Use of a Genetic Algorithm – Neural Network Hybrid Algorithm in the Search for High Efficiency Solid-State Phosphors

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Abstract: Artificial Intelligence methods have been employed in the search for solid-state phosphors with a high luminescence quantum yield. An Artificial Neural Network was used to investigate how luminescence efficiency can be linked to phosphor composition. The trained network was then coupled to a Genetic Algorithm whose role was to locate the global optimum composition in the search space. The compound Tb$_{0.039}$Gd$_{0.104}$Ce$_{0.063}$Si$_{0.401}$B$_{0.393}$O$_{\delta}$ (where $\delta$ indicates the stoichiometrically-required amount of oxygen) is estimated to be the optimum oxide composition that generates the highest green phosphor luminescence for use in tricolour white LEDs, when excited by a 400 nm light source.

Key-Words: Genetic Algorithm, Artificial Neural Network, phosphor, LED, oxide, hybrid algorithm.

1 Introduction

The use of computer-aided discovery is now common in the development of new materials and the formulation of composites [1]. In the laboratory, high-throughput (HT) experiments of value in the investigation of composites may generate large or complex data sets which are often well-suited to analysis by Artificial Intelligence (AI) methods. Recently, AI has been applied in the study of luminescent materials, where the search for solid-state phosphors with a high quantum yield is an area of considerable interest [2,3]; we report here on further progress in the field.

White-light-emitting diodes (LEDs) are present in applications such as flat-panel displays and solid-state photodetectors [4-7]. Most are phosphor-converted LEDs (pc-LEDs), in which a blue chip and a yellow phosphor combine to produce white light. While yellow phosphors for use in pc-LEDs with the YAG:Ce system are widely available commercially, white light can also be generated by coupling a UV or soft UV chip with RGB phosphors [8, 9]. The lifetime of organic luminescent materials is typically too short for this sort of application, so the RGB phosphors in white LEDs are usually comprised of inorganic oxides [10-12].

Photoluminescence, the emission of photons by excited molecules, is the result of sequential energy transfer between ions in the phosphor matrix (Fig. 1); the overall quantum efficiency of this process determines the amount of light emitted per unit of energy absorbed. Efficient non-radiative energy transfer can occur between ions with matching energy bands, with some ions acting as sensitizers by transferring energy to activator ions, which then emit.

Clusters that contain rare earth ions are especially effective sensitizers, and rare earth elements have been doped into the phosphor matrix

Fig. 1. The processes that lead to photon emission: 1 – absorption; 2 – energy transfer, with shedding of excess energy into the phosphor matrix; 3 – emission.
for over 60 years [13]. More than one rare earth element may be used in a sample to distort the local crystal structure and the crystal field, thereby affecting both the wavelength and intensity of the luminescence.

Although it is possible to develop theoretical models that include all energy transfer mechanisms in a sample to which a single dopant has been added, it is much harder to model the full set of processes that occur in a matrix containing several active luminescent centres. The difficulties can largely be circumvented if luminance can be related computationally to composition without an explicit model of the underlying interactions within the crystal being required. It is that observation which guides the work described here.

2 Formulation of high-efficiency emitters using a Genetic Algorithm
Sohn and co-workers have described the development of oxide-based RGB phosphors for tricolour white LEDs using a Genetic Algorithm-based approach [10,11]. Genetic Algorithms (GAs), a type of Evolutionary Algorithm, use adaptive computational methods to solve optimisation and search problems, seeking a global optimum in a parameter space that includes all the variables in a problem [14].

Genetic Algorithms have been widely applied in science to problems such as the automated synthesis of combinatorial compound libraries [15], drug design [16] and the study of conditions for reactions such as sucrose inversion [17], iron ore sintering [18] and vegetable oil hydrogenation [19]. Among a large number of further applications, a GA algorithm has been used to determine the free energy global minimum of a protein 3D structure from its primary structure [20] and in a search for the optimum structure of alloy nanoclusters [21].

