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Phase stability of ScN-based solid solutions for thermoelectric applications from first-principles calculations

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We have used first-principles calculations to investigate the trends in mixing thermodynamics of ScN-based solid solutions in the cubic B1 structure. 13 different $\text{Sc}_{1-x}\text{M}_x\text{N}$ ($\text{M} = \text{Y}, \text{La}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Gd}, \text{Lu}, \text{Al}, \text{Ga}, \text{In}$) and three different $\text{ScN}_{1-x}\text{A}_x$ ($\text{A} = \text{P}, \text{As}, \text{Sb}$) solid solutions are investigated and their trends for forming disordered or ordered solid solutions or to phase separate are revealed. The results are used to discuss suitable candidate materials for different strategies to reduce the high thermal conductivity in ScN-based systems, a material having otherwise promising thermoelectric properties for medium and high temperature applications. Our results indicate that at a temperature of $T = 800^\circ\text{C}$, $\text{Sc}_{1-x}\text{Y}_x\text{N}$; $\text{Sc}_{1-x}\text{La}_x\text{N}$; $\text{Sc}_{1-x}\text{Gd}_x\text{N}$, $\text{Sc}_{1-x}\text{Ga}_x\text{N}$, and $\text{Sc}_{1-x}\text{In}_x\text{N}$; and $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$ solid solutions have phase separation tendency, and thus, can be used for forming nano-inclusion or superlattices, as they are not intermixing at high temperature. On the other hand, $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, $\text{Sc}_{1-x}\text{Hf}_x\text{N}$, and $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ favor disordered solid solutions at $T = 800^\circ\text{C}$. Thus, the $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ system is suggested for a solid solution strategy for phonon scattering as Lu has the same valence as Sc and much larger atomic mass. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818415>]

I. INTRODUCTION

ScN is a promising material for medium and high temperature thermoelectric applications since it has suitable thermal and electrical properties for thermoelectric application, such as high melting point (2900 K),^{1,2} being an n-type semiconductor with indirect band gap of 0.9–1.6 eV and a wide range of electron mobility 30–172 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with carrier concentrations reported to vary from 10^{18} to 10^{22}cm^{-3} .^{3–7} In terms of thermoelectric properties, we discovered that ScN thin films have high thermoelectric power factor ($S^2\sigma$) of $2.5 \times 10^{-3} \text{ W}/(\text{m}\cdot\text{K}^2)$ at 800 K where the thermoelectric power factor is the product of Seebeck coefficient (S) and electrical conductivity (σ).⁸ Recently, this was confirmed by Burmistrova *et al.* who reported a thermoelectric power factor of ScN up to $3.3 \times 10^{-3} \text{ W}/(\text{m}\cdot\text{K}^2)$ at 840 K due to low metallic-like electrical resistivity ($7.4 \mu\Omega \text{ m}$) with retained relatively large Seebeck coefficient of $-156 \mu\text{V}/\text{K}$.⁹ These power factors are comparable to state of the art thermoelectric material such as pure Bi_2Te_3 or PbTe .^{10–12} The value is high considering that it is obtained for a nitride material without any deliberate optimization of doping and has been suggested to be related to electronic structure effects of nitrogen vacancies and oxygen incorporation.^{9,13}

However, for most practical applications, the thermoelectric figure of merit (ZT) of ScN is too low. ZT is defined as $S^2\sigma T/\kappa$, where T is the absolute temperature, κ is the sum of electrical and lattice thermal conductivity, $\kappa = \kappa_{el} + \kappa_{ph}$. For pure ScN, ZT is about 0.2–0.3 at 800 K.^{8,9} This is due to the high total thermal conductivity of about $8.3 \text{ W}/\text{m}\cdot\text{K}^2$ at 800 K.^{9,14} Thus, to improve the ZT of ScN, the lattice thermal

