08

# Ru/Sr multilayer mirrors for the spectral range $9-12$ nm

© R.A. Shaposhnikov, S.Yu. Zuev, V.N. Polkovnikov, N.N. Salashchenko, N.I. Chkhalo

Institute of Physics of Microstructures, Russian Academy of Sciences,
607680 Nizhny Novgorod, Russia
e-mail: shaposhnikov-roma@mail.ru

Received May 6, 2022
Revised May 6, 2022
Accepted May 6, 2022

The results of studies of Ru/Sr multilayer mirrors optimized for the working wavelength range of $9-12$ nm are presented in the paper. Within the framework of the presented article the strontium based multilayer structures with stable over time reflective characteristics were obtained for the first time. It is shown that Ru/Sr mirrors have the highest reflectance of all known reflective coatings, with the exception of beryllium-containing, in the spectral range of $9-12$ nm.

**Keywords:** multilayer X-ray mirrors, X-ray lithography, X-ray radiation.

DOI: 10.21883/TP.2022.08.54562.124-22

## Introduction

One of the spectral ranges of interest for applied and fundamental research is the region of soft X-ray radiation $9-12$ nm.

Among the scientific tasks, solar astronomy can be distinguished. So far, the corona of the Sun has been studied mainly in the longer wavelength part of the spectrum $17-60$ nm. This preference is largely determined by the presence of relatively high (up to 60%) reflection coefficients of multilayer mirrors (MMs) [1]. However, the ions radiating in this region are formed in the middle and lower layers of the solar corona. To study the upper layers, it is necessary to switch to a shorter wavelength range, in which, for example, FeXVIII ions emit ($\lambda = 9.34$ nm) [2]. Ensuring the highest possible temporal resolution of telescopes requires the highest possible values of reflection coefficients.

Another direction related to work in this spectral range is next-generation projection lithography. At this stage of technology development, the possibility of switching to lithography with a wavelength shorter than 13.5 nm [3,4] is being actively discussed. In the range of $10-11$ nm lie the maxima of krypton and xenon plasma radiation [5,6]. The advancement of projection lithography technology into this range is hindered by the lack of sufficient (about 60%) reflection coefficients of the MMs.

Thus, the development of these fields of science and technology is associated with the improvement of the reflective characteristics of the MMs used in optical circuits. This leads, on the one hand, to the need to improve the technological process of synthesis of multilayer structures, and on the other, to the search for alternative pairs of materials that could provide a high reflection coefficient of the mirror due to their optical properties.

The most promising spacer materials (having low absorption) in the spectral range of $9-12$ nm are yttrium and strontium. It is on their basis that it is theoretically possible to create highly reflective (over 60%) MMs. Fig. 1 shows the theoretical dependences of peak values of reflection coefficients for a number of MMs based on Y (Fig. 1, *a*) and Sr (Fig. 1, *b*).

Despite the fact that theoretically Sr-based MMs have a large reflection, the most commonly used spacer material in the range of $9-12$ nm is Y.

It should be noted that for $\lambda > 11.2$ nm, beryllium [7,8] appears to be an even more advantageous spacer material. However, due to the high toxicity of Be, its use is often limited. And in some cases up to $\lambda_L$ silicon (12.4 nm) prefer to use reflective optical elements based on yttrium.

The highest values of the reflection of the MMs based on Y were obtained for Pd/Y with boron carbide barrier layers $B_4C$ (43% at $\lambda = 9.34$ nm) [9] and Ru/Y (54% at $\lambda = 11.4$ nm) [10].

The transition to Sr-based MMs is hampered by the high chemical activity of this element. First of all, Sr interacts with moisture contained in the atmosphere, which leads to rapid oxidation of both magnetron targets of strontium and thin films in the composition of multilayer structures. At the moment, one study is known [11], in which Mo/Sr mirrors were studied. Their reflection coefficient after synthesis was 40.8% at $\lambda = 9.34$ nm. However, within 24h, it dropped to a value below 1% due to the oxidation of strontium layers. Attempts to use barrier layers, as well as a protective layer synthesized on top of the structure, did not lead to positive results.

This paper presents the results of an experimental study of MMs based on Ru/Sr. The influence of barrier layers $B_4C$ on the reflective characteristics of the MMs, as well as temporal stability, is investigated.

