.6		—		–1.9			
$PrAlO_3$ annealed in (20%) H_2/N_2	Binding energy (catalogue value)	$EB_C = 931.9$ eV		72.9 eV		531 eV			
	EB [eV] (compound)	M 932.3	S 928.1	M 73.0	S 71.05	M 529.3	S_1 531.55	S_2 527.35	S_3 523.3
	Chemical shift Δ [eV] ($\Delta = EB_M - EB_C$)	+0.4		+0.1		–1.7			

$Pr_{0.90}Al_{0.90}O_{3.09}$ 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
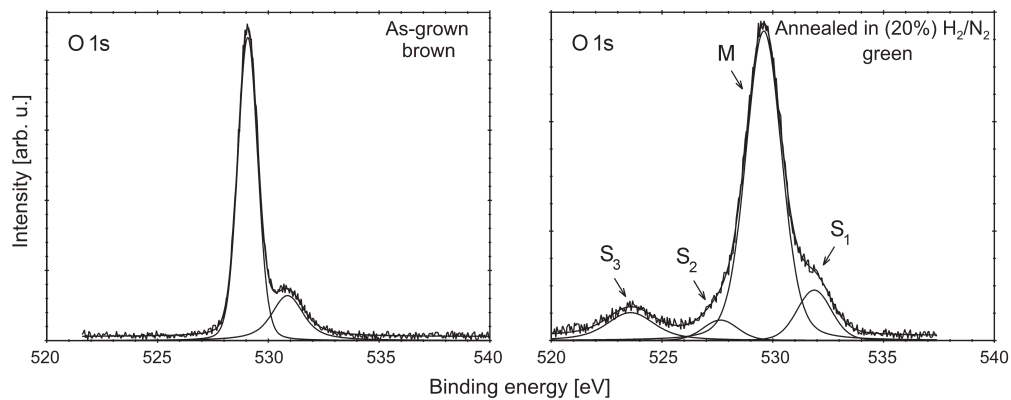
Fig. 3. XPS O 1*s* lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.
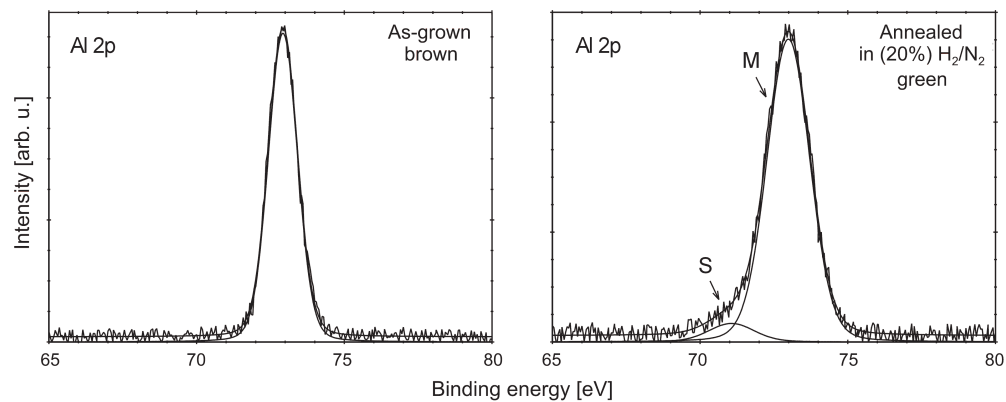
Fig. 4. XPS Al 2*p* lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.
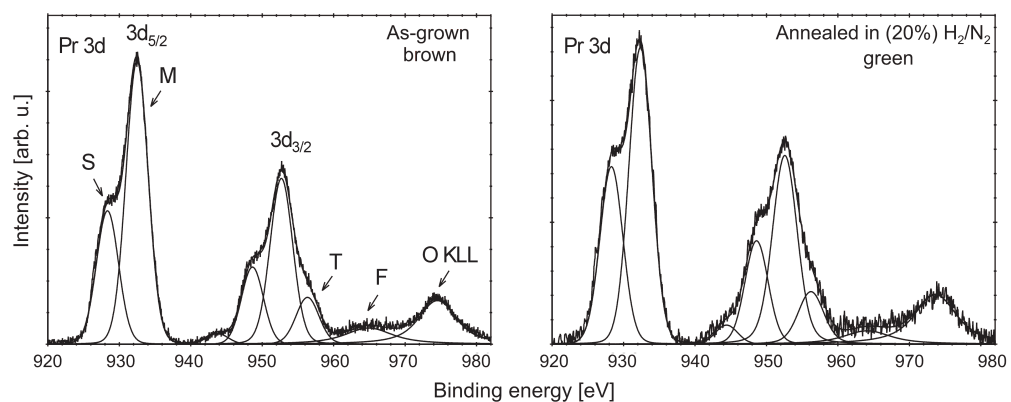
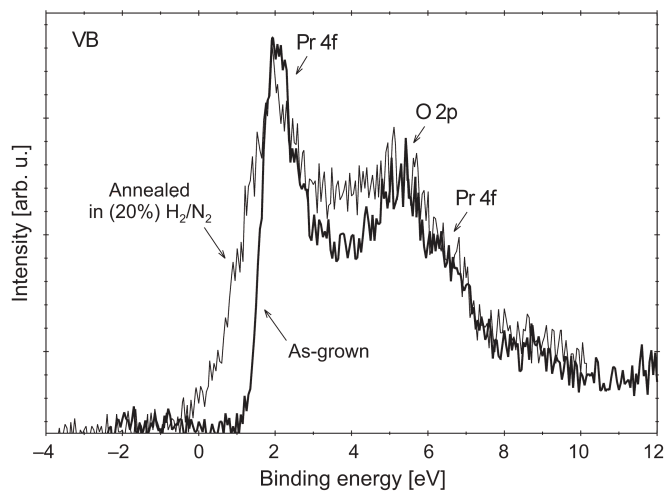Fig. 5. XPS Pr 3*d* lines of as-grown and annealed in the reducing atmosphere PrAlO$_3$ crystal.

