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Materials Letters 61 (2007) 4777–4780
materials letters
www.elsevier.com/locate/matlet

Predicting thermal conductivity of nanomaterials by correlation weighting technological attributes codes

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Received 11 December 2006; accepted 6 March 2007
Available online 14 March 2007

Abstract

A number of characteristics that include atom compositions, conditions of synthesis and the features of nanomaterials related to their commercial manufacturing have been examined as possible descriptors of a given nanostructure. Using an optimization procedure linked to the Monte Carlo method the special correlation weights have been calculated for each descriptor. A new application of the correlation weights predictive model for the thermal conductivity of nanomaterials has been developed. Statistical characteristics of the model are as follows: $n=43$, $r^2=0.8687$, $s=5.14$ W/m/K, $F=271$ (training set); $n=15$, $r^2=0.8598$, $s=4.91$ W/m/K, $F=80$ (test set).

Keywords: Nanomaterials; Thermal conductivity; Predictive modeling

1. Introduction

The Quantitative Structure–Property/Activity Relationships (QSPR/QSAR) provide efficient tools for predicting the physico-chemical properties and/or biological activities of organic [1–5], inorganic, and coordination compounds [6–8], as well as polymers [9,10]. The QSPR/QSAR modeling is based on a molecular graph that is an elucidation of molecular structure. Also, the alternative molecular graph represented by the Simplified Molecular Input Line Entry System (SMILES) notation has been tested recently [11,12]. The essence of the SMILES approach involves encoding the molecular structure using a set of special symbols that contain information about the presence of different chemical elements and various features of molecular structure, such as *cis*- and *trans*-isomerism, double and triple covalent bonds, etc.

In recent years, a new category of substances the so-called nanostructures has received a lot of attention both from the basic science as well as the industry. However, studies on the environmental effects of such structures are scarce and due to the fact that their fabrication increases every year such effects could accumulate and propagate. Therefore the development of predictive, reliable methods for their properties/activity is an important and urgent aim. Such task provides various challenges since the simple elucidation of the structure of nanomaterials by an analogy to a molecular graph has not been yet successfully accomplished. In fact, nanomaterials have complex associations of atoms involving more than many hundreds or even thousands of units [13].

The thermal properties of nanomaterials in general [14,15] and their thermal conductivity in particular [16] are essential characteristics from the point of view of nanotechnology. The present study aims to define a list of features of nanomaterials, similar to the graph of theoretical attributes of molecular structure, such as the presence of different chemical elements, single, double, and triple covalent bonds, etc. In the case of nanomaterials the role of their attributes, which could be used in constructing a thermal conductivity model may be as follows: to provide information on atom composition, temperature of synthesis, and status of the final product (ceramic, single crystal, glass, bulk and film).

2. Methods

The data on thermal conductivity of nanomaterials used in the present study was taken from the database available via the

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doi:10.1016/j.matlet.2007.03.026

Internet [17]. The twenty attributes of nanomaterials have been selected. These attributes and their codes are as follows:

1) Room temperature, 80, 100, or 150 is %A;
2) 200, or 250 is %B;
3) 273, 300, 315, or 350 is %D;
4) 400 or 425 is %E;
5) 500 or 540 is %F;
6) 600 or 650 is %G;
7) 700 is %H;
8) 800 or 875 is %I;
9) 1000 is %K;
10) 1100 is %L;
11) 1200 or 1250 is %M;
12) 1300 or 1327 is %N;
13) 1400 is %O;
14) 1530 or 1600 is %P.

The temperature is expressed in centigrade degree (Celsius). The second category of the attributes that we considered is defined by the status of the nanomaterials as commercial products. These are as follows:

15) ceramic is CER;
16) Single crystal is SIC;
17) nanomaterial produced in the form of bulk is BULK;
18) nanomaterial produced in the form of film is FILM;
19) nanomaterial produced in cubic form is CUB, and
20) nanomaterial produced in glass form is GLS.

These codes can be converted to the set of SMILES-like representations of the nanomaterials under considerations, which are shown in Table 1. It is to be noted that a comma has also been used as an attribute of the nanomaterial, since the number of commas in different lines are not the same.