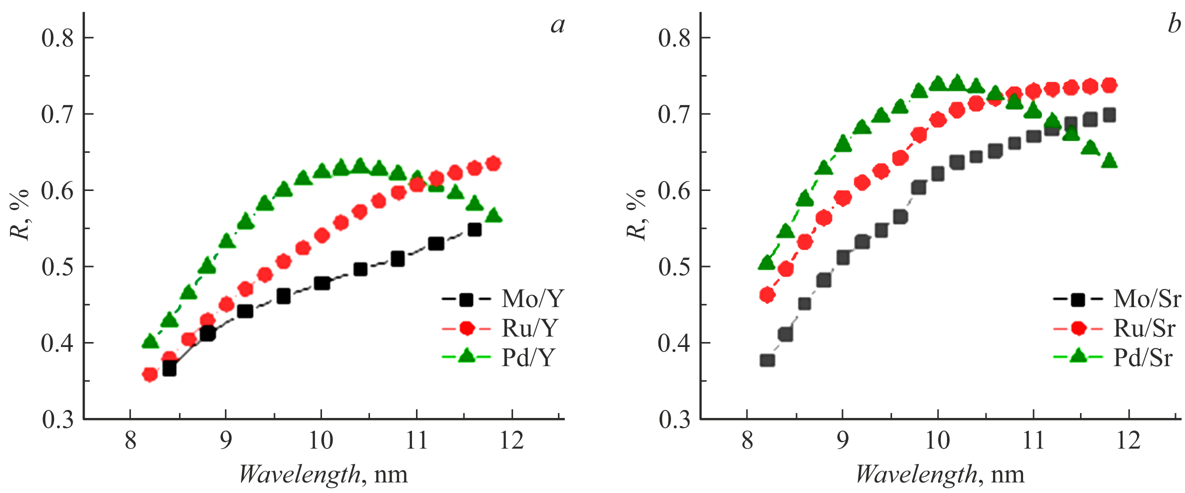


**Figure 1.** Theoretical dependence of the maximum reflection coefficient of Y-containing mirrors (*a* — squares — Mo/Y, Ru/Y —circles, Pd/Y — triangles); Sr-containing mirrors (*b* — Mo/Sr — squares, Ru/Sr — circles, Pd/Sr — triangles) of wavelength.

## 1. Experimental procedure

The MMs synthesis was carried out by magnetron sputtering on an installation equipped with four planar-type magnetrons. Such a number of magnetrons allows operating four materials within one technological cycle. This is fundamentally important for the application of the barrier layer technique. The unit is equipped with a vacuum airlock chamber for loading/unloading samples.

Stabilized current power supplies developed at IFM RAS were used as magnetron power sources. The working gas was high-purity (99.998%) argon. The pressure of the residual gases at the time of the synthesis of the structure was at the level of $10^{-7}$ mm Hg. Working gas pressure at $10^{-3}$ mm Hg. The deposition of the sprayed materials was carried out on single-crystal silicon substrates with a mean square roughness at the level of 0.2 nm.

A separate problem was the operation of a strontium target before placing it in a vacuum chamber. When interacting with the atmosphere, the oxidation of the target surface occurs in tens of seconds. This makes the target unusable. For transportation to the vacuum chamber, the target was placed in a container with toluene. The chamber itself was filled with an inert medium (argon). These precautions allowed the target to be installed inside the camera. The presence of the gateway made it possible to exclude the subsequent interaction of strontium with the atmosphere. The reflective characteristics of the MMs were measured in the hard X-ray range at a wavelength of 0.154nm on a four-crystal diffractometer PANalitycal X'Pert Pro, as well as in the soft X-ray range on a laboratory reflectometer with a monochromator spectrometer RSM-500. Learn more about diagnostic tools and methods in [12]. Samples with protective layers were also measured on the optical line of the BESSY-II synchrotron [13].

The analysis of experimental data obtained as part of these measurements, as well as their modeling carried out using the software Multifitting [14], allow us to determine the main parameters of structures: period, thickness of layers of materials, interlayer roughness.

