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The lack of an efficient emitter in the 500-600nm range is limiting the adoption of LEDs for indoor lighting applications. The degradation in performance of current InGaN alloys in this range is due to the large lattice mismatch between InN and GaN and associated alloy phase instabilities. We propose and investigate, using first-principles methods, the electronic structure of an alternative $LiMg_{1-x}Zn_xN$ alloy which has the potential to fill this gap. The small lattice mismatch between LiMgN and LiZnN, along with electronic band gaps spanning the visible range, make them, in principle, ideal candidates for white LED applications.

1 Introduction The widespread adoption of solid-state LED lighting has the capability to reduce electricity consumption for lighting applications by 50% [1, 2]. This could potentially lead to a 250 million metric ton reduction in carbon emissions for the United States alone. However, for extensive replacement of current lighting technologies with solid state alternatives, a number of obstacles need to be overcome. One of the most fundamental issues is the lack of an efficient green emitter. This is a problem both in the efficiency of green LEDs, but also more importantly in the production of efficient white light sources.

High powered white LEDs are currently produced by coating InGaN based blue emitters with a yellow phosphor; however, the lack of a red component makes this approach unsuitable for some lighting applications. White light based on a tri-chromatic red-green-blue (RGB) source offers greater flexibility in the colour-rendering index (CRI), which is needed for effective indoor lighting to satisfy the broad consumer market [3]. Tri-chromatic white light sources without the need for optical coatings are most desirable because of the energy losses associated with the conversion of photon wavelength in phosphor containing devices.

Existing emitters in the 500-600 nm (yellow-green) wavelength range exhibit efficiencies in the region of 10%, while the theoretical limit is greater than 80%. The addition of In to GaN to form InGaN alloys can be used to fill this emission range; unfortunately this system suffers from phase separation at the desired alloy compositions, which can be understood from the strain produced by the large lattice constant mismatch of GaN and InN. A solution may be found through selective chemical mutation of the cations to favourably tune the band gaps, while ensuring small mismatch. Here we propose an alternative nitride alloy system in which In is replaced by Li and Mg, and Ga is replaced by Li and Zn. Both LiMgN and LiZnN can be considered as filled tetrahedral semiconductors, with Li occupying the interstitial (½ ,½, ½) sites in the underlying zinc blende lattice [4].

In this letter we report the first-principles electronic structure of the $LiMg_{1-x}Zn_xN$ alloy system (x = 0, ¼, ½, ¾, 1). The alloys were modelled within the special quasirandom structure (SQS) approach [5] and the effect of alloy ordering is also investigated. We find that the small lattice mismatch of the $LiMg_{1-x}Zn_xN$ alloy, along with a low bowing parameter which produces a smooth band gap transition across the visible range, demonstrates the potential for substantial improvements over existing InGaN based materials in the required emission range.

2 Computational methods The $LiMg_{1-x}Zn_xN$ alloys were modelled using a 96 atom supercell. The lattice occupancies of Li and N were held constant for each system, while the SQS model was applied to distribute the Mg and Zn atoms over their available face centred cubic sublattice sites. The total energy and band structure were obtained using density functional theory [6] within the generalized gradient approximation [7] (GGA) as implemented in the VASP package [8].

A plane wave cut-off of 500 eV and a 5×5×5 Monkhorst-Pack [9] *k*-point grid were chosen. The lattice constants of the alloys were assumed to be determined by a weighted average of the equilibrium ternary constituent lattice constants, i.e. that they obey Vegard's rule [10]. The band gap bowing coefficients were obtained from

$$E_g(x)=(1-x)E_g(\mathrm{LiMgN})+(x)E_g(\mathrm{LiZnN})-bx(1-x) \qquad (1)$$

where $E_g(x)$ is the calculated band gap of the alloy at composition x.

3 Results and discussion The calculated equilibrium lattice constants of 4.999 Å (LiMgN) and 4.933 Å (LiZnN) are in excellent agreement (within 1%) with available X-ray diffraction data [11, 12]. The lowest energy gaps of 2.46 eV (LiMgN) and 0.59 eV (LiZnN) are significantly underestimated from experimental measurements of 3.2 eV [10] and 1.9 eV [11], respectively, which is a well known error of GGA. However, as the calculated bowing parameter takes into account only the changes in the band gaps for each alloy, these systematic errors are largely cancelled. We find that the bowing is almost compositionally independent at about b = 0.22 eV. Through combining this calculated bowing parameter of 0.22 eV with the experimental band gaps of LiMgN and LiZnN, and applying Equation (1), we can make an accurate prediction of the observable alloy properties. As illustrated in Fig. 1 the adjusted band gaps smoothly span the majority of the visible range from 1.9 eV (653 nm) to 3.2 eV (388 nm).

