

VUV-REFLECTION SPECTRA OF PLUMBUM MOLYBDATE SINGLE CRYSTALS

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The reflection spectra of PbMoO_4 single crystals have been studied in the energy range of $2\text{--}41\text{eV}$ with the use of synchrotron radiation at $T=300\text{ K}$. The spectral dependences of optical functions, characterizing the electron structure of the given compound, have been calculated. It has been shown that the observed structure in the reflection spectra in the range of $h\nu < 20\text{eV}$ is attributed to interband optical transitions, and at $h\nu > 20\text{eV}$ is connected with intracentral transitions in Pb^{2+} . The bulk plasma vibration energy ($h\omega = 26.5\text{eV}$) of the valence electrons has been determined. The determining role of MoO_4^{2-} tetrahedron in the formation of PbMoO_4 band structure is shown. It is assumed that the O 2p electron levels form the valence band, while the conduction band is formed by Mo 4d orbitals.

The XMeO_4 single crystals with the scheelite structure (where $X=\text{Pb,Ca,Sr}$, $\text{Me}=\text{Mo,W}$) are widely used in different acoustooptical devices as the fast deflectors of laser radiation [1], the active elements in solid-state lasers and ionizing radiation detectors in radiative-aggressive media [2]. For successful and effective usage of the given crystals in different optoelectron devices, the knowledge of their electron energy spectrum in the fundamental absorption region is necessary. The certain information about their peculiarities can be obtained from absorption and reflection investigations. In literature only several papers, dealing with the study of reflection spectra of scheelite series in the near-ultraviolet (UV) spectrum region, are known [3-7].

according to the 14 class of accuracy. The measurements were carried out in the plane perpendicular to the c -axes of the crystal.

The spectral dependences of real ϵ_1 and imaginary ϵ_2 parts of the dielectric constant ϵ , the refractive and absorption indices, n and k , respectively, the characteristic loss functions $-\text{Im}(\epsilon^{-1})$, the reduced density of states $\rho \sim \epsilon(h\nu)^2$, the effective number of the valence electrons in the unit cell n_{eff} , and the effective value of the dielectric constant $\epsilon_{0,\text{eff}}$, were calculated from the reflection spectra of PbMoO_4 by means of the Kramers-Kronig relationship according to the method described in [9].

The results of PbMoO_4 reflection spectra measurements are shown in fig.1. The spectral dependences of ϵ_1 and ϵ_2 are also presented in figure. As seen in fig.1, more than 10 reflection maxima, i.e. 3.65eV , 4.64eV , 5.08eV , 5.56eV , 6.8eV , 10.16eV , 10.97eV , 11.5eV , 12.27eV , 15.2eV , 18.1eV , are observed in the reflection spectrum in the energy range measured. The maximum reflection value at 3.65 eV is 45% . In the range of low energy values shown in fig.1 the reflection spectrum of PbMoO_4 has the similar form as other crystals with scheelite structure [3-5].

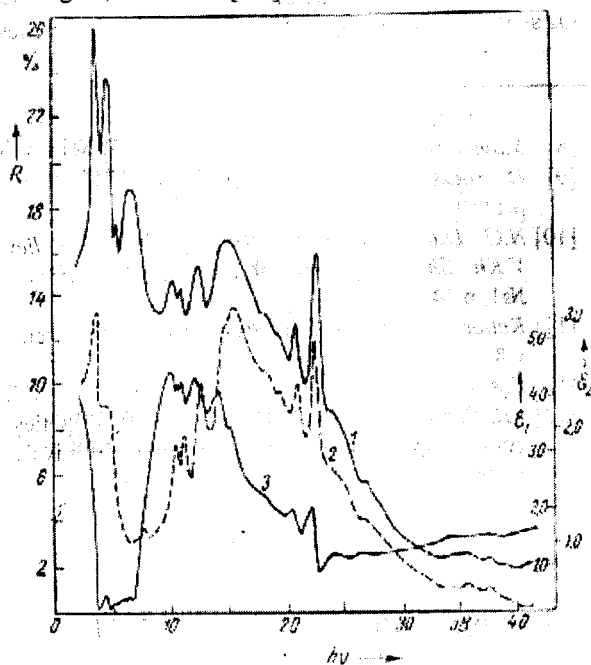


Fig.1 The spectral dependences of the reflection coefficient $R(1)$, real $\epsilon_1(2)$ and imaginary $\epsilon_2(3)$ parts of the dielectric constant in PbMoO_4 .

