UDK 546:004.032.26
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 48(1)73(2014)

ARTIFICIAL-NEURAL-NETWORK PREDICTION OF HEXAGONAL LATTICE PARAMETERS FOR NON-STOICHIOMETRIC APATITES

NAPOVEDOVANJE HEKSAGONALNIH MREŽNIH PARAMETROV Z UMETNO NEVRONSKO MREŽO

Umit Kockan[1], Fahrettin Ozturk[2,3], Zafer Evis[1,4]

[1]Micro and Nanotechnology Department, Middle East Technical University, 06800 Ankara, Turkey
[2]Department of Mechanical Engineering, Nigde University, Nigde, Turkey
[3]Department of Mechanical Engineering, The Petroleum Institute, Abu Dhabi, United Arab Emirates
[4]Department of Engineering Sciences, Middle East Technical University, 06800 Ankara, Turkey
evis@metu.edu.tr

Prejem rokopisa – received: 2013-03-21; sprejem za objavo – accepted for publication: 2013-04-23

In this study, hexagonal lattice parameters (*a* and *c*) and unit-cell volumes of non-stoichiometric apatites of $M_{10}(TO_4)_6X_2$ are predicted from their ionic radii with artificial neural networks. A multilayer-perceptron network is used for training. The results indicate that the Bayesian regularization method with four neurons in the hidden layer with a tansig activation function and one neuron in the output layer with a purelin function gives the best results. It is found that the errors for the predicted data of the lattice parameters of *a* and *c* are less than 1 % and 2 %, respectively. On the other hand, about 3 % errors were encountered for both lattice parameters of the non-stoichiometric apatites with exact formulas in the presence of the T-site ions that are not used for training the artificial neural network.

Keywords: hydroxyapatite, crystal structure, artificial neural networks, multilayer-perceptron network

V tej študiji so z uporabo umetnih nevronskih mrež napovedani heksagonalni mrežni parametri (*a* in *c*) in prostornina osnovne celice nestehiometričnega apatita $M_{10}(TO_4)_6X_2$ iz njihovih ionskih premerov. Za učenje je bila uporabljena večplastna perceptronska mreža. Rezultati kažejo, da najboljše rezultate daje Bayesianova ureditvena metoda s štirimi nevroni v skriti plasti z aktivacijsko funkcijo 'tansig' in en nevron v zunanji plasti s 'purelin'-funkcijo. Ugotovljeno je, da je napaka pri napovedanih mrežnih parametrih *a* in *c* manj kot 1 % oziroma manj kot 2 %. Po drugi plati pa se srečamo z napako 3 % pri obeh parametrih mreže nestehiometričnega apatita z natančnimi formulami pri prisotnosti ionov na T-mestih, ki niso bili uporabljeni pri usposabljanju umetne nevronske mreže.

Ključne besede: hidroksiapatit, struktura kristala, umetna nevronska mreža, večplastna perceptronska mreža

1 INTRODUCTION

Apatite is a mineral group which normally crystallizes in the space group $P6_3/m$. Apatite is the main source of the phosphorus required by plants. Apatite-group minerals have a general formula $^{IX}M1_4{}^{VII}M2_6(^{IV}TO_4)_6X_2$ (Z = 1), where the left superscripts indicate the ideal coordination numbers and are isostructural with apatite. Numerous mono-, di- and trivalent cation substitutes are found in the M sites and numerous hexa-, penta- and quadravalent polyanions can occupy the TO_4 site. The X site is usually occupied by monovalent anions, however, O^{2-} and H_2O can also reside there.[1] Apatites can be substituted by various elements, but even small amounts of substitutions can make a noticeable effect on the mechanical, thermal and optical properties.[2] Recently, apatite minerals have become very important in the fields of biomaterials, sensors, detoxification of wastes and immobilization of radioactive wastes.[2–4]

Bone is a natural composite material of a mass fraction 69–80 % inorganic phase (carbonated hydroxylapatite), 17–20 % collagen (organic component) and trace amounts of water and proteins.[5] Basically, synthetic hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) belongs to the large chemical family of calcium phosphates (CaP). CaPs are biocompatible, non-toxic, resorbable, non-inflammatory, having an excellent osteoconductive ability and bioactive property. Therefore, it is used as a bone and dental implant and for the coatings on implants, due to its similarity to the inorganic part of the bone.[6] Stability and ion-exchange capabilities mostly depend on the lattice properties. Moreover, the residual stresses in biological apatite coatings cause serious problems. These stresses may result in the wear debris and delamination that can be lethal for the patients because of the toxic effects and biomechanical failure. One of the main reasons of these drawbacks is a structural mismatch caused by the lattice-parameter differences between the substrate and the coating.[7]

It is not easy to prepare single crystals of apatites for X-ray diffraction applications and lattice-parameter determination with other diffraction techniques as electron and neutron diffractions are time consuming and not within the reach of many researchers. Moreover, vast amounts of ion-substitution possibilities exist. Neural networks can generate lattice parameters with a variety of apatite structures using limited numbers of experimental crystal study results for training the network, so that

the experimental work can be eliminated. A neural network is set to solve a relation between the inputs and outputs, which are ionic radii and lattice parameters, respectively. Hence, it is very important to construct a suitable dataset for training the neural network and find the optimum network types and parameters that can assist in generating crystal-structure entities like the lattice parameters of apatites.[8,9]