In their study, Sohn’s group drew upon a 154-membered library to screen the oxide system for green phosphors of suitable luminescent properties. Although they viewed their method as combinatorial, it is more appropriately thought of as a high-throughput experiment, since in a combinatorial experiment the nature, rather than the value, of the parameters is changed. Values for the fitness function required by the GA were determined experimentally by synthesizing and testing each compound proposed by the GA. Appropriate quantities of solutions of Gd₂O₃ and Si(OC₂H₅)₄ in nitric acid, and Tb(NO₃)₂, Mg(NO₃)₂·6H₂O, Ce(NO₃)₃, Al(NO₃)₃, and H₃BO₃ in deionised water were prepared and mixed. Water was removed and the residue was dried, pulverised and transferred into a purpose-built ceramic container and fired at 900 °C for 2 h in a neutral N₂ gas atmosphere.

Emission spectroscopy of the fired samples was studied at 400 nm, to simulate the conditions in an InGaN chip (LED light source) and luminance calculated from the emission spectrum and the visual spectral efficacy curve.

Fig. 2. The experimental method used by Sohn et al [10, 11].

Little is known theoretically about how oxide composition determines luminescence efficiency, so the use of a GA by Sohn was in principle a reasonable way to proceed. However, the need to prepare a new oxide sample in the laboratory for every evaluation of the GA fitness function is a serious limitation, so for practical reasons Sohn restricted the number of GA cycles to ten.

This use of an abbreviated period of evolution is understandable, but it carries the danger that the GA might not have converged on an optimized solution when the procedure was halted. In most published applications of GAs to scientific problems, hundreds or thousands of generations are required to locate the global optimum, so Sohn’s conclusion that the optimum composition was found within six generations must be viewed with caution.

3 A hybrid formulation algorithm
The requirement that every sample proposed by the GA be synthesized and tested imposes considerable experimental demands, as Sohn’s group appreciated. However, if luminance is already available for a number of samples of different composition, the GA can be used in a two-step procedure that requires no synthetic work.
3.1 Neural Network

The first step is to model the relationship between composition and efficiency using an Artificial Neural Network (ANN). ANNs are widely applied in science, to problems for which not enough is known about the relationships that exist within the data to allow construction of a theoretical model.

Numerous scientific tasks are in essence pattern-matching, a type of problem to which ANNs are well suited. ANNs have been used in science for spectral interpretation, and in drug design to locate molecules of desired chemical activity by determining Quantitative Structure-Activity Relationships (Q SARs) or Quantitative Structure-Property Relationships (Q SPRs) from experimental data [21, 22]. Extensive data is generated in high-throughput screening and combinatorial experiments, so ANNs are a favourite tool in their analysis [1]. ANNs have been successfully applied in process control [23], to learn relationships between control parameters and production efficiency, and by connecting electronic sensors to the input layer of an ANN, networks can be utilized to recognize complex compounds [24].

Though ANNs have many advantages in pattern-matching, their ability to extrapolate is limited, so one might question whether in the application discussed here an ANN could predict the composition of a compound whose luminance might exceed that of the best member in the training set. However, provided that the training samples cover the composition range of the dopants effectively, it is reasonable to expect that an ANN can learn the relationships between dopant concentration and luminance, and subsequently employ such rules, even if they predict a composition whose light output lies beyond the range of values found in the training set.

The nature and size of the data set determine the optimum geometry of an ANN, though determining that geometry is not always a trivial process [25]. Crucially, networks must contain fewer connections than the number of distinct training samples, otherwise the ANN may learn to recognise each sample individually at the expense of learning about the relations within the data. Sohn’s green phosphor composition library contained 154 samples, a sufficient number to train a network containing several dozen connections.

3.2 Genetic Algorithm

Once the ANN has learnt the relationships contained in this data set, the TANN is coupled to a GA. For each new sample composition created by the GA the TANN is interrogated to obtain a predicted luminance, thus avoiding the need to physically prepare and test a large number of samples. Hybrid systems that comprise a GA and an ANN have been reported before, for example in studies of the effect of adjustable GA parameters on the performance of a heterogeneous catalyst optimization process.