conductivity needs to be reduced. Standard strategies for other thermoelectric materials for lattice thermal conductivity reduction include alloying, construction of superlattices, nanoinclusions, or grain boundaries.^{10,15–22} In addition, Sc is naturally isotope-pure and ScN thus lacks, with the exception of the small effect of 0.4% ^{15}N ,²³ isotope reduction of thermal conductivity. Consequently, the possibilities to substantially reduce the thermal conductivity by alloying or nanostructure engineering are particularly promising in this material. If the thermal conductivity can be reduced, ScN-based materials could potentially be applied at elevated temperatures, possibly as high as around 800°C where diffusion can be activated. This means that the thermodynamics of mixing between ScN and the alloying or superlattice component becomes relevant. Superlattices might intermix, alloys could order or phase-separate, and nanostructures might be dissolved in the matrix. All these processes could affect, negatively or positively, thermoelectric properties. The thermodynamics of mixing is also of relevance for the possibility of bulk synthesis. Thin film growth of multicomponent nitrides are typically done at non-equilibrium conditions where metastable alloys can be formed also in immiscible systems.^{24,25} However, if there is a thermodynamic driving force for decomposition, nanostructure design can be performed by annealing of metastable thin-film alloys. There are a number of investigations demonstrating the effects of diffusion in mixed nitride systems at high temperature, in particular, in thin films. For instance, it has been found that metastable nitride alloys might phase separate both by a spinodal-decomposition mechanism, for instance, in TiAlN ,^{26,27} and by nucleation and growth as in ScAlN .²⁸ The difference has been explained in terms of volume mismatch, favoring nucleation and growth, and the electronic structure as driving forces for phase separation, allowing for spinodal decomposition.^{29–31} These decomposition mechanisms give

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different nanostructure and could give different impact on thermoelectric properties.^{28,32,33} Thus, we need to carefully select suitable materials candidates for each different approach for thermal conductivity reduction in ScN-based systems.

In this work, we perform a first-principles scan of the mixing thermodynamics and lattice spacing of ScN with 13 different nitrides and three other pnictides with possible relevance for design of thermoelectric properties. Thus, we are able to suggest candidate materials for the different design strategies to decrease the thermal conductivity of ScN-based systems at high temperatures.

II. COMPUTATIONAL DETAILS

In this study, we consider the mixing thermodynamics in order to determine phase stability of $\text{Sc}_{1-x}\text{M}_x\text{N}$ and $\text{ScN}_{1-x}\text{A}_x$ alloy systems where M consists of early transition metals (Y, Ti, Zr, Hf, V, Nb, and Ta), rare earth metals (La, Gd, and Lu) and group-13 (Ga and In) and A consists of group-15 (P, As, and Sb). These nitride systems are chosen since they all can be found in the rock salt B1 structure, although in some cases other structures are the ground state under ambient conditions. We start by considering the mixing enthalpy which is calculated as

$$\Delta H_{\text{mix}}(x) = H_{(\text{Sc}_{1-x}\text{M}_x\text{N}/\text{ScN}_{1-x}\text{A}_x)} - (1-x)H_{\text{ScN}} - xH_{\text{MN}/\text{ScA}}, \quad (1)$$

where the enthalpies are considered at zero pressure as the energies of each phase is taken at its corresponding equilibrium volume. The effect of increasing temperature can be assessed by calculation of the free energy

$$\Delta G(x, T) = \Delta H_{\text{mix}}(x) - T\Delta S(x), \quad (2)$$

where $\Delta H(x)$ is the mixing enthalpy per formula unit and the mixing entropy $\Delta S(x)$ can be estimated from the mean-field approximation