An artificial neural network (ANN) has a wide range of applications where a large amount of data is available but no reliable physical model is present.[10] The ANN is extensively used to model complex relationships between inputs and outputs. In the program, the training is first performed using the existing experimental data. By using this method, many properties like stress, strain, hardness, toughness, residual stress[11–14] and anything else that has a complex non-linear relationship with the known input variables can be determined without extensive theoretical and experimental studies. For example, the amounts of added chemicals are the input parameters that involve vast possibilities; however, the outputs that depend on the input parameters are normally determined experimentally. Generating large numbers of experimental data may be avoided by training neural networks with small numbers of experimental data if the input variables and the values that affect the searched properties, the outputs of the neural network, are known. Alloy design is particularly efficient with this method.[15]

Pattern recognition and prediction of the lattice parameters of apatites with artificial neural networks were previously studied.[9] Hexagonal lattice parameters of stoichiometric apatites were predicted using artificial neural networks.[16] However, there is not enough detail about the learning methods used for training the network and applicability of the method to non-stoichiometric apatites. The term 'non-stoichiometric' is used to state that M/TO_4, M/X or TO_4 /X ratios are different from the general formula of $M_{10}(TO_4)_6X_2$. In addition, a unit-cell-volume calculation of apatites may amplify the errors coming from the lattice-parameter predictions. The errors between the calculated and predicted unit-cell volumes of apatites were calculated. In this study, non-stoichiometric hexagonal unit-cell lattice parameters and volumes of apatites ($M_{10}(TO_4)_6X_2$), constituted by M: Ca^{2+}, Cd^{2+}, Pb^{2+}, Sr^{2+}, Zn^{2+}, La^{3+}, Y^{3+}; T: As^{+5}, Cr^{+5}, P^{5+}, V^{5+}, Si^{+4}; and X: F^{-}, Cl^{-}, OH^{-}, Br^{-1}, were predicted from their elemental ionic radii using an ANN. Each ion site accepted up to three substitutions and a wide variety of coupled substitutions were investigated. In addition, mathematical formulas were derived for the calculation of the lattice parameters using average ionic radii as independent variables.

2 METHODS

In an ANN, the learning methods compare the predicted outputs with the actual results.[17] Typically 60–80 % of the data is used for training the network, while the rest is used for testing and validating the data. At the end of the training process, the test data is used to check the ability of the network to predict new data.[18] A multilayer-perceptron (MLP) model that maps the sets of input data onto a set of appropriate output with supervised learning and batch training was used because of its high non-linear regression performance.[19] A single hidden layer with different numbers of processing units and various learning methods were experimented to achieve the highest network performance. Sigmoid transfer functions for the hidden layer and linear transfer function for the output layer were used.

Some of the frequent algorithms use a first-order derivative while others use a second-order derivative of the error functions to determine the delta value which is used to adjust the weights of the network.[20] In this study, backpropagation algorithms were used. The experimented backpropagation methods in this study were resilient backpropagation (RP), gradient descent with momentum and adaptive learning rate backpropagation (GDX), levenberg-marquardt backpropagation (LM) and scaled conjugate gradient backpropagation (SCG). In addition to these methods, bayesian regularization (BR), which is a generalization method based on LM, was used.

The backpropagation method is useful for finding a network's weight gradient $\nabla\eta(w)$ easily.[16,21] The details regarding this method were given in a previous study.[16] The performance function of most of the networks is MSE, but the generalization can be improved by modifying the performance function with the mean square of weights and biases. By using this new performance function, the weights and biases were minimized, so the network performance increased.[16,19] The performance ratio is hard to optimize. To do this, the BR method can be used. This method reveals the network parameters (weights and biases) that are being effectively used. This method is especially useful when the inputs and targets fall in the range of [–1,1] or are scaled to fit this range.[19]

An MLP neural network was used for the prediction of hexagonal lattice parameters of apatites from their average ionic radii at the individual sites of M, T, and X. The average ionic radii were calculated by separately giving weight to each ion at sites M, T, and X. The weights given are the mole numbers corresponding to each ion of the apatite formula. Then, the ionic radius of each ion was multiplied by its weight and the values were added to each site. Finally, the value for each site was divided by the corresponding total weight and the average ionic radius for each site was calculated.

Lattice parameters for the training dataset were retrieved from the Joint Committee on Powder Diffraction Standards (JCPDS) database and literature[22,23] with the addition of two extra databases[24,25] and the ionic radii were found from a handbook.[26] The constructed dataset was used for training the network with a proper learning method, neuron number in the hidden layer and activation functions. After training the network, the lattice

parameters of non-stoichiometric apatites were predicted by constructing a test dataset. The outputs of the test dataset were not introduced to the software, so that the prediction accuracy could be verified by comparing the neural networks' lattice-parameter predictions with the experimental data. The formulas and lattice parameters of the apatites that were used for testing, were retrieved from the literature.[27–32] In addition, the volumes of the apatites in the test dataset were calculated using the following equation:[33]

$$V = 2.589 \times a^2 \times c \quad (1)$$

where a and c are the lattice parameters of the hexagonal unit cell.