3.3 Training the Neural Network

The hybrid system was programmed in Java. Typical execution times on a 2 GHz PC were 10-15 minutes for the ANN and 3-4 minutes for the GA.

The ANN architecture was a feed-forward multilayer network with logistic activation functions, in which an input node was available for each of the seven elements in the oxide sample; a value for the luminance was predicted through a single output node. The number of hidden nodes in the ANN was selected during network testing. Six samples were removed from the 154-membered composition library to leave a training set of 148 samples.

Networks that contained between three and seven nodes in a single hidden layer were tested, each for up to 2,000,000 learning cycles, at initial learning rates ranging from 0.01 to 0.75. Each network configuration was tested several times, starting from random connection weights, and the predicted luminance used as a measure of the performance of the network.

A variety of combinations of activation and output luminance functions were examined; the best performance was achieved when coupling the output luminance function given in equation 1

\[ f_{\text{lum}}(x) = 400 \times (x - 0.2) \]  

in which \( x \) is the activation level of the output node, with the activation function,

\[ f_{\text{act}}(I_o) = \frac{1}{1 + e^{0.5 - I_o}} \]

in which \( I_o \) is the integrated input signal to the node. \( f_{\text{lum}} \) distributes luminance values between 0 and 240 across the most responsive region of the logistic function, while tolerating higher values. \( f_{\text{act}} \) is the logistic activation function shifted by 0.5 in the positive \( x \)-direction. This modification maintains positive connection weights, to counteract a bias towards negative values which may emerge, since the mean of the training set values is in the lower operating range of the output luminance function.
Over a range of trials, it was found that a network containing five hidden nodes in a single layer leads to the lowest mean error (Fig. 3.). Networks that contain fewer than five hidden nodes failed to fully learn the rules in the data, while larger networks were susceptible to overfitting.

An appropriate learning rate is essential for effective learning. At any stage of training, the current learning rate depends upon both the initial rate, and on the total number of learning cycles to be executed, so the values of these parameters should be optimized simultaneously. The lowest prediction error, of less than 5% in a network with five hidden nodes and trained for 1,000,000 epochs, used an initial learning rate of 0.25.

3.4 Optimization of Genetic Algorithm parameters
Each GA string encoded the composition of a trial compound, defining the number of moles of each element in the molecular formula. The average luminance of the population, the highest luminance and the corresponding sample composition values were tracked as a function of generation.

Just as the degree to which a neural network is able to learn is correlated with network geometry and the values of the training parameters, so the effectiveness of the GA is influenced by the values of the parameters that define the evolution of the population. A large number of preliminary GA runs were performed to determine the effect of the population size on the speed of convergence and quality of solution, and to select the optimum parameters to be used in the hybrid system.

Stochastic remainder selection was used in the GA to select strings into the parent pool. The offspring generation was created through single-point crossover. The crossover and mutation rates were selected through experiments with a variety of combinations of values during this testing. GA populations between 10 and 500 were tested with crossover rates that ranged from 0.6 to 0.9 and mutation rates from 0.05 to 0.2, for up to 10,000 generations, both with and without elitism.

A population size of 40 strings was found to retain sufficient genetic diversity for the algorithm to converge reliably on solutions close to the global optimum (Fig. 5.); improved solutions continue to appear over a period of several hundred generations, with convergence promoted through the use of elitism. The algorithm was normally run for 1,000 generations, with convergence to an unchanging solution typically occurring around generation 500.
Fig. 6. Average and highest luminance as a function of generation; the crossover rate, $p_c$, was 0.6.

Fig. 7. Average and highest luminance as a function of generation; the crossover rate, $p_c$, was 0.8.

The rate of convergence was found to depend markedly on the crossover rate. An increase in the value of $p_c$ from 0.6 to 0.8 results in an increase of the speed of convergence without a reduction in the quality of the final solution (Figs 6, 7).