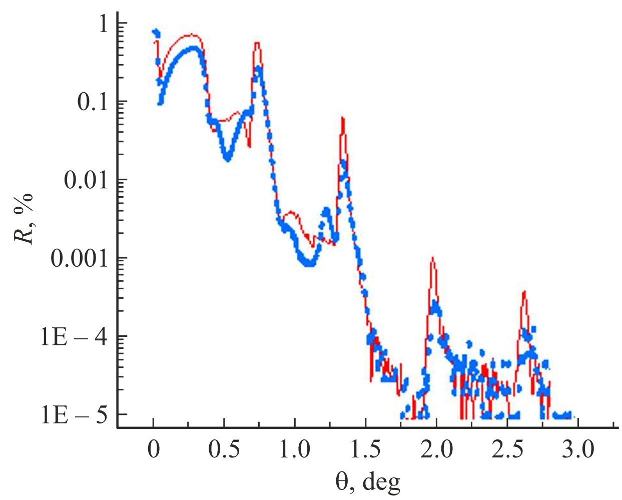


**Figure 2.** Angular dependence of the reflection coefficient of the Ru/Sr mirror at a wavelength of 0.154 nm, measured on the day of synthesis (solid curve) and 2 weeks after synthesis (dotted curve).

It should be noted that as part of this study, no distinction is made between the actual roughness and mixing of materials at the interface. By interlayer roughness we mean their overall effect. Therefore, we will use the term „transition boundary“.

## 2. Experimental results and discussion

The first series of experiments was devoted to the study of two-component MMs Ru/Sr. Fig. 2 shows the results of measuring the dependence of the reflection coefficient of the Ru/Sr mirror on the angle of radiation slip in the hard

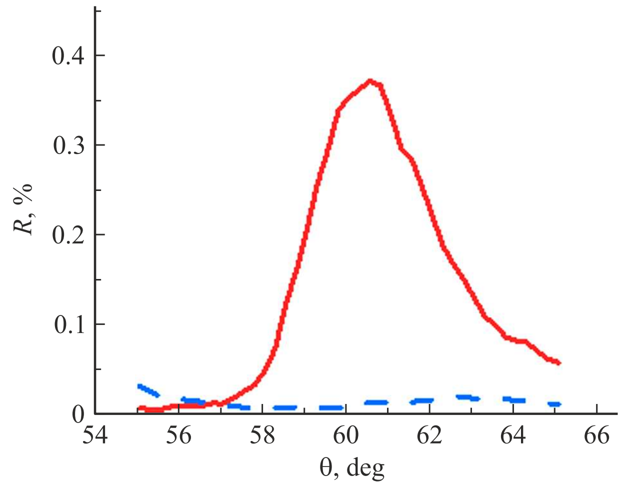


**Figure 3.** Angular dependence of the reflection coefficient of the Ru/Sr mirror at a wavelength of 11.4 nm, measured on the day of synthesis (solid curve) and 2 weeks after synthesis (dotted curve).

X-ray range on the day of synthesis and after 2 weeks. Fig. 3 shows the results of measuring the reflection coefficient of the same MMs at an operating wavelength of 11.4 nm.

From the presented dependencies, it can be seen that the maximum reflection coefficient of the Ru/Sr structure immediately after synthesis was 37% ($\lambda = 11.4$ nm), however, subsequent measurements showed a strong degradation of the reflective characteristics of the mirror, which is due to both mixing of materials in the structure and its oxidation.

The mixing of materials (an increase in the transition boundaries) is indicated by a decrease in the distant (3rd and 4th) diffraction orders in Fig. 2. The oxidation is indicated by the „sagging“ of the inter-peak (between the critical angle and the first order of diffraction, as well as between the first and second orders) sections in the same figure.

Modeling shows that initially the transition boundaries had the following values: Ru-on-Sr 1.1 nm, Sr-on-Ru 0.51 nm. After 2 weeks , they made up: Ru-on-Sr 3 nm, Sr-on-Ru 0.73 nm. Thus, there is a significant asymmetry of borders. The model also included the oxidation of the upper $N = 20$ periods.

At the end of a series of studies of two-component structures, the question of the influence of the upper protective layer was studied. It is assumed that the oxidation of the structure occurs from above. This means that applying a relatively thick protective film over the entire structure will reduce this negative effect. As such a film, we chose a ruthenium film with a thickness of 10 nm.

Fig. 4 shows the angular dependences of the reflection coefficients at $\lambda = 0.154$ nm, taken immediately after the synthesis of the structure with a protective layer of Ru and a month later.