$$S_{\text{mf}} = -k_B \{x \ln(x) + (1-x) \ln(1-x)\}, \quad (3)$$

where x is the fraction of considered solid solution material. This formula is a simplification of the real entropy and is used to obtain a guideline for effect of temperature on phase stability. Vibrational contributions are not included but are believed to be of no critical importance for the ability to draw qualitative conclusions about mixing trends at temperatures up to around 1000 K, which was noted for the related system TiAlN (Ref. 34) and probably related to the high melting point of these nitrides. All calculations in this work were performed based on first-principles density functional calculations using the Kohn-Sham equations³⁵ and Projector Augmented Wave (PAW) method³⁶ as implemented in the Vienna *Ab-initio* Simulation Package (VASP) code.^{37,38} Two exchange-correlation energy approximations had been used in this study, (i) the generalized gradient approximation as given by Perdew-Burke-Ernzerhof (GGA-PBE)³⁹ for early transition metals, group-13 and-15 and (ii) the generalized gradient approximation with a Hubbard Coulomb term,⁴⁰ the U term, applied only to 4f orbitals. The effective values (U - J) are selected according to the

determination in Ref. 41 as 6.5 eV, 8 eV, and 9.5 eV for La, Gd, and Lu, respectively. Note that in Ref. 41, they showed that for empty-, full-, and half-filled with strong spin-splitting of 4f band, the 4f-states are positioned far below or above the Fermi level. Correspondingly, the exact value of the U should have a small effect on mixing energetics.

In this study, to reveal the mixing trends, we have selected three types of configurations to each of the ScN based solid solutions. First, the clustering state is considered by the separate calculation of the pure binary nitrides. Second, substitutionally disordered solid solutions of $\text{Sc}_{1-x}\text{M}_x\text{N}$ and $\text{ScN}_{1-x}\text{A}_x$ on the underlying rock salt (B1) lattice are generated using a special quasirandom structures (SQSs)⁴²-based approach for the composition $x = 0.25, 0.50$, and 0.75. To obtain converged total energies, 128 atoms supercells are used, which are based on a $4 \times 4 \times 4$ repetition of the fcc-unitcell and consisting of 64 atoms on each sublattice. The pair correlation functions, quantifying the configurational state of a structure,^{32,43} are for these SQS structures identical to the ideal disordered system on the first two nearest neighbor shell and differing with less than 0.04 on the first seven shells for all compositions. Finally, ordered configurations are represented by the B1-L1₀ (CuAu) and B1-L1₁ (CuPt) ordering with composition $x = 0.50$ for all systems in this study. These two structures are chosen since they represent the maximum ordering possible on the first and second metal coordination shells, respectively, on the fcc lattice. These two coordination shells are often dominating the effective cluster interactions and thus, the energies of B1-L1₀ and B1-L1₁ should contrast strongly to the phase separated state and together with clustering and the SQS structure give a good estimate of the energy span of different $\text{Sc}_{0.5}\text{M}_{0.5}\text{N}$ and $\text{ScN}_{0.5}\text{A}_{0.5}$ alloys. The B1-L1₁ structure has also been predicted as the ground state in the isostructural $\text{Zr}_{0.5}\text{Gd}_{0.5}\text{N}$ (Ref. 44) and has been observed experimentally for $\text{Ti}_{0.5}\text{W}_{0.5}\text{N}$.³³ In addition, we included in this study also the ScTaN_2 -type hexagonal structure (space group $P6_3/mmc$) consisting of alternating layer of Sc-N-Ta-N-Sc. This structure can be considered an inherent nanolaminate (more details, see, Refs. 45 and 46) which possibly could give interesting thermoelectric properties as in similar systems such as misfit layered cobaltates or TiS_2 .⁴⁷⁻⁴⁹ A plane wave cut-off of 400 eV was used with the k-point mesh of $7 \times 7 \times 7$ points for 128 cells and $21 \times 21 \times 21$ points for the binary system. In all systems, the internal coordinates of atoms were fully relaxed and in the case of ordered alloys also the cell shape was relaxed.