The optimal descriptor used in the present study is defined as

$$\mathrm{DCW} = \prod_{k=1}^{N} \mathrm{CW}(\mathrm{CA}_k) \quad (1)$$

where CA_k is the code of the k-th attribute; $\mathrm{CW}(\mathrm{CA}_k)$ is the correlation weight of the CA_k; and N is the number of attributes for a given nanomaterial.

Using the Monte Carlo optimization [3–10,18] for the training set one can calculate the values of all $\mathrm{CW}(\mathrm{CA}_k)$, which produce large values of correlation coefficients between thermal conductivity and the DCW. The numerical data on the CW (CA_k) obtained using Eq. (1) is then used to calculate DCW for each nanomaterial from the training set. An application of the Least Squares method allows to define the thermal conductivity:

$$\mathrm{TC} = C_0 + C_1 * \mathrm{DCW} \quad (2)$$

The predictive ability of Eq. (2) must be validated with nanomaterials of an external validation set. In the present study, the separation of the considered species into training and validation sets has been done randomly, but applying two constraints: (1) all attributes must be presented in the training

Table 1
Experimental and calculated thermal conductivity values (Eq. (3)) for the training and test sets

No.	Codes of the attributes (CA_k) of nanomaterials	DCW	Experimental	Calculated
Training set				
1	Al,N,BULK,CER,%A	1.00386	30.10	30.45
2	Al,N,BULK,CER,%G	1.00104	20.06	19.16
3	Al,Al,O,O,O,BULK,SIC	1.00838	50.00	48.55
4	Al,Al,O,O,O,BULK,CER,%O	0.99828	5.43	8.11
5	Al,Al,O,O,O,BULK,CER,%B	1.00163	22.78	21.53
6	Al,Al,O,O,O,BULK,CER,%C	1.00023	19.64	15.92
7	Al,Al,O,O,O,BULK,CER,%E	0.99903	10.66	11.12
8	Al,Al,O,O,O,BULK,CER,%F	0.99939	14.63	12.56
9	Al,Al,O,O,O,BULK,CER,%I	0.99868	6.69	9.72
10	Al,Al,O,O,O,BULK,CER,%K	0.99833	6.27	8.31
11	Al,Al,O,O,O,BULK,SIC,%A	1.00490	43.05	34.62
12	Al,Al,O,O,O,BULK,SIC,%D	1.00209	19.65	23.37
13	Al,Al,O,O,O,BULK,SIC,%I	1.00081	12.12	18.24
14	B,N,BULK,CER,%D	1.00402	28.72	31.09
15	B,N,BULK,CER,%K	1.00238	26.63	24.53
16	Cr,B,B,BULK,%A	1.00277	26.12	26.09
17	Mo,Si,Si,BULK,CER,%B	1.00587	53.92	38.50
18	Mo,Si,Si,BULK,CER,%F	1.00362	22.15	29.49
19	Mo,Si,Si,BULK,CER,%G	1.00419	23.83	31.77
20	Mo,Si,Si,BULK,CER,%L	1.00051	17.14	17.04
21	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%B	0.99985	6.06	14.40
22	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%E	0.99725	4.60	3.99
23	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%G	0.99818	4.18	7.71
24	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%I	0.99691	3.97	2.63
25	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%M	0.99554	3.76	-2.85
26	Al,Al,Al,Al,Al,Al,O,O,O,O,O,O,O,O,O,Si,Si,O,O,O,O,BULK,CER,%O	0.99650	3.76	0.99
27	Si,C,FILM,CUB,%G	1.00115	27.14	19.60
28	Si,C,FILM,CUB,%I	0.99987	21.32	14.48
29	Si,C,FILM,CUB,%M	0.99850	2.47	9.00
30	Si,C,FILM,CUB,%N	1.00488	34.57	34.54
31	Si,C,FILM,CUB,%P	0.99847	1.34	8.88
32	Si,O,O,BULK,CER,%C	0.99790	1.04	6.59
33	Si,O,O,BULK,CER,%I	0.99635	1.67	0.39
34	Si,O,O,BULK,CER,%P	0.99496	2.51	-5.18
35	Si,O,O,BULK,GLS,%A	0.99862	1.38	9.48
36	Si,O,O,BULK,GLS,%B	0.99748	0.59	4.91
37	Si,O,O,BULK,GLS,%B	0.99748	0.88	4.91
38	Si,O,O,BULK,GLS,%C	0.99610	1.28	-0.61
39	Si,O,O,BULK,GLS,%D	0.99583	1.36	-1.69
40	Si,O,O,BULK,GLS,%D	0.99583	1.43	-1.69
41	Si,O,O,BULK,GLS,%F	0.99526	1.62	-3.97
42	Si,O,O,BULK,GLS,%G	0.99582	1.72	-1.73
43	Si,O,O,BULK,GLS,%H	0.99669	1.80	1.75
Validation set				
1	Al,N,BULK,CER,%E	1.00011	22.15	15.44
2	Al,Al,O,O,O,BULK,CER,%A	1.00277	25.08	26.09
3	Al,Al,O,O,O,BULK,CER,%D	0.99996	15.47	14.84
4	Al,Al,O,O,O,BULK,CER,%G	0.99996	8.99	14.84