Fig. 8. Average and highest luminance as a function of generation; the mutation rate, $p_m$, was 0.05.

Fig. 9. Average and highest luminance as a function of generation for a GA run with a mutation rate, $p_m$, of 0.2.

Figures 8 and 9 show that variation in the mutation rate $p_m$ from 0.05 to 0.2 had only a modest effect upon the speed of convergence. The use of elitism, combined with stochastic remainder selection, allows the use of a fairly aggressive mutation rate and a value of 0.2 for $p_m$ was used in the final system.

3.5 Hybrid system parameter optimisation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. hidden nodes</td>
<td>5</td>
</tr>
<tr>
<td>ANN Learning rate</td>
<td>0.25</td>
</tr>
<tr>
<td>ANN No. of learning cycles</td>
<td>1000000</td>
</tr>
<tr>
<td>Population</td>
<td>40</td>
</tr>
<tr>
<td>No. of GA cycles</td>
<td>1000</td>
</tr>
<tr>
<td>GA crossover rate</td>
<td>0.8</td>
</tr>
<tr>
<td>GA mutate rate</td>
<td>0.2 per string</td>
</tr>
</tbody>
</table>

Table 1. Key parameters.

Key parameter values are listed in Table 1.

Once the values of all adjustable parameters had been selected, the hybrid system was executed repeatedly to investigate the accuracy and reproducibility of the results. Each instance of network training generates a different ANN model, since learning starts from a unique, random set of connection weights; nevertheless all converged networks should reach a similar conclusion about how luminance is related to composition. Consequently, the GA should in turn converge on approximately the same composition each run, provided that the ANN has trained effectively.
Figure 10 shows the average and highest luminance values during a typical run with optimized parameters. The best solution achieved by the GA during this run was 273.68. In contrast, the highest luminance value attained by Sohn and his co-workers was 198.89.

Table 2 contains the composition of the samples of highest luminance from five separate hybrid system runs. It is apparent that the model effectively eliminates magnesium- and aluminium-containing compounds in the search for the phosphor of highest luminance. Figure 11 shows how the elemental composition of the highest luminance string in the population varies as the calculation proceeds, confirming that the amounts of Magnesium and Aluminium decrease to negligible levels during the first two hundred generations. The composition of the highest luminance string is close to that of the optimum composition after 260 generations. While the hybrid approach described here and the combined computational-experimental method of Sohn are not equivalent, Figure 11 does suggest that were the time available for further laboratory-based experiments, Sohn’s approach might well have yielded samples of luminance greater than the value of 199 that they reported.

Table 2. Compositions predicted by five successive runs of the hybrid system.

<table>
<thead>
<tr>
<th>Run</th>
<th>Tb</th>
<th>Gd</th>
<th>Ce</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>B</th>
<th>Luminance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0432</td>
<td>0.1005</td>
<td>0.0588</td>
<td>3.71 \times 10^{-9}</td>
<td>0.4102</td>
<td>8.35 \times 10^{-7}</td>
<td>0.3873</td>
<td>268.951</td>
</tr>
<tr>
<td>B</td>
<td>0.0379</td>
<td>0.0973</td>
<td>0.0618</td>
<td>6.81 \times 10^{-9}</td>
<td>0.3975</td>
<td>7.22 \times 10^{-8}</td>
<td>0.4055</td>
<td>265.477</td>
</tr>
<tr>
<td>C</td>
<td>0.0398</td>
<td>0.1021</td>
<td>0.0601</td>
<td>4.23 \times 10^{-7}</td>
<td>0.4011</td>
<td>9.01 \times 10^{-8}</td>
<td>0.3969</td>
<td>273.682</td>
</tr>
<tr>
<td>D</td>
<td>0.0349</td>
<td>0.1057</td>
<td>0.0646</td>
<td>6.72 \times 10^{-9}</td>
<td>0.4063</td>
<td>5.88 \times 10^{-8}</td>
<td>0.3885</td>
<td>270.306</td>
</tr>
<tr>
<td>E</td>
<td>0.0393</td>
<td>0.1146</td>
<td>0.0689</td>
<td>5.1 \times 10^{-14}</td>
<td>0.3916</td>
<td>2.85 \times 10^{-9}</td>
<td>0.3856</td>
<td>267.714</td>
</tr>
</tbody>
</table>