III. RESULTS AND DISCUSSION

Below we report the results of our systematic investigation of mixing thermodynamics in the $\text{Sc}_{1-x}\text{M}_x\text{N}$ and $\text{ScN}_{1-x}\text{A}_x$ systems. The section is organized such that the different candidate systems are divided in subsections depending on the location of M (or A) place in the periodic table.

A. $\text{Sc}_{1-x}\text{Y}_x\text{N}$

The calculated mixing enthalpy of the $\text{Sc}_{1-x}\text{Y}_x\text{N}$ solid solution is shown in Figure 1(a). $\text{Sc}_{1-x}\text{Y}_x\text{N}$ exhibits a

FIG. 1. (a) Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, B1-L1₀ and B1-L1₁ ordered solid solution and ScTa₂N₂-type structure phase, respectively, of Sc_{1-x}Y_xN, as a function of YN content. (b) Calculated equilibrium lattice parameter for rocksalt (B1) Sc_{1-x}Y_xN solid solution as a function of YN content. The black line indicates Vegard's rule. Experimental data from the work of Gregoire *et al.* are shown with stars.⁵⁰

positive symmetric mixing enthalpy curve for the random solid solution over entire composition with the highest value of about 0.12 eV/f.u. at $x = 0.50$. For the considered ordered alloys, the B1-L1₁ compound is similar to the SQS in enthalpy while the B1-L1₀ and the ScLaN₂ structure are considerably higher. Thus, Sc_{1-x}Y_xN shows an energetic driving force for phase separation into ScN and YN. The reason can be seen from Table I; the calculated binary lattice parameters are $a_{\text{ScN}} = 4.52 \text{ \AA}$ and $a_{\text{YN}} = 4.92 \text{ \AA}$. This means that YN has a lattice parameter 9% larger than ScN translating to a volume mismatch of 29%. This mismatch prevents the Sc_{1-x}Y_xN system from being thermodynamically stable as a solid solution. Moreover, Figure 1(b) shows the calculated lattice parameter of Sc_{1-x}Y_xN solid solution. The plot shows a positive deviation from the linear Vegard's rule. This behavior has been observed previously for highly size-mismatched nitride solid solutions such as Sc_{1-x}Al_xN²⁸ and Ti_{1-x}Gd_xN⁴⁴ and has been explained with the asymmetry of the binding energy curves making it more difficult to drastically compress the larger nitride as compared to expand the smaller. When we include the effect of temperature at $T = 800 \text{ }^\circ\text{C}$ and study the free energy of mixing, the result still shows positive symmetric mixing free energy curve with small drop in magnitude. This result confirms that even at high temperature, ScN and YN will tend to phase separate if

TABLE I. Calculated equilibrium and experimental lattice parameters for rocksalt (B1) of Sc_{1-x}M_xN solid solution as a function of MN content, where M = Y, Ti, Hf, Zr, V, Nb, Ta, Ga, In, La, Gd, and Lu for Sc sublattice mixtures and B1 solid solutions of ScN_{1-x}A_x as a function of ScA content where A = P, As, and Sb for N sublattice mixtures.

Materials	Calculated lattice parameter/experimental lattice parameter (Å)				
	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1.0$
Sc _{1-x} Y _x N	4.52/4.50, ^a	4.63	4.73	4.83	4.92/4.89, ^a 4.91 ^c
Sc _{1-x} Ti _x N	4.512 ^b	4.44	4.37	4.31	4.25/4.25 ^b
Sc _{1-x} Zr _x N		4.54	4.56	4.58	4.60/4.58 ^c
Sc _{1-x} Hf _x N		4.52	4.52	4.53	4.53/4.52 ^c
Sc _{1-x} V _x N		4.41	4.31	4.22	4.12/4.12 ^c
Sc _{1-x} Nb _x N		4.48	4.47	4.46	4.45/4.39 ^c
Sc _{1-x} Ta _x N		4.47	4.45	4.43	4.42/4.36 ^c
Sc _{1-x} Ga _x N		4.47	4.43	4.39	4.27
Sc _{1-x} In _x N		4.57	4.62	4.66	4.71
Sc _{1-x} La _x N		4.77	5.01	5.21	5.34/5.29 ^c
Sc _{1-x} Gd _x N		4.64	4.76	4.88	4.98/4.98 ^d
Sc _{1-x} Lu _x N		4.53	4.56	4.58	4.61
ScN _{1-x} P _x		4.74	4.94	5.15	5.31/5.30 ^c
ScN _{1-x} As _x		4.81	5.08	5.32	5.49/5.46 ^e
ScN _{1-x} Sb _x		5.01	5.41	5.68	5.89