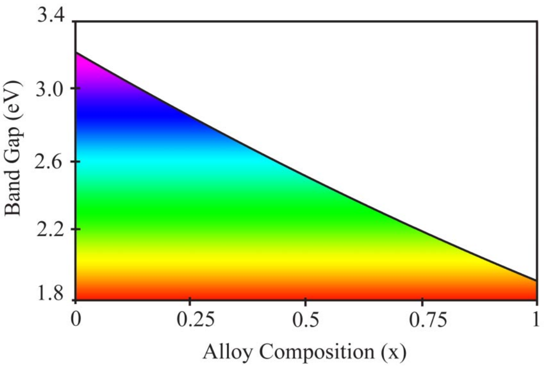

Figure 1 Fundamental direct band gap at Γ as a function of alloy composition. This was calculated taking the experimental values for LiMgN and LiZnN and the GGA bowing parameter.

As spontaneous lattice ordering is possible depending on the preparatory conditions, in addition to the random SQS generated configurations, we have also calculated the stoichiometric $\mathrm{LiMg_{0.5}Zn_{0.5}N}$ alloy in four ordered superlattice configurations: alternating planes of Mg and Zn aligned along (i) (001) in a CuAu type (1×1) structure, (ii) (110) in a Y2 type (2×2) superlattice, (iii) (111) in a CuPt type (1×1) structure and (iv) (201) ordering in a chalcopyrite type (2×2) structure. These orderings are illustrated in Fig. 2 and the resulting energetic and electronic data are summarized in Fig. 3.

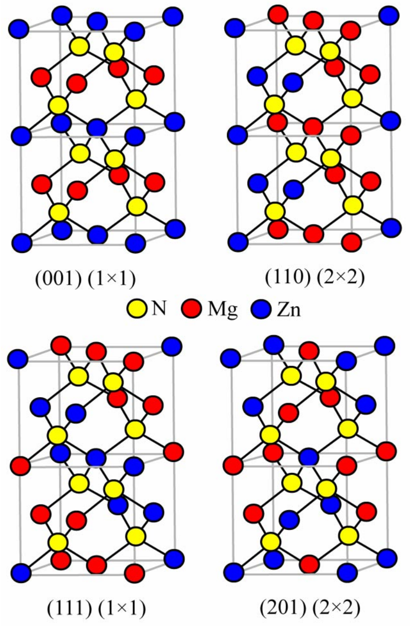

Figure 2 Crystal structure representation of the four ordered cation $\mathrm{LiMg_{0.5}Zn_{0.5}N}$ superlattices examined. The Li atoms have been removed for clarity.

The mixing enthalpies of each ordered configuration, calculated relative to LiMgN and LiZnN, all lay within a small 16 meV energy range. The energetic ordering of (001) > (201) > (110) > (111) is consistent with previous observations [13] that while (111) alignment results in the highest energy configurations for systems with large lattice constant mismatch, in lattice matched systems it is one of the most favourable; the inverse holds true for the (201) superlattice. Large charge variation in the Y2 and CuPt structures contribute to an enhanced Madelung energy [14]. The intrinsic geometric frustration induced by the high symmetry of the CuAu structure results in a small positive enthalpy of +4 meV with respect to the relaxed bulk constituents. The SQS generated structure results in a negative formation enthalpy of -4.3 meV, similar in magnitude to the (201) ordered structure. This negative formation energy is quite unusual in semiconductor alloys. As the random, (201), (110) and (111) alignments are all favourable, with negative formation energies, the energetic data predict that stable long range ordering could be accessible under appropriate temperature and growth conditions.

The calculated electronic band gaps of the stable random and ordered (201) configurations are close in energy, in the region of 2.5 eV, while the CuPt and Y2 configurations result in reduced band gaps of 2.42 eV and 2.47 eV respectively. Ordered (111) CuPt alignment is known to result in the largest band level repulsions between the Γ and L states, causing the CBM to shift down in energy, resulting in its lower fundamental gap [15]. As we are only considering fully ordered systems in our simulations, these ordering effects will be exaggerated compared to the mixture that will occur in real systems. However, the results do infer that there will be some opportunity to fine-tune the band gap through altering growth conditions.

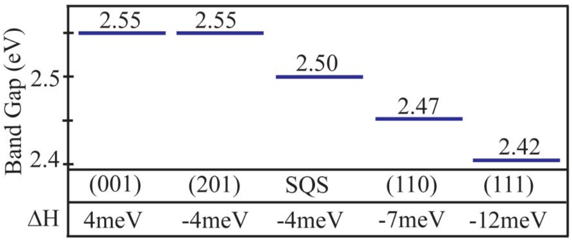

Figure 3 Fundamental direct band gaps at Γ and formation enthalpy for the random (SQS) and the four ordered x = ½ alloys.

4 Conclusion

We have reported the results of an electronic structure study of the $LiMg_{1-x}Zn_xN$ alloy system using the SQS approach to generate the random distribution of lattice sites. The calculated equilibrium lattice constants confirm the low lattice mismatch between LiMgN and LiZnN and are in excellent agreement with the experimentally determined values. The effect of alloy ordering was examined for the x = ½ composition which indicates that (111) CuPt alignment is most favourable, resulting in a more negative mixing enthalpy than that of the random alloy. This stable ordered superlattice has a band gap 80 meV lower than the SQS phase. We have therefore demonstrated the potential of a new alloy system that has a band gap tuneable throughout the visible range, with very small lattice mismatch and minimal bowing. Experimental tests for our predictions are called for.

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