3 RESULTS AND DISCUSSION

After all the data were collected, several network parameters were identified such as the type of the network, the number of hidden layers, learning methods and normalization functions. The best parameters found for each learning method are given in **Table 1**. The number of neurons in the hidden layer varied between four and seven with the tangent sigmoid function in the hidden layer and pure linear function in the output layer.

The previous works showed that the lattice parameters of apatites depend strongly on the average ionic radii of the M, T and X sites,[9] so to calculate the average ionic radius of each site, the weights were given to the M, T and X sites, with each site accepting up to three ions.The datasets prepared for training the network showed that the data should be kept as small as possible to prevent large deviations of the results and overfitting. After some trial and error, a refined dataset was prepared for the neural-network application as seen in **Table 2**.

In this study, the Matlab Neural Network Toolbox, version 4, was used for training and testing the network. After experimenting with different learning types and neuron numbers for the MLP network, it was seen that all the learning types, except for the BR and the GDX, produced correlation coefficients higher than 0.99. However, their prediction results were not equally successful. The LM, SCG, and BR methods produced satisfactory results, but only the BR method was capable of giving both high-correlation coefficients and most accurate prediction results, so the BR was used as the primary choice for training and testing throughout this study. The network parameters were optimized in order to obtain

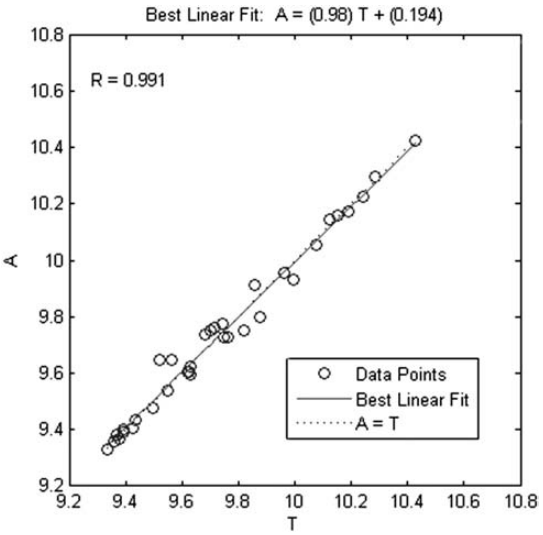

Figure 1: Linear correlation of outputs and targets for lattice parameter *a*
Slika 1: Linearna odvisnost rezultatov in ciljev za mrežni parameter *a*

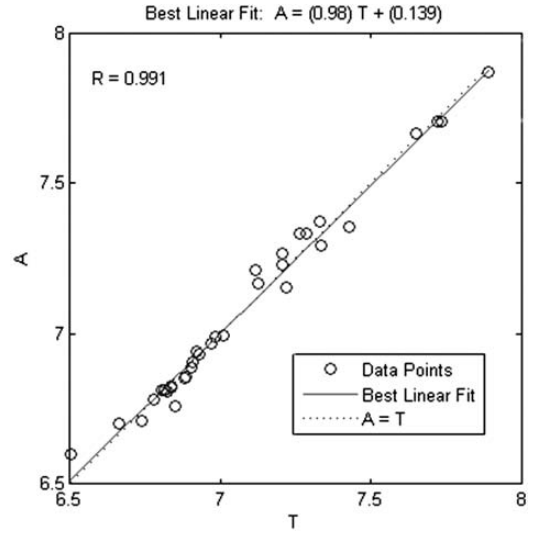

Figure 2: Linear correlation of outputs and targets for lattice parameter *c*
Slika 2: Linearna odvisnost rezultatov in ciljev za mrežni parameter *c*

Table 1: Training parameters for each learning method
Tabela 1: Parametri usposabljanja za vsako metodo učenja

Learning method	Number of neurons in the hidden layer	Activation function used for hidden layer	Activation function used for output layer	Epoch	Momentum coefficient	Learning rate	Train goal
BR	4	tansig	purelin	1000	–	–	–
GDX	7	tansig	purelin	5000	0.8	0.05	1e-3
LM	4	tansig	purelin	400	–	–	15e-4
RP	6	tansig	purelin	5000	–	–	1e-3
SCG	7	tansig	purelin	3000	–	–	177e-5 1e-3 (for *c*)

Table 2: Training dataset and percent errors for the outputs
Tabela 2: Podatki za usposabljanje in napaka rezultatov