^aReference 50.

^bReference 52.

^cReference 66.

^dReference 67.

^eReference 68.

diffusion is activated in the system. Experimentally, thin films of Sc_{1-x}Y_xN solid solutions have been deposited by Gregoire *et al.*⁵⁰ As can be seen in Fig. 1(b) the measured lattice spacing has good agreement with our calculations which is a strong indication that the films are solid solutions and not phase separated. PVD synthesis is a non-equilibrium technique well known to be able to grow films of metastable solid solutions in thermodynamically immiscible nitride alloy systems due to limited diffusion during growth.²⁶ Our calculations predict that a high temperature annealing experiment carried out on such films would result in an initiation of phase separation when diffusion is activated. Since the driving force for separation in Sc_{1-x}Y_xN is the volume mismatch, phase separation would need the nucleation of large enough domains that could relax to the respective lattice spacing corresponding to the composition of the domains. On the other hand, fully coherent spinodal decomposition is not predicted to take place.

B. Sc_{1-x}Ti_xN, Sc_{1-x}Zr_xN, and Sc_{1-x}Hf_xN

Figure 2(a) shows the calculated mixing enthalpies of Sc_{1-x}Ti_xN, Sc_{1-x}Zr_xN, and Sc_{1-x}Hf_xN solid solution system. All of the systems in this alloy family show lower mixing enthalpy than Sc_{1-x}Y_xN system and even negative for Sc_{1-x}Zr_xN and Sc_{1-x}Hf_xN disordered solid solutions over the entire composition range. The curves also show a considerable asymmetry with respect to equi-atomic concentrations, especially in Sc_{1-x}Ti_xN case where there is a strong deviation. These results show that ScN has higher tendency

FIG. 2. (a) Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, B1- $L1_0$ and B1- $L1_1$ ordered solid solutions and ScTaN_2 -type structure phase of $\text{Sc}_{1-x}\text{M}_x\text{N}$, as a function of MN content where $\text{M} = \text{Ti}, \text{Zr}$, and Hf , respectively. (b) Calculated equilibrium lattice parameter for rocksalt (B1) $\text{Sc}_{1-x}\text{M}_x\text{N}$ solid solution as a function of MN content where $\text{M} = \text{Ti}, \text{Zr}$, and Hf , respectively. The black line indicates Vegard's rule. For $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, the experimental data from Gall *et al.* are shown with stars.⁵²