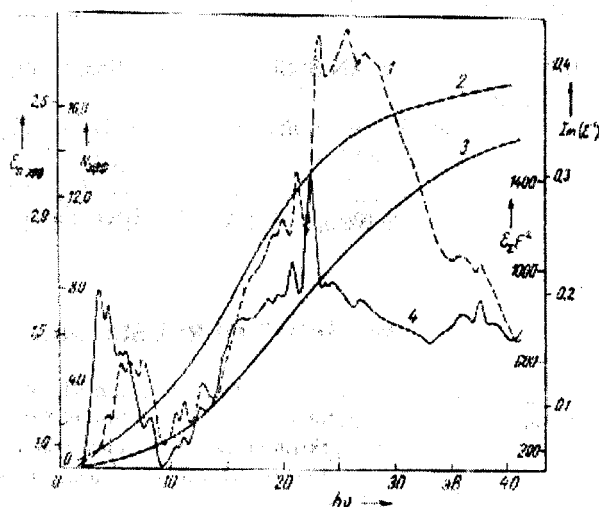


Fig.2 The spectra of the effective value of the dielectric constant $\epsilon_{0,\text{eff}}(1)$, the reduced density of states $\rho \sim \epsilon(h\nu)^2(2)$, the effective number of the valence electrons in the unitcell $n_{\text{eff}}(3)$, the characteristic loss functions $-\text{Im}(\epsilon^{-1})(4)$ in PbMoO_4 .

In the present paper the reflection spectra of PbMoO_4 crystals in vacuum UV region are first investigated with the use of the storage ring of synchrotron center IYAF CO AN RF as the radiation source [8]. The energy region under study was $2\text{--}41\text{eV}$. The PbMoO_4 single crystals grown by the Czochralski method were investigated. The samples with the sizes of $10 \times 8 \times 6\text{ mm}$ cut off along the principal axes of the crystal were mechanically treated, their surfaces were treated

The spectra of ϵ_1 and ϵ_2 well correlate with the reflection spectrum and reach the maximum values in the region

$h\nu=3+16\text{eV}$. The low values of ε_1 and ε_2 indicate on a high degree of ionization of the given crystals. At $h\nu>18\text{eV}$ the decay of optical functions of ε_1 and ε_2 is observed. The $\varepsilon_2(h\nu)^2$, $-\text{Im}(\varepsilon^{-1})$, n_{eff} and $\varepsilon_{0,\text{eff}}$ spectra are shown in fig.2. As seen from the $\varepsilon_2(h\nu)^2$ spectra, the density of states at the optical transitions at 18.1 and 22.2eV is rather high. The analysis of the $-\text{Im}(\varepsilon^{-1})$ spectrum allows to determine the energy of plasma vibrations of free electrons, $\hbar\omega=26.5\text{eV}$. The dependence of $\varepsilon_{0,\text{eff}}$ on the energy $h\nu$ for PbMoO_4 has also a distinct saturation region at energies of $h\nu>21\text{eV}$. It means that the transitions corresponding to the two absorption bands with the maxima at 3.65 and 15.2eV make the most contribution to $\varepsilon_{0,\text{eff}}$. The low value of $\varepsilon_{0,\text{eff}}$ in saturation region also points on the essential role of the optical transitions from the deep d bands to $\varepsilon_{0,\text{eff}}$. The spectral dependence of n_{eff} indicates its continuous increase with distinct steps of growth at 3.65, 15.2 and 30eV, respectively. As n_{eff} is determined only by the behaviour of ε_2 and presents a total oscillator strength, then given steps of growth on the curve of n_{eff} point on the appearance of the new types of optical transitions in the investigated photon energy region.

The band structure calculations [10] and the similarity of reflection spectra of the crystals with scheelite structure in the low-energy spectrum region [3-7] points on the essential role of the MoO_4^{2-} tetrahedral groups in the formation of their band structure [3, 5-7, 10-12].