	Apatite formula	Average radius *M*	Average radius *T*	Average radius *X*	*a*/(10^{-1} nm)	*c*/(10^{-1} nm)	*a* output	*c* output	Error (%) (*a*)	Error (%) (*c*)
1	$Ca_5 (PO_4)_3 OH$	1	0.38	1.37	9.424	6.879	9.4037	6.8499	0.215	0.423
2	$Ca_5 (VO_4)_3 (OH)$	1	0.54	1.37	9.818	6.981	9.7524	6.9889	0.668	0.113
3	$Ca_5 (CrO_4)_3 OH$	1	0.55	1.37	9.683	7.01	9.7353	6.9945	0.540	0.221
4	$Ca_5 (PO_4)_3 F$	1	0.38	1.33	9.367	6.884	9.3817	6.855	0.157	0.421
5	$Ca_5 (PO_4)_3 Cl$	1	0.38	1.81	9.52	6.85	9.6457	6.7576	1.320	1.349
6	$Ca_5 (AsO_4)_3 Cl$	1	0.46	1.81	10.076	6.807	10.057	6.8122	0.189	0.076
7	$Ca_5 (PO_4)_3 Br$	1	0.38	1.96	9.761	6.739	9.7262	6.7111	0.357	0.414
8	$Cd_5 (PO_4)_3 OH$	0.95	0.38	1.37	9.335	6.664	9.3293	6.7003	0.061	0.545
9	$Cd_5 (PO_4)_3 Cl$	0.95	0.38	1.81	9.625	6.504	9.6019	6.6	0.240	1.476
10	$Sr_5 (PO_4)_3 Cl$	1.18	0.38	1.81	9.859	7.206	9.91	7.2671	0.517	0.848
11	$Sr_5 (CrO_4)_3 Cl$	1.18	0.55	1.81	10.125	7.328	10.144	7.3722	0.188	0.603
12	$Sr_5 (PO_4)_3 Br$	1.18	0.38	1.96	9.9641	7.207	9.9553	7.2315	0.088	0.340
13	$Sr_5 (PO_4)_3 OH$	1.18	0.38	1.37	9.745	7.265	9.7731	7.3304	0.288	0.900
14	$Sr_5 (PO_4)_3 F$	1.18	0.38	1.33	9.7174	7.2851	9.7597	7.3331	0.435	0.659
15	$Pb_5 (PO_4)_3 Cl$	1.19	0.38	1.81	9.993	7.334	9.9297	7.2928	0.633	0.562
16	$Pb_5 (AsO_4)_3 Cl$	1.19	0.46	1.81	10.24	7.43	10.226	7.3553	0.137	1.005
17	$Pb_5 (PO_4)_3 OH$	1.19	0.38	1.37	9.877	7.427	9.7969	7.3545	0.811	0.976
18	$Ba_5 (PO_4)_3 OH$	1.35	0.38	1.37	10.1904	7.721	10.175	7.707	0.151	0.181
19	$Ba_5 (PO_4)_3 F$	1.35	0.38	1.33	10.153	7.733	10.159	7.7079	0.059	0.325
20	$Ba_5 (PO_4)_3 Cl$	1.35	0.38	1.81	10.284	7.651	10.296	7.668	0.117	0.222
21	$Ba_5 (CrO_4)_3 OH$	1.35	0.55	1.37	10.428	7.89	10.423	7.8724	0.048	0.223
22	$Ca_{7.684} Sr_{2.316} (PO_4)_6 (OH)_2$	1.041688	0.38	1.37	9.4955	6.9718	9.4762	6.9692	0.203	0.037
23	$Ca_{3.616} Sr_{6.384} (PO_4)_6 (OH)_2$	1.114912	0.38	1.37	9.6313	7.1246	9.6244	7.1669	0.072	0.594
24	$Ca_{8.98} Sr_{1.02} (PO_4)_6 (OH)_2$	1.01836	0.38	1.37	9.4352	6.9087	9.4345	6.9031	0.007	0.081
25	$Ca_{4.03} Cd_{0.97} (PO_4)_3 (OH)$	0.9903	0.38	1.37	9.391	6.837	9.3881	6.8215	0.031	0.227
26	$Ca_{3.98} Cd_{1.02} (PO_4)_3 F$	0.9898	0.38	1.33	9.379	6.834	9.3647	6.8252	0.152	0.129
27	$Ca_{3.475} Cd_{1.525} (PO_4)_3 F$	0.98475	0.38	1.33	9.36	6.812	9.3566	6.8103	0.036	0.025
28	$Ca_5 (PO_4)_3 F_{0.41} Cl_{0.59}$	1	0.38	1.6132	9.5485	6.8237	9.5379	6.8072	0.111	0.242
29	$Sr_6 Ca_4 (PO_4)_6 F_2$	1.108	0.38	1.33	9.63	7.22	9.5936	7.1525	0.378	0.935
30	$Sr_{7.3} Ca_{2.7} (PO_4)_6 F_2$	1.1314	0.38	1.33	9.565	7.115	9.646	7.2127	0.847	1.373
31	$Ca_{9.37} Sr_{0.63} (PO_4)_6 F_2$	1.01134	0.38	1.33	9.3902	6.9011	9.4012	6.8878	0.117	0.193
32	$Ca_5 (PO_4)_3 F_{0.17} Cl_{0.83}$	1	0.38	1.7284	9.6205	6.7761	9.6012	6.7798	0.201	0.055
33	$Ca_5 (AsO_4)_3 F$	1	0.46	1.33	9.75	6.92	9.7251	6.9385	0.255	0.267
34	$Ca_5 (AsO_4)_3 OH$	1	0.46	1.37	9.7	6.93	9.7503	6.931	0.519	0.014
				Average percent errors of outputs					0.299	0.472

Table 3: Testing the dataset and percent errors for non-stoichiometric apatites
Tabela 3: Preizkus nabora podatkov in delež napake pri nestehiometričnih apatitih

