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Photoelectron spectroscopy of Ba-doped lead germanate – $Pb_5Ge_3O_{11}$

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XPS electronic structure measurements of barium-doped lead germanate ($Pb_5Ge_3O_{11}$) single crystals along the principal directions revealed a deviation of stoichiometry, which was the reason for the structural disorder and broadening of the core level lines.

Key words: *lead germanate; single crystal; photoelectron spectroscopy*

1. Introduction

Lead germanate ($Pb_5Ge_3O_{11}$) is a ferroelectric crystal, which attracts attention due to its applicability in electro-optical devices related to its pyroelectric and photorefractive effects [1–3]. The influence of dopant elements – Ba, Ca, Sr, Cu, Mn, La, Nd, Gd – on the electro-optical properties of lead germanate was investigated. Doping affects e.g., the pyroelectric coefficient as well as spontaneous polarisation and causes a distinct shift in the temperature of the para-ferroelectric phase transition. Its crystal structure consists of layers arranged alternately along the *c* axis within a Pb frame. These layers consist of germanate groups: GeO_4 tetrahedra and Ge_2O_7 double tetrahedra (Fig. 1) [4]. The properties of lead germanate show a marked anisotropy due to the uniaxial structure, e.g. in electric permittivity, piezoelectric and electrostrictive constants, refractive index, electro-optic coefficients, and elastic constants. The electric conduction of undoped lead germanate crystals is thermally activated, with the activation energy E_a varying from 0.64 to 0.83 eV. Barium ions influence the electric conduction, lowering the activation energy to 0.35–0.51 eV, depending on concentration. Moreover, Ba-doping enhances the pyroelectric coefficient, decreases spontaneous polarisation, and increases coercive field values [5].

The aim of this work is to examine the influence of barium doping on the electronic structure of lead germanate. $Pb_5Ge_3O_{11}$ single crystals, pure and doped with Ba,

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were measured by XPS. Changes in the full width at half maximum with increasing Ba content were observed. The core levels are sensitive to chemical surroundings, therefore XPS spectroscopy is very useful for characterising the chemical environment of elements, especially in the case of disordered materials. According to Lewis et al. [6], core-level X-ray photoelectron spectroscopy probes the local potentials at lattice sites in a solid and hence it should be able to provide information both on averaged site potentials in a disordered alloy and on fluctuations around those averages.

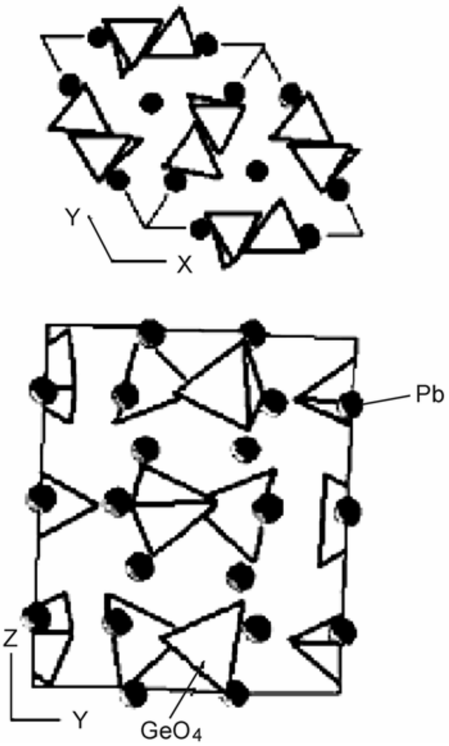

Fig. 1. Projection of the crystal structure on the basal plane after [4]