Table 1 (*continued*)

No.	Codes of the attributes (CA_k) of nanomaterials	DCW	Experimental	Calculated
Validation set				
5	Al,Al,O,O,O,BULK,CER,%M	0.99731	5.85	4.23
6	B,N,BULK,CER,%H	1.00489	27.00	34.58
7	Mo,Si,Si,BULK,CER,%E	1.00326	30.93	28.05
8	Mo,Si,Si,BULK,CER,%I	1.00291	19.23	26.65
9	Al,Al,Al,Al,Al,O,O,O, O,O,O,O,O,Si,Si,O,O,O, O,BULK,CER,%C	0.99845	5.43	8.80
10	Al,Al,Al,Al,Al,O,O,O, O,O,O,O,O,Si,Si,O,O,O, O,BULK,CER,%K	0.99655	3.76	1.19
11	Si,O,O,BULK,CER,%E	0.99670	1.25	1.79
12	Si,O,O,BULK,CER,%M	0.99499	2.09	-5.06
13	Si,O,O,BULK,GLS,%B	0.99748	0.67	4.91
14	Si,O,O,BULK,GLS,%D	0.99583	1.32	-1.69
15	Si,O,O,BULK,GLS,%E	0.99490	1.50	-5.42

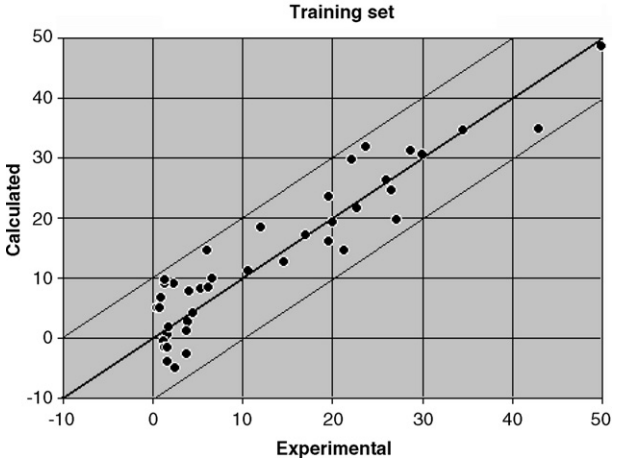

Fig. 1. Plot of experimental versus calculated values of thermal conductivity for the training set.

set; and (2) the diapasons of the thermal conductivity values for training and validation sets must be similar.

3. Results and discussion

Statistical characteristics of the models (obtained in three runs of Monte Carlo optimization) similar to that in Eq. (2) are statistically characterized by: first probe $R_t^2=0.8667$, $R_v^2=0.8576$; second probe $R_t^2=0.8672$, $R_v^2=0.8579$; and third probe $R_t^2=0.8672$, $R_v^2=0.8598$, where R_t and R_v are the correlation coefficients between thermal conductivity and the DCW for the training and validation sets, respectively. Thus, the statistical quality of the models based on the optimal descriptor calculated with Eq. (1) is reproduced and the statistical quality of these models is quite good for both the training and the validation sets. The numerical values of the $CW(CA_k)$ are as follows:

CW(Si)=1.0019472, CW(SIC)=1.0052753, CW(O)=0.9981051, CW(Mo)=1.0008205, CW(N)=0.9986408, CW(GLS)=1.0013297, CW(Cr)=0.9917891, CW(FILM)=0.9965605, CW(C)=1.0022444, CW(Al)=1.0030147, CW(B)=1.0059944, CW(CUB)=1.0064568, CW(BULK)=1.0022868, CW(CER)=1.0031430, CW(,)=1.0000785, CW(%P)=0.9910215, CW(%O)=0.9920073, CW(%N)=0.9973768, CW(%M)=0.9910473, CW(%L)=0.9900339, CW(%K)=0.9920577, CW(%I)=0.9924094, CW(%H)=0.9945386, CW(%G)=0.9936741, CW(%F)=0.9931158, CW(%E)=0.9927537, CW(%D)=0.9936795, CW(%C)=0.9939484, CW(%B)=0.9953345, and CW(%A)=0.9964697.