	Apatite formula	Average radius *M*	Average radius *T*	Average radius *X*	*a*/(10^{-1} nm)	*c*/(10^{-1} nm)	*a* output	*c* output	Error (%) for (*a*)	Error (%) for (*c*)
1	$Ca_{9.75} Y_{0.25} (PO_4)_6 (OH)_{1.75} F_{0.25}$	0.9975	0.38	1.365	9.406	6.874	9.3969	6.8433	0.097	0.447
2	$Ca_{9.5} Y_{0.5} (PO_4)_6 (OH)_{1.75} F_{0.25}$	0.995	0.38	1.365	9.408	6.877	9.3928	6.836	0.162	0.596
3	$Ca_{9.25} Y_{0.75} (PO_4)_6 (OH)_{1.75} F_{0.25}$	0.9925	0.38	1.365	9.384	6.86	9.3888	6.8286	0.051	0.458
4	$Ca_{9.75} Al_{0.25} (PO_4)_6 (OH)_2$	0.9885	0.38	1.37	9.4248	6.8812	9.3853	6.8162	0.419	0.945
5	$Ca_{9.5} Al_{0.5} (PO_4)_6 (OH)_2$	0.977	0.38	1.37	9.4252	6.892	9.3677	6.782	0.610	1.596
6	$Ca_{9.25} Al_{0.75} (PO_4)_6 (OH)_2$	0.9655	0.38	1.37	9.4218	6.8807	9.3509	6.7475	0.753	1.936
7	$Ca_{9.5} Mg_{0.82} (PO_4)_6 (OH)_2$	0.9778	0.38	1.37	8.8133	6.8215	9.3688	6.7843	6.303	0.545
8	$Ca_{9.5} Zn_{0.31} (PO_4)_6 (OH)_2$	0.9918	0.38	1.37	8.8972	6.8427	9.3905	6.8259	5.544	0.246
9	$Ca_{9.5} La_{0.14} (PO_4)_6 (OH)_2$	1.0004	0.38	1.37	9.3135	6.8346	9.4044	6.8512	0.976	0.243
10	$Ca_{9.5} Y_{0.23} (PO_4)_6 (OH)_2$	0.9976	0.38	1.37	8.9013	6.8548	9.3998	6.843	5.600	0.172
11	$Ca_{9.5} In_{0.17} (PO_4)_6 (OH)_2$	0.9965	0.38	1.37	8.832	6.8101	9.398	6.8397	6.409	0.435
12	$Ca_{9.5} Bi_{0.10} (PO_4)_6 (OH)_2$	1.0003	0.38	1.37	9.3442	6.8457	9.4042	6.8509	0.642	0.076
13	$Ca_{9.7} Y_{0.2} (PO_4)_6 (OH)_2$	0.9980	0.38	1.37	9.4072	6.877	9.4004	6.844	0.072	0.480
14	$Ca_{9.55} Y_{0.3} (PO_4)_6 (OH)_2$	0.9970	0.38	1.37	9.377	6.859	9.3987	6.841	0.231	0.262
15	$Ca_{9.4} Y_{0.4} (PO_4)_6 (OH)_2$	0.9959	0.38	1.37	9.399	6.8734	9.3971	6.838	0.020	0.515

16	$Ca_{9.25}\ Y_{0.5}\ (PO_4)_6\ (OH)_2$	0.9949	0.38	1.37	9.388	6.8662	9.3954	6.8349	0.079	0.456
17	$Ca_{9.1}\ Y_{0.6}\ (PO_4)_6\ (OH)_2$	0.9938	0.38	1.37	9.3496	6.8544	9.3937	6.8318	0.472	0.330
18	$Ca_{8.55}\ Y_{0.7}\ (PO_4)_6\ (OH)_2$	0.9924	0.38	1.37	9.3384	6.8448	9.3915	6.8278	0.569	0.248
19	$Ca_{9.95}(PO_4)_{5.71}(CO_3)_{0.20}\ (OH)_2$	1	0.373	1.37	9.410	6.879	9.3535	6.8418	0.600	0.541
20	$Ca_{9.46}(PO_4)_5(CO_3)_{1.00}\ (OH)_{1.78}$	1	0.343	1.37	9.394	6.894	9.1013	6.8047	3.116	1.295
21	$Ca_{9.88}(PO_4)_{5.76}(CO_3)_{0.24}F_{1.49}(OH)_{0.51}$	1	0.3712	1.3402	9.382	6.891	9.3241	6.8432	0.617	0.694
22	$Ca_{9.34}(PO_4)_{4.79}(SO_4)_{1.04}(CO_3)_{0.16}(OH)_{1.78}$	1	0.3724	1.37	9.427	6.879	9.3491	6.8411	0.8264	0.5510
23	$La_{8.65}Sr_{1.35}(SiO_4)_6O_{2.32}$	1.0503	0.40	1.40	9.7100	7.2254	9.6257	7.012	0.8682	2.9535
24	$La_{8.65}Sr_{1.35}(GeO_4)_6O_{2.32}$	1.0503	0.53	1.40	9.9120	7.3236	9.8341	7.1225	0.7859	2.7459
25	$La_9Sr_1(SiO_4)_{5.5}(AlO_4)_{0.5}O_{2.25}$	1.045	0.4117	1.40	9.7111	7.2290	9.6746	7.0095	0.3759	3.0364
26	$La_{9.5}(SiO_4)_{5.5}(AlO_4)_{0.5}O_2$	1.03	0.4117	1.40	9.7260	7.2002	9.6509	6.967	0.7722	3.2388
27	$La_{9.33}(SiO_4)_6O_2$	1.03	0.40	1.40	9.721	7.187	9.5919	6.9546	1.3281	3.2336
28	$La_{9.33}(SiO_4)_2(GeO_4)_4O_2$	1.03	0.4867	1.40	9.870	7.257	9.8336	7.0343	0.3688	3.0688
29	$La_{9.33}(SiO_4)(GeO_4)_5O_2$	1.03	0.5083	1.40	9.902	7.276	9.8325	7.05	0.7019	3.1061
30	$La_{9.33}(GeO_4)_6O_2$	1.03	0.53	1.40	9.912	7.283	9.8124	7.064	1.0048	3.0070