Obviously, unlike the case shown in Fig. 2, this structure is quite stable with respect to oxidation. However, the successful application of a protective coating does not eliminate the problem of extended transitional boundaries.

At the second stage, the influence of barrier layers $B_4C$ deposited on the conditionally „bad“, i.e. a longer Ru-to-Sr interface, was studied. Such a structure had the form sub/Sr/$B_4C$/Ru, where „sub“ denotes the substrate. Fig. 5 shows the results of measuring the angular dependences of the reflection coefficient of this mirror in the hard X-ray region (Fig. 5, *a*) and at the working wavelength (Fig. 5, *b*), as well as the results their modeling.

The period of the studied mirror was $d = 5.87$ nm, the average thicknesses of the layers, according to the model, were: $d\text{Ru} = 2.45$ nm, $d\text{B}_4\text{C} = 0.4$ nm, $d\text{Sr} = 3.02$ nm. The length of the Ru-to-Sr transition border has changed. Even considering $d\text{B}_4\text{C} = 0.4$ nm, it was 0.7 nm. This led to a significant increase in the measured reflection coefficient. From the dependence presented in Fig. 5, it can be seen that the maximum reflection coefficient at the working wavelength is 11.4 nm $R = 62.4\%$.

To study the temporal stability of the reflective characteristics of this structure, additional measurements of its reflection coefficient were carried out at a wavelength of 0.154 nm and at a wavelength of 11.4 nm on the day of synthesis, 9 days after synthesis and 19 days after synthesis. The measurement data are shown in Fig. 6. The data presented in Fig. 6 demonstrate that the Ru/Sr MMs with barrier layers $B_4C$ has significantly better temporal stability of reflective characteristics in comparison with the two-component structure. Thus, the reflection coefficient of the Ru/Sr structure optimized for a wavelength of 11.4 nm fell to values of 1% in 15 days, while the reflection coefficient of the sub/Sr/$B_4C$/Ru structure two months after synthesis is at the level of 60%.

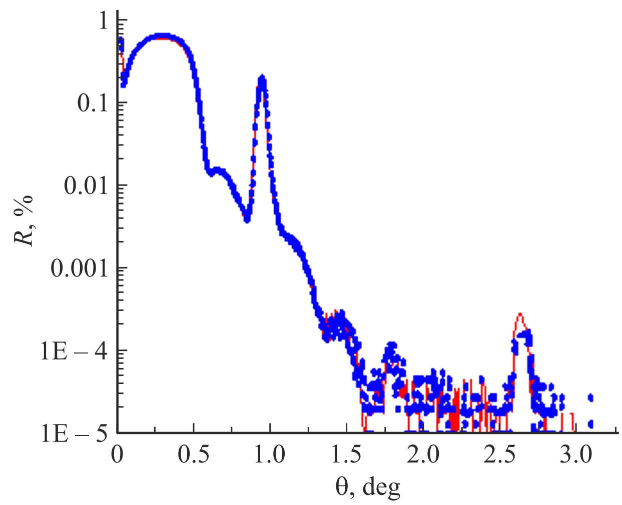


**Figure 4.** Dependence of the reflection coefficient Ru/Sr of a multilayer mirror with a protective layer Ru. The solid curve corresponds to the measurement taken immediately after synthesis, the dotted curve corresponds to the measurement taken a month after synthesis.