to form solid solution with TiN , ZrN , and HfN than with YN . When we consider the effect of lattice parameter mismatch of this system, there is a small degree of lattice mismatch between ScN and ZrN or HfN but still high lattice mismatch between ScN and TiN (see Table I and Fig. 2(b)). In addition, TiN , ZrN , and HfN have one extra d electron as compared to ScN and YN . This extra d electron can affect mixing energetics as has been found previously for the alloy of TiN with AlN .³² However, in opposite to the alloys of TiN , ZrN , and HfN with AlN , for $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, and $\text{Sc}_{1-x}\text{Hf}_x\text{N}$ system, the extra d -electron can delocalize also over the Sc -sites which has empty $3d$ - t_{2g} states. This results in a negative contribution to the enthalpy of mixing in these systems, and as can be observed in Fig. 2(a), to an asymmetric shape of the mixing enthalpy curve with respect to composition. The composition asymmetry shows that it is more favorable to dissolve a small amount of Ti , Zr , and Hf into ScN than a small amount of Sc in TiN , ZrN , and HfN . This is qualitatively in line with the calculations of the dilute case in Ref. 51. It can be understood since the extra d -electrons with t_{2g} symmetry from Ti , Zr , and Hf has to occupy gradually higher energies of the empty Sc $3d$ t_{2g} state when their concentrations in the alloys increase. Since the lattice mismatch of ZrN and HfN with ScN is small, the effect of electronic structure dominates and yields a negative mixing enthalpy unlike TiN that has a large lattice mismatch that compensates for the electronic structure effect. In the case of $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, the ordered B1- $L1_0$ phase is higher in energy than the disordered solid solution and has a mixing enthalpy with respect to TiN and ScN of 0.060 eV/f.u. The B1- $L1_1$ order on the other hand is lower and has a negative mixing enthalpy of -0.08 eV/f.u. The favoring of the B1- $L1_1$ order has previously been observed for B1 systems, in particular, with size mismatch between the cations

$\text{Zr}_{0.50}\text{Gd}_{0.50}\text{N}$,⁴⁴ $\text{Ti}_{0.50}\text{W}_{0.50}\text{N}$,³³ and explained by the ability for relaxation of the metal-nitrogen bond lengths in this particular ordered structure where all second-nearest neighbor pairs on the metal fcc-sublattice are of different kinds.³² For $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, the B1- $L1_0$ order is just below the disordered solid solution with a mixing enthalpy of -0.088 eV/f.u. In this system with a small size difference, the B1- $L1_1$ phase is just above the SQS result. For $\text{Sc}_{1-x}\text{Hf}_x\text{N}$, both ordered structures are almost degenerate with the SQS with the B1- $L1_1$ being lowest with H_{mix} of -0.153 eV/f.u. In all these three systems, concentration appears to be the determining factor for the mixing thermodynamics rather than different configurations. Indeed, the estimation of mixing free energy including the mean field entropy at 800°C clearly favors disordered solid solutions in $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, and $\text{Sc}_{1-x}\text{Hf}_x\text{N}$ systems. Our calculated lattice parameters of $\text{Sc}_{1-x}\text{Ti}_x\text{N}$ solid solution are in agreement with existing experiments as can be seen in Fig. 2(b). The experiments by Gall *et al.* show that it is indeed possible to synthesize $\text{Sc}_{1-x}\text{Ti}_x\text{N}$ solid solution thin films by reactive magnetron sputtering.⁵² The authors identified the solid solutions to be single phase B1 structure and did not report any signs of ordering. However, as for the $\text{Sc}_{1-x}\text{Y}_x\text{N}$ case above, we are not aware of attempts to anneal such $\text{Sc}_{1-x}\text{Ti}_x\text{N}$ solid solutions to allow for ordering or phase separation by high temperature induced diffusion.

C. $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$

The calculated mixing enthalpies of $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$ solid solution are shown in Figure 3(a). The results show that they have similar tendency as the systems described in Sec. III B; that is, low and negative mixing enthalpy and asymmetric curve meaning that

FIG. 3. (a) Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, B1- $L1_0$ and B1- $L1_1$ ordered solid solution and ScTaN_2 -type structure of $\text{Sc}_{1-x}\text{M}_x\text{N}$, as a function of MN content where $\text{M} = \text{V}$, Nb , and Ta , respectively. (b) Calculated equilibrium lattice parameter for rocksalt (B1) $\text{Sc}_{1-x}\text{M}_x\text{N}$ solid solution as a function of MN content where $\text{M} = \text{V}$, Nb , and Ta , respectively. The black line indicates Vegard's rule.