Table 4: Percent errors for the calculated volumes
Tabela 4: Delež napake pri izračunanih prostorninah

	Apatite formula	*V* (unit cell)	*V* (predicted)	Error (%) volume
1	$Ca_{9.75}\ Y_{0.25}\ (PO_4)_6\ (OH)_{1.75}\ F_{0.25}$	1574.5	1564.5	0.639
2	$Ca_{9.5}\ Y_{0.5}\ (PO_4)_6\ (OH)_{1.75}\ F_{0.25}$	1575.9	1561.4	0.917
3	$Ca_{9.25}\ Y_{0.75}\ (PO_4)_6\ (OH)_{1.75}\ F_{0.25}$	1564.0	1558.4	0.356
4	$Ca_{9.75}\ Al_{0.25}\ (PO_4)_6\ (OH)_2$	1582.5	1554.4	1.773
5	$Ca_{9.5}\ Al_{0.5}\ (PO_4)_6\ (OH)_2$	1585.1	1540.8	2.793
6	$Ca_{9.25}\ Al_{0.75}\ (PO_4)_6\ (OH)_2$	1581.4	1527.5	3.406
7	$Ca_{9.5}\ Mg_{0.82}\ (PO_4)_6\ (OH)_2$	1371.8	1541.7	12.387
8	$Ca_{9.5}\ Zn_{0.31}\ (PO_4)_6\ (OH)_2$	1402.4	1558.4	11.123
9	$Ca_{9.5}\ La_{0.14}\ (PO_4)_6\ (OH)_2$	1534.9	1568.8	2.209
10	$Ca_{9.5}\ Y_{0.23}\ (PO_4)_6\ (OH)_2$	1406.2	1565.4	11.322
11	$Ca_{9.5}\ In_{0.17}\ (PO_4)_6\ (OH)_2$	1375.3	1564.0	13.720
12	$Ca_{9.5}\ Bi_{0.10}\ (PO_4)_6\ (OH)_2$	1547.5	1568.6	1.365
13	$Ca_{9.7}\ Y_{0.2}\ (PO_4)_6\ (OH)_2$	1575.6	1565.8	0.624
14	$Ca_{9.55}\ Y_{0.3}\ (PO_4)_6\ (OH)_2$	1561.4	1564.5	0.200
15	$Ca_{9.4}\ Y_{0.4}\ (PO_4)_6\ (OH)_2$	1572.1	1563.3	0.555
16	$Ca_{9.25}\ Y_{0.5}\ (PO_4)_6\ (OH)_2$	1566.7	1562.0	0.299
17	$Ca_{9.1}\ Y_{0.6}\ (PO_4)_6\ (OH)_2$	1551.3	1560.8	0.613
18	$Ca_{8.55}\ Y_{0.7}\ (PO_4)_6\ (OH)_2$	1545.4	1559.1	0.889
19	$Ca_{9.95}(PO_4)_{5.71}(CO_3)_{0.20}\ (OH)_2$	1577.0	1549.7	1.731
20	$Ca_{9.46}(PO_4)_5(CO_3)_{1.00}\ (OH)_{1.78}$	1575.1	1459.3	7.352
21	$Ca_{9.88}(PO_4)_{5.76}(CO_3)_{0.24}F_{1.49}(OH)_{0.51}$	1570.4	1540.3	1.917
22	$Ca_{9.34}(PO_4)_{4.79}(SO_4)_{1.04}(CO_3)_{0.16}\ (OH)_{1.78}$	1582.7	1548.1	2.188
23	$La_{8.65}Sr_{1.35}(SiO_4)_6O_{2.32}$	1763.7	1682.1	4.63
24	$La_{8.65}Sr_{1.35}(GeO_4)_6O_{2.32}$	1862.9	1783.3	4.269
25	$La_9Sr_1(SiO_4)_{5.5}(AlO_4)_{0.5}O_{2.25}$	1765.0	1698.6	3.764
26	$La_{9.5}(SiO_4)_{5.5}(AlO_4)_{0.5}O_2$	1763.4	1680.0	4.727
27	$La_{9.33}(SiO_4)_6O_2$	1758.3	1656.6	5.787
28	$La_{9.33}(SiO_4)_2(GeO_4)_4O_2$	1830.3	1761.1	3.782
29	$La_{9.33}(SiO_4)(GeO_4)_5O_2$	1847.0	1764.6	4.461
30	$La_{9.33}(GeO_4)_6O_2$	1852.5	1760.9	4.947

the best results with the BR method. Four processing elements and the tansig activation function were used in the hidden layer, while the purelin function was used in the output layer.