2. Experimental

Pure lead germanate, $Pb_5Ge_3O_{11}$, and the barium-doped, $Pb_5Ge_3O_{11}$:Ba, single crystals were grown from a melt using the Czochralski technique. The monocrystalline samples were prepared from a boule, transparent light yellow in colour, grown along the [001] direction. The orientation was verified using the standard Laue technique [7–9]. Three $Pb_5Ge_3O_{11}$ single crystals, pure and doped with 10% and 25% of barium, were cut along the *b* and *c* principal directions. The *a* direction is not a principal one but is perpendicular to the *b* and *c* axes (Fig. 2). XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatised Al K_α X-ray radiation (1486.6 eV). A hemispherical mirror analyser was used to analyse the energy of electrons, with the energy resolution of about 0.3 eV. All measurements were performed for monocrystalline samples broken perpendicular to the *a, b,* and *c* directions under UHV conditions at 10^{-8} Pa. In each case, a neutraliser was used due to the charge effect that occurs for non-conducting dielectric samples. The binding energy was determined by reference to the C 1s component set at 285 eV. Each peak of the recorded spectrum is characteristic of a certain electron energy level of a certain element. The electron binding energies are characteristic of each element. The measured binding energies, however, are not absolutely constant, but depend on the chemical environments of functional groups due to the modification of the valence electron distribution. These differences in the electron binding energies in relation to pure elements are called chemical shifts. For XPS investigations it is important to determine the relative concentrations of various constituents. The Multipak Physical Electronics programme enables the quantification of XPS spectra, utilising the peak area and peak height sensitivity factor [10]. The calculation of the standard atomic concentration provides the ratio of each component to the sum of the other elements considered in the data. Only those elements, for which the specific lines were clearly visible in the spectrum, were considered. For these lines, the Shirley background was subtracted, the limit of the region of the lines was individually selected, and the integration was then done. The area following sensitivity factors were used: 9.000 for Pb 4f, 7.343 for Ba $3d_{5/2}$ and 0.733 for O 1s. The accuracy of this method is ±10%.

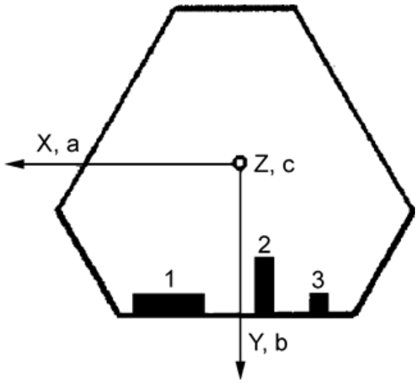

Fig. 2. The crystal habit of a boule pulled along the *c* axis and a sketch of the samples cut for XPS measurements along the: *a* axis – sample 1, *b* axis – sample 2, c axis sample 3

3. Results and discussion

The XPS spectra of the single crystals recorded in the energy range of 0–1400 eV show some contamination with carbon (Fig. 3). The chemical compositions of the pure crystal and the ones doped with 10% and 25% Ba, calculated using the XPS spectra, are collected in Table 1. For all the measured crystals, a lower than nominal concentration of oxygen is observed, indicating the presence of oxygen vacancies. Moreover, an enhanced concentration of germanium, which has the smallest ionic radius in the compound, is observed. This suggests the presence of some germanium as an interstitial atom.

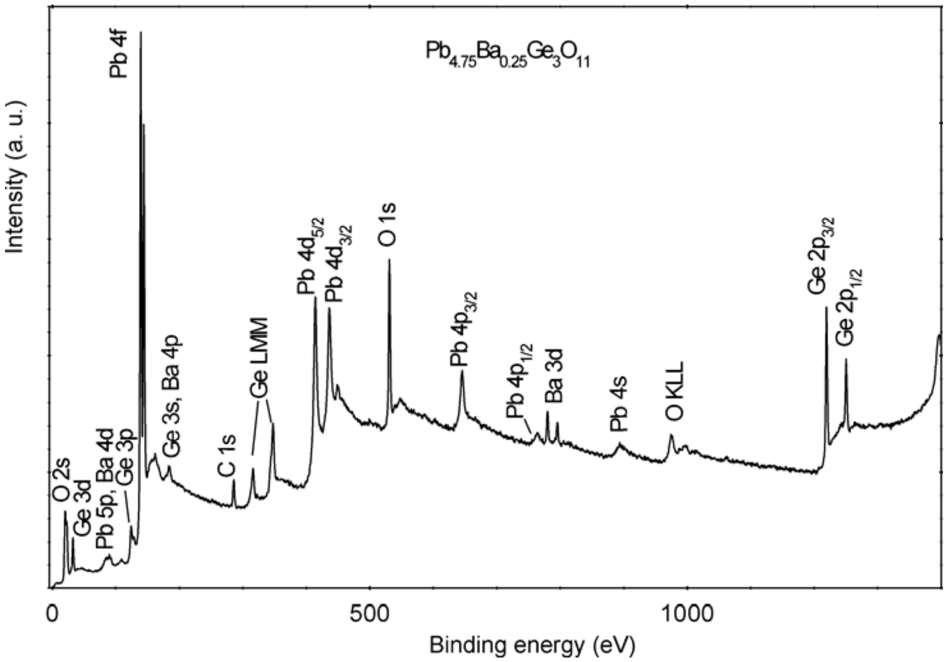

Fig. 3. XPS spectrum of $Pb_5Ge_3O_{11}$: 25% Ba in a wide energy range

Table 1. Chemical compositions of pure and Ba-doped $Pb_5Ge_3O_{11}$

Element	Ba content [wt. %]								
	0			10			25		
	a axis	*b* axis	*c* axis	*a* axis	*b* axis	*c* axis	*a* axis	*b* axis	*c* axis
Pb	5.00	4.86	5.00	5.01	5.00	4.69	5.00	4.86	4.76
Ge	3.28	3.48	3.53	3.30	3.50	3.22	3.21	3.39	3.57
O	10.73	10.66	10.47	10.55	10.43	10.98	10.55	10.50	10.45
Ba	–	–	–	0.14	0.07	0.11	0.24	0.25	0.22