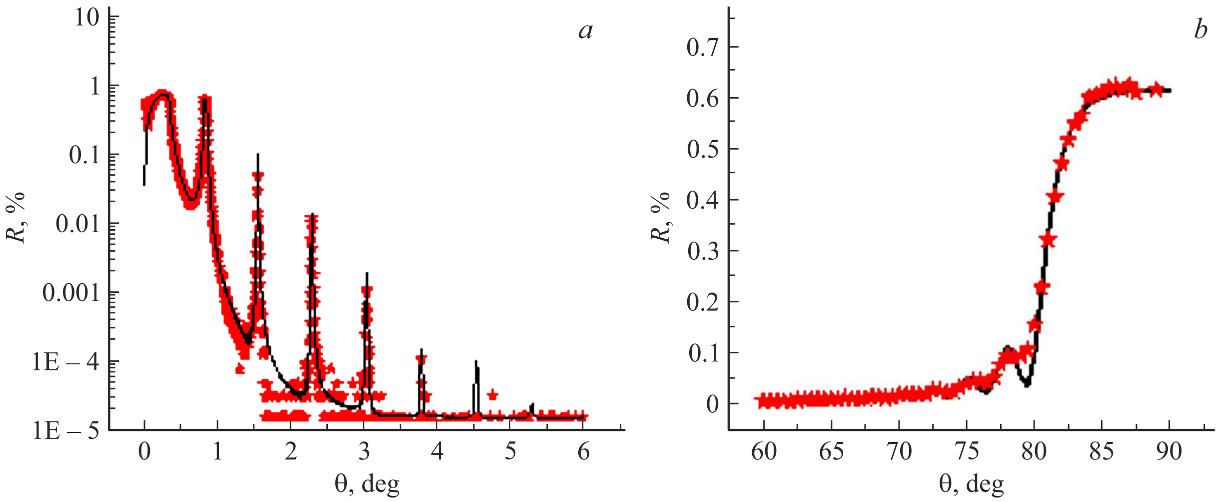


**Figure 5.** Angular dependences of the reflection coefficient sub/Sr/$B_4C$/Ru-mirrors in the hard X-ray range (*a*) and at the working wavelength (*b*). The stars correspond to experimental measurements, a solid curve — modeling performed in the Multifitting program.

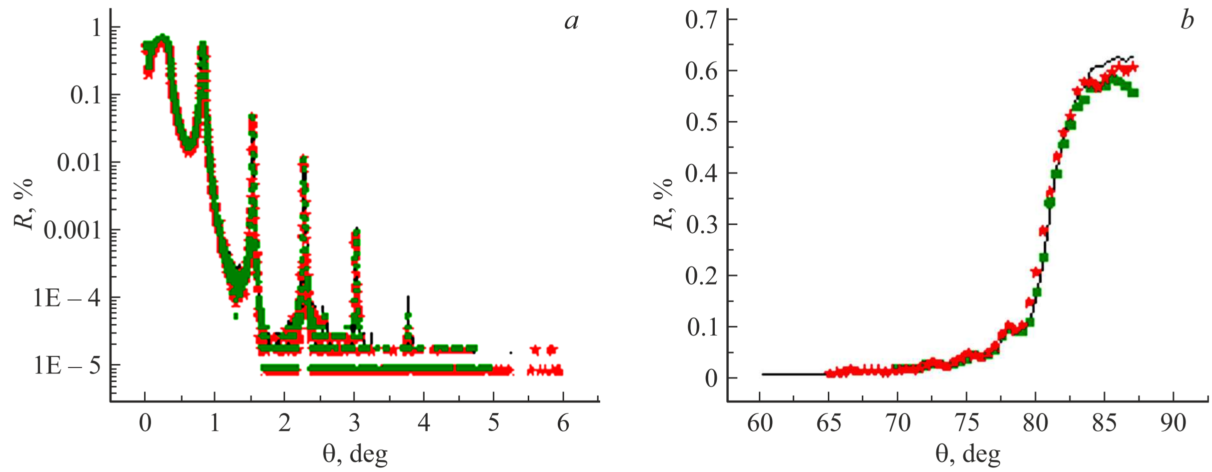


**Figure 6.** Measurement of the reflection coefficient of sub/Sr/$B_4C$/Ru structures at a wavelength of 0.154 nm (*a*) and at a wavelength of 11.4 nm (*b*) in the day of sputtering (solid curve), 9 days after sputtering (red stars (in the online version)) and 19 days after sputtering (green squares (in the online version)).

Thus, it can be concluded that the addition of barrier layers is critically important in the synthesis of strontium-based mirrors. It should be noted that the application of layers $B_4C$ to another boundary (sub/$B_4C$/Sr/Ru structure) did not allow the formation of a mirror with stable reflective characteristics.

The next stage of research was the synthesis of MMs type sub/Sr/$B_4C$/Ru, optimized for an operating wavelength of 9.34 nm. The results of measurements of the angular dependence of the reflection coefficient at a wavelength of 9.34 nm are shown in Fig. 7. It can be seen from the presented data that the structure has a record value of the reflection coefficient $R = 48\%$ at a wavelength of 9.34 nm, which shows the prospects for the application and further research of strontium-based multilayer structures.

The result of the final experiment with simultaneous application of both the protective layer Ru and barrier layers $B_4C$ is shown in Fig. 8 (measurements were performed on the optical line of the BESSY-II synchrotron).