A training dataset constructed from thirty-four data entries was used for the prediction of non-stoichiometric apatites. This dataset was trained using the BR method with four neurons in the hidden layer. The tansig activation function was used in the hidden layer, while the purelin function was used for the output layer. The training dataset can be seen in **Table 2**. The coefficient of determination, R^2, was 0.981 for both lattice parameters as seen in **Figures 1** and **2**. In both figures the vertical axis (*A*) represents the predicted value, while the horizontal axis (*T*) represents the experimental value. In addition, the average error percentage was 0.299 % and 0.472 % for the lattice parameters *a* and *c*, respectively. The results indicate that that training was precise.

After the training of the model, a test dataset constructed from non-stoichiometric apatites was used to predict their lattice parameters. The results of the predictions can be seen in **Table 3**. The data in the first six lines from **Table 3** were not charge balanced and approximate formulas for the apatites were used for the prediction. The errors for the lattice parameters were less than 1 % for *a* and 2 % for *c*. The data in lines seven to eighteen from **Table 3**[27] contained an error of about 5 % due to the measurement errors. The predicted lattice parameters from the approximate formulas of these apatites confirmed the error in the measurements. Four of the generated results had an error of about 5 % for lattice parameter a, but the rest of the predictions were completed with an error of less than 1 % for both lattice parameters.

The data after line nineteen from **Table 3** included virtually exact formulas taken from the literature. The error margins given in these studies for certain apatite formulas were not taken into account to get the results of exact formulas. These apatites produced less accurate results compared to the previous data in the same dataset. The errors for lattice parameter *a* were generally less than or around 1 % with a maximum of 3.116 %. However, the errors for lattice parameter *c* were varying around 3 % which was significantly higher compared to lattice parameter *a*. This was probably due to the complex T sites associated with these apatites. Some of the ions at the T site used for testing the network were not included in the dataset of the training network due to the insufficient experimental data and this resulted in decreased prediction accuracy. Even under these circumstances, the errors for both lattice parameters did not get significantly higher than 3 %.

The volume calculations for the apatites given in **Table 3** are given in **Table 4**. The apatite volumes were calculated successfully except for four cases with an error of about 5 % for lattice parameter a. In addition, the results for the apatites after the nineteenth data entry in **Table 4** were varying significantly, so reliable volume calculations for the apatites with the complex T sites were not possible. These results show that if a training dataset could be improved with the apatites involving different arrangements at the T sites, even the lattice parameters of highly non-stoichiometric apatites could be predicted with high accuracies.

The predictions can be reproduced using equations 2 and 3 for lattice parameters *a* and *c*, respectively. These equations were derived using the final weights and activation functions of the network trained with the BR method:

$$a = -3.5488 \cdot F_1 + 2.0679 \cdot F_2 + 2.1481 \cdot F_3 - \\ -4.6425 \cdot F_4 + 3.6454 \quad (2)$$

$$c = -1.8272 \cdot F_1 + 1.8272 \cdot F_2 + 2.1636 \cdot F_3 - \\ -1.9986 \cdot F_4 + 1.7878 \quad (3)$$

$$F_1 = \frac{2}{1 + exp(-2 \cdot E_1)} \quad (4)$$

The F_i values in these equations are the activation functions of each neuron in the hidden layer, calculated with equation 4. E_i is the weighted sum and its value for the corresponding F_i can be calculated using the equations and final weights given in **Tables 5** and **6** for lattice parameters *a* and *c*, respectively. In **Tables 5** and **6**, C_1, C_2, and C_3 are the final weights of the network corresponding to the average ionic radii R_A, R_B, and R_C, respectively. C_4 is the bias for each processing element.

Table 5: Weights between the input and hidden layer for lattice parameter *a*

Tabela 5: Uteži med vnosom in skritimi plastmi za mrežni parameter *a*

i	$E_i = C_1 \times R_M + C_2 \times R_T + C_3 \times R_X + C_4$			
	C_1	C_2	C_3	C_4
1	–0.29121	–0.37429	–0.93008	–0.68189
2	2.1243	–0.84122	–0.72689	–1.3309
3	–1.0465	–2.5549	0.6731	1.4169
4	–0.075195	–4.125	–0.091451	1.1377

Table 6: Weights between the input and hidden layer for lattice parameter *c*

Tabela 6: Uteži med vnosom in skritimi plastmi za mrežni parameter *c*

i	$E_i = C_1 \times R_M + C_2 \times R_T + C_3 \times R_X + C_4$			
	C_1	C_2	C_3	C_4
1	–0.52211	–0.49087	–0.25122	0.054422
2	0.52211	0.49087	0.25122	–0.054422
3	1.0851	–0.95392	–0.34973	0.51105
4	–0.45506	–1.021	0.044623	0.29596