For the pure crystals broken perpendicular to the *a* and *c* directions, the nominal concentration of lead was found. A decrease in the concentration of lead, however, was observed for the crystal broken perpendicularly to the *b* axis. For the crystal doped with 10% of barium, which has the ionic radii similar to lead and the same oxidation state, the concentrations of oxygen and germanium were similar as for the pure crystal. In the planes (*b*,*c*) and (*a*,*c*), the lead concentration is nominal. This indicates that barium is in the interstitial positions. For the (*a*,*b*) plane, lead concentration is lower than the nominal one and in this plane probably only barium atoms are in the Pb sites.

A similar effect is observed for the crystal doped with 25% Ba. Narrow and almost symmetric lines are observed for the planes (*a*,*c*) and (*a*,*b*) where barium probably replaced Pb ions. For the (*b*,*c*) plane, where the concentration of Ba and Pb ions is enhanced, a broadening of the line occurs due to structural disorder. An example is shown in Fig. 4.

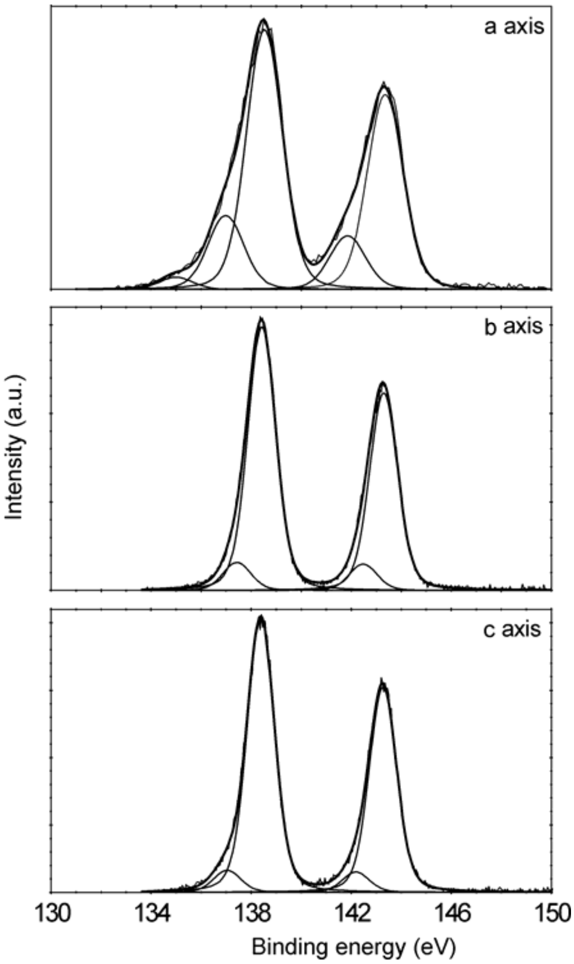

Fig. 4. Pb 4f lines for crystals broken perpendicularly to the *a*, *b*, and *c* directions

The XPS lines are much narrower for these planes (see Table 1) which exhibit the chemical composition in agreement with the nominal one, suggesting a better structural order. It is worthwhile to notice that these directions are the principal ones. For the *a* direction (not principal), all measured lines are broadened due to a more random arrangement of atoms. Moreover, barium ions are probably located not exactly in the lead sites in this direction. These two effects influence the electrostatic charges on the crystal lattice sites. The satellite lines at lower binding energies may be partly related to a not fully neutralized surface and/or partly to disorder, corresponding to the distortion of germanate groups. It is known that variations in bond length and bond angles, such as in amorphous silicon, cause static charge fluctuations in the network [11]. Local variations of valence charge affect electronic structure and lead to a homogeneous broadening of the Si 2p core level, similar to the obtained results.

4. Conclusions

XPS electronic structure measurements of barium-doped lead germanate crystals along perpendicular directions revealed variations in crystal stoichiometry, related to structural disorder and a broadening of the core level lines.

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