A thick protective layer significantly increases the absorption in the structure, and the reflection becomes noticeably lower: about 40% at a wavelength of 9.34 nm. Given the good temporal stability of the reflective characteristics of the sub/Sr/$B_4C$/Ru structure without a protective layer, it can be concluded that there is no need for an upper protective film.

## 3. Conclusion and future plans

As part of the study presented, multilayer structures based on Ru/Sr were synthesized by magnetron sputtering. In the course of research, Ru/Sr structures were obtained with a reflection coefficient of $R = 37\%$ at a wavelength of 11.4 nm. However, the study of the temporal stability

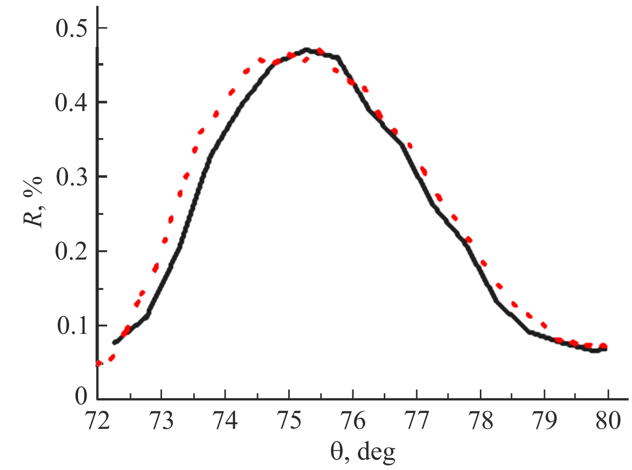


**Figure 7.** Measurements of angular dependences of the reflection coefficient of a multilayer structure sub/Sr/$B_4C$/Ru at an operating wavelength of 9.34 nm. The solid curve corresponds to the measurement taken on the day of synthesis, the dotted curve corresponds to the measurement taken 3 months after synthesis.

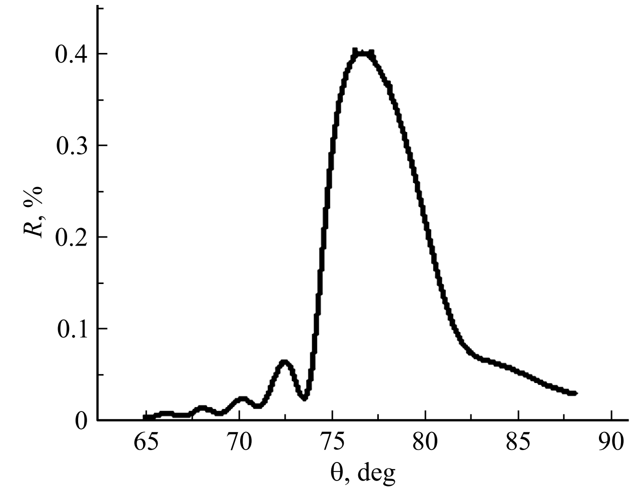


**Figure 8.** The dependence of the reflection coefficient of the Ru/Sr mirror with boron carbide barrier layers on the angle of incidence of radiation measured on the optical line of the BESSY-II synchrotron.

of the reflective characteristics showed that 2 weeks after synthesis, the reflection coefficient of the structure drops to a value of about 1%, which makes its practical use impossible.

It is shown that a significant improvement in temporal stability was achieved by introducing $B_4C$ into the structure of barrier layers. Multilayer X-ray mirrors sub/Sr/$B_4C$/Ru were obtained, which had a reflection coefficient of $R = 62\%$ at a wavelength of 11.4 nm. The repeated measurements of the angular dependence of the reflection coefficient showed that its value does not fall below 60% for at least two months after synthesis. The results obtained also exceed the previously obtained values of the reflection coefficient of multilayer structures sub/Y/$B_4C$/Ru.

As part of the study, multilayer structures of sub/Sr/$B_4C$/Ru optimized for a wavelength of 9.34 nm were also obtained. The obtained values of the reflection coefficient of these structures are $R = 48\%$ and significantly exceed the currently known record values of the reflection coefficient of Pd/Y structures ($R = 43\%$) optimized for this wavelength. Thus, it can be concluded that as part of this study, multilayer structures were obtained with a record value of the reflection coefficient at wavelengths of 9.34 and 11.4 nm, which demonstrates the prospects of using strontium-based multilayer structures to work in the spectral range of 9–12 nm.