these systems favor formation of solid solutions due to the effect of small lattice mismatch (see Table I) and effect of electronic structures, where V, Nb, and Ta have 2 extra d electrons that can delocalize in the alloy with ScN. Figure 3(b) shows the deviation of lattice parameter with composition. It is a negative deviation from linear Vegard's rule, as in the previous system. At $x = 0.50$, all three systems show a very low mixing enthalpy for ScTaN_2 -type structure, making this the ground state structure of the $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$ systems at $x = 0.50$. These results of our calculation agree with the fact that this phase has been experimentally synthesized in bulk as ScTaN_2 and $\text{ScNbN}_{2-\delta}$.^{45,46} Our results indicate that the corresponding phase, ScVN_2 , should exist in the Sc-V-N system. However, the latter system might deserve a more detailed future study as calculations have obtained energies for WC-type VN to be lower than the experimentally observed B1 VN phase making predictions in the VN-related system more difficult.⁵³

The stability of the ScTaN_2 phase can be explained by considering its structure. It consists of a layered structure with two subsystems which are rocksalt ScN-like and a hexagonal related structure of TaN (WC structure type).⁴⁵ When we consider the ground state structure of the binary phase of TaN and NbN, there are competitive phases with hexagonal base structure (TaN has ϵ -phase structure and NbN has WC structure).^{54–56} These two binary systems have lower formation enthalpy than their rocksalt phase as plotted in Figure 4. Since ScN has the rocksalt structure and NbN and TaN have a hexagonal base structure as their lowest energy state, the combination of these two building blocks into a layered structure give, together with a possibility to delocalize Nb and Ta d -electrons also over the ScN-layers, an energetic driving force for this system to stabilize ScTaN_2 structure.

FIG. 4. Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, ScTaN_2 -type structure phase including their competitive hexagonal phase for (a) $\text{Sc}_{1-x}\text{Nb}_x\text{N}$ and (b) $\text{Sc}_{1-x}\text{Ta}_x\text{N}$. The dotted line indicates new equilibrium line. The value for WC, NbN, and ϵ -TaN are obtained from Refs. 54 and 56, respectively.

This can be seen by the ScTaN_2 structure being below also the line connecting the B1-ScN with hexagonal types of TaN and NbN. Moreover, the ScTaN_2 phase in these two material systems are stable also at $T = 800^\circ\text{C}$ at least in comparison with the free energy of the disordered B1 solid solutions.

D. $\text{Sc}_{1-x}\text{Al}_x\text{N}$, $\text{Sc}_{1-x}\text{Ga}_x\text{N}$, and $\text{Sc}_{1-x}\text{In}_x\text{N}$

The group-13 nitrides AlN, GaN, and InN crystallize in the hexagonal wurtzite structure as their ground state but can be transformed into the rock salt phase under high pressure. The B1 rock salt phase of AlN created at high pressure can be metastable also at ambient conditions⁵⁷ while B1 GaN has been stabilized as thin interlayers.⁵⁸ AlN is also known to be soluble as a metastable rock salt alloy in several rock salt transition metal nitrides, in particular, $\text{Ti}_{1-x}\text{Al}_x\text{N}$.²⁶ Thus, for our purpose, it is of interest to investigate their mixing tendency with ScN.

Figure 5(a) shows the calculated mixing enthalpy of ScN with rock-salt GaN and InN while in the ScAlN system the H_{mix} data are taken from our previous work²⁹ and included for comparison. Figure 5(a) shows that both the GaN and InN containing systems have lower, but still positive, mixing enthalpy than the $\text{Sc}_{1-x}\text{Al}_x\text{N}$ meaning that GaN and InN have energetic driving force for isostructural phase separation with ScN but weaker than ScAlN. B1 GaN and InN have smaller lattice mismatch with ScN than rocksalt AlN does (Table I), which is the probable explanation for the lower mixing enthalpies. We note that our calculated value of the lattice parameter of B1 GaN, 4.27 Å, is considerably higher than the value 4.1 Å reported for GaN stabilized as a multilayer with TiN.⁵⁸ As all our other lattice spacing are showing excellent agreement with experiments, and that an extrapolation of the high-pressure lattice constant of B1 GaN

to zero pressure seems to result in a value close to our,⁵⁹ a reinvestigation of thin film multilayer stabilized GaN would be of interest.