It is known that the chemical bond in tetraoxyanions is realized by the valence s , p and d - electrons of metal and

$2p$ -electrons of oxygen [3, 5, 10]. In the indicated complex tetraoxyanions the d -electron density of the central atom transforms through the irreducible representations of t and e symmetries, and the $2p$ - electrons of oxygen transform through the t , e , t_1' and a_1 symmetries [10-12]. Theoretical calculations and experimental investigations of mutual position of the X -ray spectra of oxygen and the central atom [11] allow to conclude that for the MoO_4^{2-} tetrahedron, the molecular orbitals, involving the $2p$ -electron density of oxygen are the upper occupied levels, and the d -states of molybdenum characterize the vacant molecular orbitals of the given complex. In this case, the conduction band in PbMoO_4 is splitted into two subbands separated by $\Delta=10.5\text{eV}$. Such splitting is typical for electron states of the d -transition elements in the crystal field [12, 13]. A high value of Δ in PbMoO_4 is connected probably with the role of the heavy Pb atom involved in the scheelite lattice. Due to its large ionic radius and mass, it can considerably effects on the d -state of MoO_4 .

The analysis of the reflection spectra in PbMoO and other compounds containing Pb and Bi, at $h\nu>20\text{eV}$, and also the X -ray photoelectron spectra of tetraoxyanions of transition metals [7,11,12] allow to assert that the observed triplet in the reflection spectrum (20.82; 22.53; 23.83 eV) is caused by intracentral transitions $5d_{5/2} \rightarrow 6p_{3/2}$, $5d_{3/2} \rightarrow 6p_{1/2}$, $5d_{3/2} \rightarrow 6p_{3/2}$ in the Pb ion. But the spectrum peculiarities at $h\nu>30\text{eV}$ (35.4 and 37.55 eV) can be attributed to $\text{O}2s \rightarrow \text{Pb}6p$ transitions. Undoubtedly, some peculiarities take

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MOLİBDAT-QURĞUSUN MONOKRİSTALLARINDA VUB QAYTARMA SPEKTRİ

Sinxrotron şüalanma ilə $T=300\text{ K}$ da 2-dən 41 eV qədər enerji intervalında PbMoO_4 monokristallarında qaytarma spektri öyrənilmişdir. Bu birləşmələrin elektron quruluşunu xarakterizə edən optik funksiyaların spektral asılılıqları hesablanmışdır. Qeyd edilmişdir ki, qaytarma spektrində $h\nu<20\text{ eV}$ oblastında müşahidə olunan struktura zonalarası keçidlərlə, $h\nu>20\text{ eV}$ isə Pb^{2+} daxili keçidlər ilə əlaqədardır. Valent elektronların plazma rəqslərinə uyğun enerjisi təyin edilmişdir ($h\omega=26,5\text{ eV}$). Göstərilmişdir ki, MoO_4^{2-} tetraedri PbMoO_4 sona strukturunun formalaşmasında əsas rol oynayır. O $2p$ elektron səviyyəsinin valent zonanı, $\text{Mo}4d$ orbitalın isə keçirici zonanı təşkil etdiyi söylənilmişdir.

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ВУФ-СПЕКТРЫ ОТРАЖЕНИЯ МОНОКРИСТАЛЛОВ МОЛИБДАТА СВИНЦА

Изучены спектры отражения монокристаллов PbMoO_4 в интервале энергий от 2-41 эВ с использованием синхротронного излучения при $T=300\text{ K}$. Рассчитаны спектральные зависимости оптических функций, характеризующих электронное строение данного

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соединения. Показано, что наблюдаемая структура в спектрах отражения в области $h\nu < 20$ эВ связана с межзонными оптическими переходами, а при $h\nu > 20$ эВ внутрицентровыми переходами в Pb^{2+} . Определена энергия объемных плазменных колебаний ($h\omega = 26,5$ эВ) валентных электронов. Показана основополагающая роль MoO_4^{2-} тетраэдра в формировании зонной структуры $PbMoO_4$. Сделано предположение о том, что электронные уровни O2p образуют валентную зону, а зона проводимости образована $Mo4d$ орбиталями.

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