Materials Research Bulletin 98 (2018) 206–212

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Prediction of perovskite and other ternary oxide multilayers as mirrors for soft X-rays

Kaihang Luo[a], Shanyuan Niu[a], Dhyey Shah[b], Amogh Lonkar[b], Yang Liu[a], Jayakanth Ravichandran[a,*]

[a] Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089, USA
[b] Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089, USA

ARTICLE INFO

Keywords:
Ceramics
Oxides
Optical materials
Optical properties
Multilayers

ABSTRACT

We propose multilayers of perovskite and related ternary oxides with a general formula of ABO_3 as high reflectivity mirrors, especially for use in water window region (2.3–4.4 nm). The high reflectivity combinations of oxide multilayers were deduced using evolutionary search algorithms such as genetic algorithms, and the calculation speed was accelerated *via* parallel computing methods We also propose a figure of merit for X-ray reflectivity in periodic multilayers systems, which can simplify the future efforts on identifying material combinations, and the search through this multi-dimensional parameter space. The highest reflectivity value was found to be over 33% at 3.1 nm in the water window region. The effect of interface roughness was simulated and the decrease in reflectivity was found to be modest for practically achievable roughness values. This work establishes the foundation for future experimental and theoretical studies towards achieving high reflectivity x-ray mirrors of complex oxide multilayers.

1. Introduction

X-ray mirrors are widely used in biological imaging [1], next generation lithography [2], atto-second spectroscopy [3,4], X-ray telescopes [5–7] *etc.* Biological imaging using X-rays provides several advantages such as operation in ambient conditions, wide range of excitation conditions (energy, incident photon flux), high spatial resolution, and the ability to deduce wide range of structural and chemical information using element specific excitations [8]. Particularly, imaging and spectroscopy in the K absorption edges of carbon and oxygen encompassing the X-ray wavelength of 2.3 nm–4.4 nm, also known as water window region, is ideal to study a wide range of biological systems [9]. Despite these obvious advantages, the development of X-ray optics in this wavelength regime for a full-fledged microscope has remained challenging.

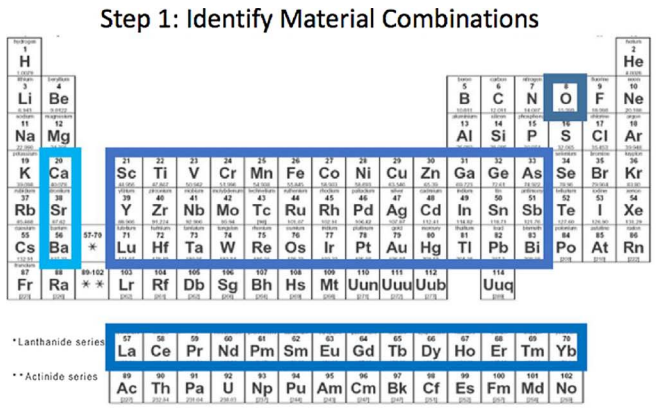
2. Background

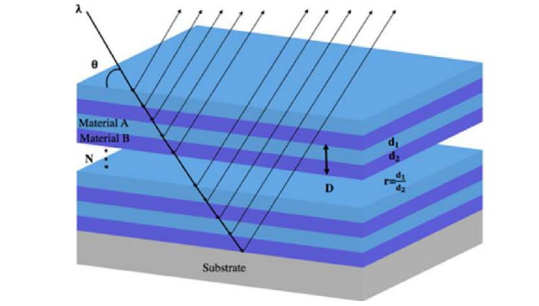
As the refractive index contrast between all the elements, and hence, the materials are small, multilayers of materials, with large index mismatch, are required to create constructive interference between many reflections to achieve sizeable reflectivity. To this end, the absorption edges of elements in the desired wavelength of operation is used to maximize the index mismatch between layers [6,10,11]. In the past, metallic multilayers have been successfully used as X-ray condenser mirrors, but their efficiency have remained much lower than the theoretically achievable values [1,12,13]. While the highest theoretical reflectivity of such a flat mirror was predicted to be 64%, the practical maximum reflectivity in multilayer mirrors achieved is only 15% [12]. The primary reason for such low efficiency is the large interdiffusion coefficients of the metallic components that results in diffuse interfaces with high degree of roughness [9,12]. Recently, several ionic materials such as nitrides and oxides have been considered as alternatives for metallic multilayers. Nitride/Boron Carbide/metal multilayers have shown large reflectivity as high as 23% in the soft X-ray regime [14], Therefore, it is imperative to design and explore multilayer systems *with low interdiffusion coefficients*, which can be grown epitaxially or in amorphous form with abrupt interfaces to achieve large reflectivity and stability in practice.