## Funding

The study was carried out with the financial support of the Russian Federation represented by the Ministry of Science and Higher Education, agreement No.075-15-2021-1350 dated October 5, 2021 (internal number 15.SYN.21.0004).

## Conflict of interest

The authors declare that they have no conflict of interest.

## References

[1] S.A. Bogachev, N.I. Chkhalo, S.V. Kuzin, D.E. Pariev, V.N. Polkovnikov, N.N. Salashchenko, S.V. Shestov, S.Y. Zuev. Appl. Optics, **55** (9), 2126–2135 (2016).
[2] D. Martínez-Galarce, R. Soufli, D. L. Windt, M. Bruner. Opt. Eng., **59** (2), 095102-1–095102-15 (2013).
[3] N.I. Chkhalo, N.N. Salashchenko. AIP Advan., 3 (8), 082130 (2013).
[4] A.D. Akhsakhalyan, E.B. Klyuenkov, A.Ya. Lopatin, V.I. Luchin, A.N. Nechai, A.E. Pestov, V.N. Polkovnikov, N.N. Salashchenko, M.V. Svechnikov, M.N. Toropov, N.N. Tsybin, N.I. Chkhalo, A.V. Shcherbakov. Poverkhnost'. Rentgenovskie, sinkhrotronnye i nejtronnye issledovaniya, **1**, 5–24 (2017). (in Russian).
[5] A.N. Nechai, S.A. Parakhin, A.Ya. Lopatin, V.N. Polkovnikov, D.G. Reunov, N.N. Salashchenko, M.N. Toropov, N.I. Chkhalo, N.N. Tsybin. Kvant. elektron., **50**, 4 408–413 (2020) (in Russian). DOI: 10.1070/QEL17269
[6] N.I. Chkhalo, S.A. Garakhin, A.Ya. Lopatin, A.N. Nechay, A.E. Pestov, V.N. Polkovnikov, N.N. Salashchenko, N.N. Tsybin, S.Yu. Zuev. AIP Advan., **8**, 105003 (2018).
[7] V.N. Polkovnikov, N.N. Salashchenko, M.V. Svechnikov, N.I. Chkhalo. UFN, **190**, 92–106 (2020). (in Russian). DOI: 10.3367/UFNr.2019.05.038623
[8] Yu.A. Weiner, S.A. Garakhin, S.Yu. Zuev, A.N. Nechai, R.S. Pleshkov, V.N. Polkovnikov, N.N. Salashchenko, M.V. Svechnikov, M.G. Sertsu, R.M. Smertin, A. Sokolov, N.I. Chkhalo, F. Shafers. Poverkhnost'. Rentgenovskie, sinkhrotronnye i nejtronnye issledovaniya, **2**, 3–14 (2020). (in Russian). DOI: 10.31857/S1028096020020168
[9] D.L. Windt, E.M. Gullikson. Appl. Opt., **54** (18), 5850 (2015).

[10] V.N. Polkovnikov, R.A. Shaposhnikov, N.I. Chkhalo, N.N. Salashchenko, N.A. Dyuzhev, F.A. Pudonin, G.D. Demin. Kratkie soobshcheniya po fizike FIAN, **12**, 58–60 (2021). (in Russian).
[11] B. Sae-Lao, C. Montcalm. Opt. Lett., **26** (7), 468–470 (2001).
[12] S.S. Andreev, A.D. Akhsakhalyan, M.A. Bibishkin, N.I. Chkhalo, S.V. Gaponov, S.A. Gusev, E.B. Kluenkov, K.A. Prokhorov, N.N. Salashchenko, F. Schäfers, S.Yu. Zuev. Centr. Europ. J. Phys., **1**, 191–209 (2003).
[13] A. Sokolov, P. Bischoff, F. Eggenstein, A. Erko, A. Gaupp, S. Künstner, M. Mast, J.S. Schmidt, F. Senf, F. Siewert, T. Zeschke, F. Schäfers. Rev. Sci. Instrum., **87** (5), 052005 (2016). https://doi.org/10.1063/1.4950731
[14] M. Svechnikov. J. Appl. Cryst., **53**, 244–252 (2020). https://doi.org/10.1107/S160057671901584X