The average composition of samples in Table 2 is Tb_{0.039}Gd_{0.104}Ce_{0.063}Si_{0.401}B_{0.393}O_{5} with average luminance estimated to be 269.2 ± 4% (the error was estimated from the network training error). The luminance of the proposed compound is comparable with that of a commercially available ZnS:Cu,Al green phosphor.

Table 3 shows the compositions of all strings in the population in the last generation of a typical run, ordered by decreasing luminance. The top fifteen strings are similar to that of optimum composition, while, as one would anticipate, those near the bottom of the table are of poor quality, because of the disruption caused in the strings by the genetic operators.
4 Discussion
The compound predicted by the hybrid system as having the highest luminance comprises the same elements as that proposed by Sohn, but is primarily boron- and silicon-based, indicating a borosilicate phosphor matrix. By contrast, Sohn’s compound is primarily silicon and is therefore essentially a silicate phosphor matrix. A number of studies have shown that a borosilicate phosphor matrix is a
medium for the activator ions that emit, not itself the origin of the emission [26].

Rare-earth elements are usually doped into the matrix to achieve higher luminescence [27]. In phosphors of this type the optical transitions connect energy levels of a given 4f configuration. The 4f electron shell is well shielded by the 5s² and 5p⁶ shells, therefore, the energy levels originating from the 4f⁰ configuration relate to states in which the chemical bonding is the same [5]. Consequently, the rare-earth doped phosphor matrices exhibit very specific and favourable luminescent properties.

Cerium and terbium co-doping has been widely reported in phosphor matrices [28], including the borosilicate system [29]. Since the proposed compound contains small amounts of both cerium and terbium, it is instructive to examine the energy levels of the two ions and the energy transfer process between them that leads to luminescence.

Moon and co-workers [29] studied energy transfer between Ce³⁺ and Tb³⁺, whose energy levels are resonant in borosilicate glasses (Fig. 12). They recognised that donor Ce³⁺ ions act as sensitizers by transferring absorbed energy to Tb³⁺ ions via a non-radiative mechanism. Spectroscopic overlap near 425 nm of the strong Ce³⁺ emission band and the weak band from Tb³⁺ emission is a necessary condition for Ce³⁺ to Tb³⁺ energy transfer.

![Fig. 12. The energy level system of Ce³⁺ and Tb³⁺ ions in borosilicate glass.](image)

From time-resolved spectra, Moon et al determined that the Ce³⁺ to Tb³⁺ energy transfer process has a 20 ns time delay and leads to quenching of the shorter-wavelength side of the Ce³⁺ emission band [29].

In a study of energy transfer between Tb³⁺ and Ce³⁺ ions, Changhong and Fuxi [30] established that the emission intensity of Tb³⁺ (⁵D₄ → ⁷F₅, 542 nm) in (Ce³⁺ / Tb³⁺) doubly doped glass is much higher than in glass singly-doped with Tb³⁺, suggesting luminescent sensitization of Tb³⁺ by Ce³⁺. By measuring the energy transfer efficiency from Ce³⁺ to Tb³⁺ they showed that the transfer probability is proportional to the square of the total ion concentration. It follows that the transfer probability is inversely proportional to the sixth power of the average inter-ion distance, which is consistent with a dipole-dipole resonant non-radiative process.