In this article, we theoretically study the X-ray reflectivity of complex transition metal ternary oxide multilayer systems to identify high reflectivity candidates. As metallic multilayers suffer from diffuse and rough interfaces, alloy formation, and oxidation due to heating or high temperature operation, alternative materials systems especially oxides has been considered [14,15]. As oxygen doesn't absorb X-rays in this wavelength regime, oxides naturally present themselves as an able

* Corresponding author.
E-mail address: jayakanr@usc.edu (J. Ravichandran).

http://dx.doi.org/10.1016/j.materresbull.2017.10.018
Received 11 June 2017; Received in revised form 23 September 2017; Accepted 10 October 2017
Available online 16 October 2017





Step 3: Identify correlation between maximum reflectivity and Figure of Merit

Combination	FOM	R
$CaTiO_3/GdMnO_3$	28.13	28.43
$SrVO_3/LaAlO_3$	5.10	1.86
$CaTiO_3/NdNiO_3$	30.32	32.64
$KNbO_3/BaZrO_3$	9.98	5.57
$YMoO_3/NdFeO_3$	9.45	7.18
$BaVO_3/NdCoO_3$	8.97	12.52
$ScAlO_3/NdCoO_3$	31.82	28.29
...	...	...

Step 4: Identify the maximum reflectivity of high figure of merit material combinations

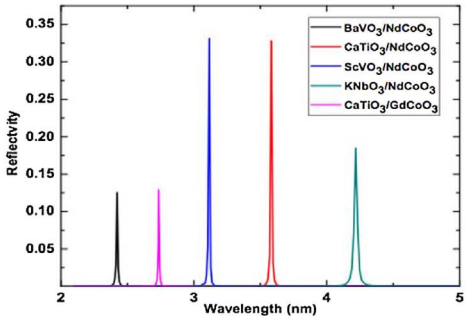


Fig. 1. Schematic of the four steps used to obtain the maximum soft x-ray reflectivity periodic multilayer combinations for perovskite and related ternary oxides to be used in the water window region. Step 1 identifies all the ternary oxide material combinations for the periodic multilayer to construct a database of materials. Step 2 identifies the maximum possible reflectivity achievable in a periodic multilayer of a given material combination amongst the training sets. The multilayer parameters include d_1, d_2, D and r, where d_1 and d_2 are layer thickness, D is total thickness, r is the ratio between top layer thickness and total period layer thickness. Step 3 correlates the training set's maximum reflectivity to material parameters to construct a plausible figure of merit (FOM). Step 4 uses this figure of merit to predict new material combinations amongst the database of materials identified in Step 1 and their maximum reflectivity values and corresponding multilayer parameters.

substitute for metals. Perovskite and other ternary oxides with ABO_3 structure show large chemical and structural diversity due to the ability to accommodate a wide range of cationic species in the A, and B-sites, and hence are ideally suited to provide the necessary flexibility to identify such combinations [16]. Further, these oxides possess stronger ionic bonds, and a close packed structure that leads to low diffusion coefficients under all conditions [17,18], and superior resistance to oxidation or other chemical changes, when compared to metals. As a result, perovskite and related oxide multilayers exhibit much lower interface roughness compared to traditional metallic multilayers [19–24]. Over the years, the growth of perovskite oxides has been perfected to ensure high quality materials with abrupt interfaces, and this feature is key to obtain high reflectivity mirrors in practice [25]. In fact, the structural perfection of complex oxide superlattices have led to demonstrations of acoustic Bragg cavities and mirrors [26], coherent phonon transport [27]. Further the ability to grow high quality perovskite oxides on silicon [28,29] opens a direct route to prepare large area mirrors for practical applications on the wafer scale using thin film deposition methods such as sputtering, PLD *etc* [30–32]. These features make them attractive candidates for X-ray mirrors, which require stability over long periods of time and harsh operation conditions.

3. Methods

The interaction between electromagnetic radiation and matter is dictated by the complex refractive index $n = 1 - \delta + i\beta$. Within the X-ray region, the real part of the refractive index is close to unity for most materials and air, and the imaginary part is vanishingly small, except at the absorption edge, as noted earlier. This causes very weak reflections of X-ray at the air/material or any material/material interface under most wavelength and incidence angles. This problem can be solved by employing X-ray multilayers, where the constructive interference of the reflections from the interfaces in alternating thin layers of material produces large reflectivity under optimal conditions. The method to calculate reflectivity for a multilayer system is essentially a layer based iteration procedure, which was simplified using transformation matrix approaches. This calculation is carried out by solving the Fresnel equations, which describes the law of reflection and transmission of radiation at the interfaces of two homogeneous media. Such theoretical studies can simulate ideal specular reflection at multilayer interfaces, but in practice, the interface roughness or any interface imperfections will introduce a perceptible amount of diffuse scattering at the interfaces. Our simulation was also adopted to calculate the effect of such roughness on the Fresnel coefficients and hence, the reflectivity of the multilayer structure. Such interface imperfections or roughness were characterized using an interface profile function, which is the normalized average value along the z direction of the dielectric function [33]. This approach has already been successfully used to simulate the reflectivity of metallic multilayer, and expect this approach to be fully applicable to the oxide systems too.

The refractive index for a given material can be deduced from the atomic scattering factors and other relevant material parameters [34]. We prepared a master list of materials containing 242 perovskite and other related ternary oxides for which the refractive indices were calculated from the database from The Center for X-ray Optics, Lawrence Berkeley National Laboratory [35]. The selection of materials for the multilayers from this list was dictated by two objectives: (1) to maximize the difference between the real part of refractive index for the two materials, and (2) to minimize the imaginary part to minimize absorption losses. The elements with absorption edge within water