Fig. 6. XPS valence band 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. Pajaczkowska *et al.* [14] showed that existence of interstitial oxygen ions in the SrPrGaO$_4$ crystal lattice influenced the coloration of the crystal. The SrPrGaO$_4$ as-grown crystals were dark green with some red stripes and after annealing in H$_2$-N$_2$ 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 PrAlO$_3$ as-grown sample is similar to that of the Pr$_2$O$_3$. 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 $3d_{3/2}$ and $3d_{5/2}$ lines are split due to final-state configurations of $4f^3\underline{L}$ (where $\underline{L}$ denotes the hole on the O $2p$ valence band) on the low binding energy side (marked as S) and of $4f^2$ on high binding energy side (marked as M) [15, 16]. The Pr $3d_{3/2}$ 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 PrAlO$_3$ samples are similar except one feature. The Pr $3d_{3/2}$ line at about 965 eV for the as-grown PrAlO$_3$ sample (marked as F) has higher intensity than for the annealed sample. This peak may be attributed to $4f^3\underline{L}^2$ final state which indicates the presence of Pr^{4+} ions [15, 18]. The weak $4f^3\underline{L}^2$ satellite predicts mainly trivalent Pr and only a small amount of Pr^{4+}.

In Figure 6, a comparison of the valence band of the as-grown and annealed in reducing atmosphere PrAlO$_3$ 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 $4f$ band maximum at ca. 2 eV below the Fermi energy level and the O $2p$ band at ca. 2 eV above. The Pr $4f$ 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_2O_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 $3d_{3/2}$ 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.

References

[1] PAWLAK D.A., LUKASIEWICZ T., CARPENTER M., MALINOWSKI M., DIDUSZKO R., KISIELEWSKI J., *Czochralski crystal growth, microstructure and spectroscopic properties of PrAlO₃ perovskite*, Journal of Crystal Growth **282**(1-2), 2005, pp. 260–9.

[2] MOUSSA S.M., KENNEDY B.J., HUNTER B.A., HOWARD C.J., VOGT T., *Low temperature structural studies on PrAlO₃*, Journal of Physics Condensed Matter **13**(9), 2001, pp. L203–9.