The role of Gadolinium, which is also present in the proposed compound, has been studied by Baccaroa and co-workers [28]. They achieved a significant enhancement of photoluminescence for Ce(Tb)-doped and Gd-enriched phosphors compared to those that were Gd-free, due to nearly resonant energy migration through the Gd sub-lattice. A high concentration of Gd³⁺ ions (> 20%) is required for this migration and this mechanism is not unique to Gd³⁺; it has also been observed in Tb³⁺ and Eu³⁺ compounds [31]. However, due to the
stability of the half-filled shell in the Gd\(^{3+}\) (4f\(^7\)) ion, the excited level (\(6P_{7/2}\)) lies at a much higher energy than in these ions. Thus, the Gd\(^{3+}\) ion emits photons in the UV region at around 315 nm [32]. These optical transitions within the 4f shell are parity and spin forbidden, so the oscillator strength is low and Gd\(^{3+}\) requires sensitizing by another species.

Blasse [32] confirmed that in a Ce-Gd-Tb system, Ce\(^{3+}\) acts as a sensitizer by absorbing energy from the excitation source and Tb\(^{3+}\) acts as an activator by trapping the excitation energy that migrates along the Gd\(^{3+}\) sub-lattice. The energy transfer process can be represented as:

\[
\text{excitation} \rightarrow \text{Ce}^{3+} \rightarrow \text{Gd}^{3+} \rightarrow \text{Gd}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow h\nu
\]

Excitation is via the 4f \(\rightarrow\) 5d transition of Ce\(^{3+}\) (4f\(^4\)). The relaxed excited state of Ce\(^{3+}\) is in resonance with the Gd\(^{3+}\) 6P levels and energy transfer occurs. Sensitization of Tb\(^{3+}\) occurs due to good overlap between the Gd\(^{3+}\) emission and the 4f \(\rightarrow\) 5d absorption bands of Tb\(^{3+}\). The Gd\(^{3+}\) ions play an intermediate role in the energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) via processes of high quantum efficiency.

Nehru and co-workers [33] prepared a green phosphor system by co-doping Tb\(^{3+}\) (15\%) with Ce\(^{3+}\) (15\%) in a borosilicate matrix. Although they believed that high concentrations of Ce\(^{3+}\) and Tb\(^{3+}\) are required to achieve maximum emission, de Hair [34] demonstrated that energy transfer from Gd\(^{3+}\) to Tb\(^{3+}\) is complete at relatively low concentrations. Since the price of Tb\(^{3+}\) doped phosphors is dependent mainly on the terbium content [34], co-doping of Gd\(^{3+}\) and Tb\(^{3+}\) ions is commercially advantageous.

5 Discussion and Conclusions

The potential application of a luminescent material depends on choice of a suitable excitation wavelength. Preparation and screening of a phosphor for a particular application is a time-consuming procedure, a process that can be enhanced through the analysis of phosphor composition libraries as described here. Although the ANN/GA hybrid has been applied here to the optimization of composition of a specific type of material, the development of new materials is in reality largely application independent, so the method is very versatile.

This sort of study may facilitate not just the development of luminescent materials for a particular purpose, but may also promote a new approach for achieving multi-spectral LEDs. Given sufficient understanding of the dependence of luminous efficiency on excitation wavelength, emission of a spectrum of colours from a single LED is possible, by coating the LED with a blend of phosphors and varying the excitation energy from the chip.

Recently, two-phase phosphors with self-adjusting emission wavelengths have been proposed as a way of overcoming the difficulty of manufacturing chromatically equivalent LEDs [35]. A two-phase phosphor combines one phosphor whose emission intensity decreases with increase in excitation wavelength radiation, with a second whose emission intensity increases as the excitation wavelength is increased [35]. Random fluctuations during manufacturing make it difficult to produce chromatically equivalent LEDs, so this innovative design has a significant commercial value.

A clear understanding of how luminous efficiency varies with excitation wavelength is essential in the design of two-phase phosphors; application of the hybrid system in development of such solid-state phosphors is likely to be productive through modeling of the relationship between luminous efficiency; phosphor composition and the excitation wavelength.

References:


Physics Research Section

a-Accelerators Spectrometers Detectors and Associated Equipment