4 CONCLUSIONS

In this research, hexagonal lattice parameters and unit cell volumes of non-stoichiometric apatites of $M_{10}(TO_4)_6X_2$ were predicted from their ionic radii by an ANN. The results reveal that the lattice-parameter errors for the results of the apatites by the ANN were less than 1 % for *a* and 2 % for *c*, respectively. However, the non-stoichiometric apatites with virtually exact formulas generated the errors of up to around 3 % for both lattice parameters because of their complex T sites. These results indicate that the hexagonal lattice-parameter prediction of the non-stoichiometric apatites with both approximate and exact formulas were reliable, provided that their T sites do not contain large quantities of ions except for the ones used for the training dataset. It is suggested that the accuracy of the predictions could be improved if the training dataset could be modified with the apatites containing different elements at the T sites to overcome the complexity, so that a wider range of possibilities could be investigated for demanding applications where strict lattice parameters are needed for the apatites with the desired elements.

5 REFERENCES

[1] M. Kohn, J. Rakovan, J. M. Hughes, Phosphates: Geochemical, Geobiological and Materials Importance, Mineralogical Society of America, 2002

[2] B. Wopenka, J. D. Pasteris, Mater Sci Eng C, 25 (**2005**), 131–43

[3] S. Peroos, Z. Du, N. H. de Leeuw, Biomater, 27 (**2006**), 2150–61

[4] M. I. Dominguez, J. Carpena, D. Borschnek, M. A. Centeno, J. A. Odriozola, J. Rose, Journal of Hazard Mater, 150 (**2008**), 99–108

[5] J. C. Goes, S. D. Figueiro, A. M. Oliviera, A. A. M. Macedo, C. C. Silva, N. M. P. S. Ricardo, A. S. B. Sombra, Acta Biomater, 3 (**2007**), 773–8

[6] E. Pecheva, T. Petrov, C. Lungu, P. Montgomery, L. Pramatarova, Chem Eng J, 137 (**2008**), 144–53

[7] S. Zhang, Y. S. Wang, X. T. Zeng, K. Cheng, M. Qian, D. E. Sun, W. J. Weng, W. Y. Chia, Eng Fract Mech, 74 (**2007**), 1884–93

[8] J. C. Elliott, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Elsevier, 1994

[9] P. Wu, Y. Z. Zeng, C. M. Wang, Biomater, 25 (**2004**), 1123–30

[10] S. Malinov, W. Sha, Comp Material Science, 28 (**2003**), 179–98

[11] A. Bezazi, S. G. Pierce, K. Worden, E. H. Harkati, Int J Fatigue, 29 (**2007**), 738–47

[12] R. P. Cherian, L. N. Smith, P. S. Midha, Artif Intell Eng, 14 (**2000**), 39–44

[13] M. Col, H. M. Ertunc, M. Yilmaz, Mater & Des, 28 (**2007**), 488–95

[14] C. Karatas, A. Sozen, S. Erguney, Expert Syst Appl, 36 (**2009**), 3514–21

[15] H. K. D. H. Bhadeshia, ISIJ Int, 39 (**1999**), 966–79

[16] U. Kockan, Z. Evis, J Appl Crystal, 43 (**2010**), 769–79

[17] Z. Zhang, K. Friedrich, Comp Sci Tech, 63 (**2003**), 2029–44

[18] P. A. Lucon, R. P. Donovan, Composites Part B, 38 (**2007**), 817–23

[19] H. Demuth, M. Beale, M. Hagan, Matlab Neural Network Toolbox 6, Users Guide, The Mathworks Inc., 2008

[20] S. Samarasinghe, Neural Networks for Applied Sciences and Engineering, Taylor&Francis, 2007

[21] S. I. Gallant, Neural Network Learning and Expert Systems, The MIT Press, 1993

[22] K. Boughzala, E. B. Salem, A. B. Chrifa, E. Gaudin, K. Bouzouita, Mater Res Bull, 42 (**2007**), 1221–9

[23] B. Hamdi, H. E. Feki, J. Savariault, A. B. Salah, Mater Res Bull, 42 (**2007**), 299–311

[24] http://webmineral.com/data/Svabite.shtml.

[25] http://webmineral.com/data/Johnbaumite.shtml.

[26] D. R. Lide, Handbook of Chemistry and Physics, Taylor&Francis, 2003

[27] T. J. Webster, E. A. Massa-Schlueter, J. L. Smith, E. B. Slamovich, Biomater, 25 (**2004**), 2111–21

[28] B. Basar, Z. Evis, Mater Sci Tech, 25 (**2009**), 794–8

[29] Z. Evis, J Ceram Soc Japan, 114 (**2006**), 1001–4

[30] M. Veiderma, K. Tonsuaadu, R. Knubovets, M. Peld, J Organometal Chem, 690 (**2005**), 2638–43

[31] L. Leon-Reina, J. M. Porras - Vazquez, E. R. Losilla, M. A. G. Aranda, Solid State Ionics, 177 (**2006**), 1307–15

[32] J. E. H. Sansom, A. Najib, P. R. Slater, Solid State Ionics, 175 (**2004**), 353–5

[33] Z. Evis, Ceram Inter, 33 (**2007**), 987–91