[3] KENNEDY B.J., PRODJOSANTOSO A.K., HOWARD C.J., *Powder neutron diffraction study of the high temperature phase transitions in NaTaO₃*, Journal of Physics Condensed Matter **11**(33), 1999, pp. 6319–27.

[4] HOWARD C.J., STOKES H., *Group-theoretical analysis of octahedral tilting in perovskites*, Acta Crystallographica Section B: Structural Science **54**(6), 1998, pp. 782–9.

[5] KENNEDY B.J., VOGT T., MARTIN C.D., PARISE J.B., HRILJAC J.A., *Pressure-induced phase transition in PrAlO₃*, Chemistry of Materials **14**(6), 2002, pp. 2644–8.

[6] HOWARD C.J., KENNEDY B.J., CHAKOUMAKOS B.C., *Neutron powder diffraction study of rhombohedral rare-earth aluminates and the rhombohedral to cubic phase transition*, Journal of Physics Condensed Matter **12**(4), 2000, pp. 349–65.

[7] CARPENTER M.A., HOWARD C.J., KENNEDY B.J., KNIGHT K.S., submitted to Physical Review B.

[8] LIU Z., ZHENG Z., HUANG X., LU Z., HE T., DONG D., SUI Y., MIAO J., SU W., *The Pr⁴⁺ ions in Mg doped PrGaO₃ perovskites*, Journal of Alloys and Compounds **363**(1-2), 2004, pp. 60–2.

[9] Czochralski J., *Ein neues Verfahren zur Messung der Kristallisationsgeschwindigheit der Metalle*, Zeitschrift für Physikalische Chemie **92**, 1918, pp. 219–21.

[10] Moulder J., Stickle W., Sobol P., Bomben K., [In] *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics 1995.

[11] Multipak Software Version 6, Physical Electronics 1998.

[12] Talik E., Kruczek M., Sakowska H., Ujma Z., Gała M., Neumann M., *XPS characterisation of neodymium gallate wafers*, Journal of Alloys and Compounds **377**(1-2), 2004, pp. 259–67.

[13] Pawlak D.A., Ito M., Dobrzycki L., Wozniak K., Oku M., Shimamura K., Fukusa T., submitted to Journal of Materials Research.

[14] Pajaczkowska A., Novoselov A., Klimm D., Talik E., Uecker R., *Does valency of Pr ions influence color of SrPrGaO$_4$ single crystals?*, Crystal Growth and Design **4**(3), 2004, pp. 497–501.

[15] Felner I., Yeshurun Y., Hilscher G., Holubar T., Schaudy G., Yaron U., Cohen O., Wolfus Y., Yacoby E.R., Klein L., Potter F.H., Rastomjee C.S., Egdell R.G., *Crystal structure, magnetic properties, X-ray-photoemission-spectroscopy, and specific-heat measurements on Pr$_2$BaO$_4$ and PrBaO$_3$*, Physical Review B: Condensed Matter **46**(14), 1992, p. 9132.

[16] Ogasawara H., Kotani A., Potze R., Sawatzky G.A., Thole B.T., *Praseodymium 3d- and 4d-core photoemission spectra of Pr$_2$O$_3$*, Physical Review B: Condensed Matter **44**(11), 1991, pp. 5465–9.

[17] Schmeisser D., *The Pr$_2$O$_3$/Si(001) interface*, Materials Science in Semiconductor Processing **6**(1-3), 2003, pp. 59–70.

[18] Lutkehoff S., Neumann M., Ślebarski A., *3d and 4d X-ray-photoelectron spectra of Pr under gradual oxidation*, Physical Review B: Condensed Matter **52**(19), 1995, pp. 13808–11.

[19] Grassmann A., Strobel J., Saemann-Ischenko G., Johnson R.L., *Electronic structure of electron-doped superconducting cuprates studied by photoelectron spectroscopy*, Physica B: Condensed Matter **163**(1-3), 1990, p. 261.

[20] Dujardin C., Pedrini C., Gacon J.C., Petrosyan A.G., Belsky A.N., Vasil'ev A.N., *Luminescence properties and scintillation mechanisms of cerium- and praseodymium-doped lutetium orthoaluminate*, Journal of Physics Condensed Matter **9**(16), 1997, pp. 5229–43.