Using the CWs for the first nanomaterial from Table 1 one can calculate the DCW using the following relationship: DCW=CW(Al)*CW(,)*CW(N)*CW(,)*CW(BULK)*CW(,)*CW(CER)*CW(,)*CW(%A)=1.0030147*1.0000785*0.9986408*1.0000785*1.0022868*1.0000785*1.0031430*1.0000785*0.9964697=1.0038572≈1.00386.

The model calculated with the above numerical data for the CW (AC_k) is as follows:

$$TC\ (W/m/K) = -3988.1 + 4003.1*DCW$$

$n=43$, $r^2=0.8667$, $s=5.18$ (W/m/K), $F=271$ (training set)
$n=15$, $r^2=0.8576$, $s=4.99$ (W/m/K), $F=78$ (test set)

The experimental and calculated values (Eq. (3)) of thermal conductivity for the training and validation sets are shown in Table 1.

Negative values of the thermal conductivity model can be considered as being close to zero. Graphically this model is represented for the training and test sets in Figs. 1 and 2, respectively.

It should be noted that the correlation between thermal conductivity and the molecular structure of "classical" organic compounds is not transparent and straightforward. A model for thermal conductivity described in Ref. [19] is based on nine descriptors (nine-variable correlation). Most of these descriptors have quantum chemical origin. At present an approach that allows for the representation of information concerning molecular structure of nanomaterials is under development. However, the calculation of quantum chemical descriptors for nanomaterials is hardly possible. Moreover, topological (2D) and stereo chemical (3D) descriptors are also unavailable for nanostructures. Most probably quantum chemical predictions for nanomaterials will remain scarce in the foreseeable future.

Although our study does not include molecular parameters obtained from the quantum chemical calculations, the descriptor calculated with Eq. (1) could be redefined in order to reflect the influence of any available parameters (numerical, yes/no-characteristics, conditions of manufacturing, etc.) of nanomaterials for further modeling of their physicochemical and biochemical properties.

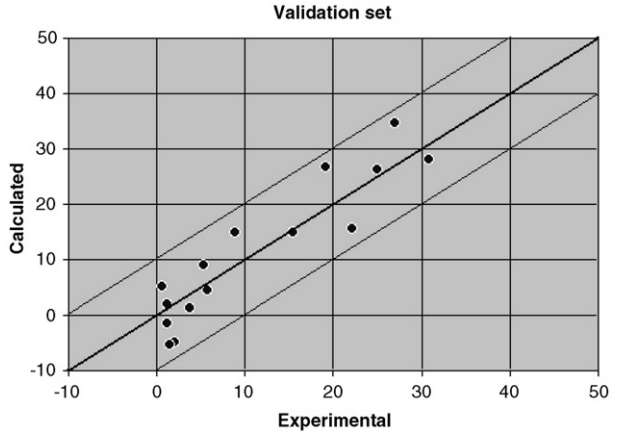

Fig. 2. Plot of experimental versus calculated values of thermal conductivity for the validation set.

We conclude that the descriptor calculated using Eq. (1), being optimized with forty three nanomaterials of the training set, gives a reasonably good prediction of the thermal conductivity for fifteen nanomaterials of the external validation set.

Acknowledgements

The authors would like to thank for the support from the High Performance Computational Design of Novel Materials (HPCDNM) – Contract #W912HZ-06-C-0057 and the Development of Predictive Techniques for Modeling Properties of NanoMaterials Using New OSPR/ASAR Approach Based on Optimal NanoDescriptors – Contract #W912HZ-06-C-0061 Projects funded by the Department of Defense through the U. S. Army Engineer Research and Development Center, Vicksburg, MS.

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