When the temperature is considered at 800°C a fraction of the composition range becomes stable with respect to isostructural decomposition. The calculated lattice parameters of the $\text{Sc}_{1-x}\text{Ga}_x\text{N}$ solid solution show a positive deviation from the linear Vegard's rule (Figure 5(b)). For $\text{Sc}_{1-x}\text{In}_x\text{N}$ the lattice parameters follow Vegard's rule almost exactly. Al, Ga, and In do not have d -electrons, they do not even have non-occupied d -states close to the Fermi level like ScN and YN. Therefore, there is no such electronic delocalization effect as has been discussed for the two previous families of systems contribution to mixing energy. On the other hand, the electronic structure effect opposing mixing as in the TiAlN system is not present either as the non-bonding t_{2g} states of ScN is unoccupied.²⁹ This indicates that the only driving force for isostructural phase separation in this alloy family is the lattice mismatch of ScN and the group 13-nitride. During the first stages of spinodal decomposition, the coherence of the lattice is kept intact and the different decomposition products cannot relax their volume. Thus, spinodal decomposition is unlikely in these systems. There is one concern for this material system on their structure after phase separation. Since our study considers ScN-based solid solutions, the mixing enthalpies of Figure 5(a) are calculated with respect to the rocksalt phase. However, as mentioned above, the binary phase structure at ambient pressure of AlN, GaN, and InN are wurtzite structure. We believe that these alloy systems should tend to phase separate through nucleation and growth of rocksalt ScN and wurtzite AlN, GaN, or InN. This has been shown in the previous theoretical and experimental study on $\text{Sc}_{1-x}\text{Al}_x\text{N}$ system by Höglund *et al.*²⁸ They synthesized metastable rocksalt $\text{Sc}_{1-x}\text{Al}_x\text{N}$ by

FIG. 5. (a) Comparison of the calculated mixing enthalpies of substitutionally disorder solid solution, B1- $L1_0$ and B1- $L1_1$ ordered solid solution and ScTaN_2 -type structure of $\text{Sc}_{1-x}\text{M}_x\text{N}$, as a function of MN content where $M = \text{Al}, \text{Ga}$, and In , respectively. The value for $\text{Sc}_{1-x}\text{Al}_x\text{N}$ obtained from Ref. 29. (b) Calculated equilibrium lattice parameter for rocksalt (B1) $\text{Sc}_{1-x}\text{M}_x\text{N}$ solid solution as a function of MN content. The black line indicates Vegard's rule. The experimental lattice spacings obtained by Höglund *et al.* for $\text{Sc}_{1-x}\text{Al}_x\text{N}$ is shown with stars.²⁸

reactive magnetron sputtering up to about $x = 0.50$.^{28,30} When subject to high temperature nucleation and growth of wurtzite, AlN was observed in domain boundaries. This contrasted to the observation of spinodal isostructural B1 decomposition in their comparison with $\text{Ti}_{1-x}\text{Al}_x\text{N}$ system that was initiated already at temperatures around 800 °C.³² Furthermore, it has been shown that the crystal structure of as-deposited physically vapor deposited $\text{Sc}_{1-x}\text{Al}_x\text{N}$ thin films exhibit wurtzite structure solid solution when the system is rich in Al.⁶⁰ A difference to AlN is that in GaN and InN the B1 phase is considerably higher in energy relative to the ground state B4 phase. In the case of GaN-rich $\text{Sc}_{1-x}\text{Ga}_x\text{N}$, we observe unusually large local lattice relaxations in our supercell calculations, possibly indicating instability of the B1 phase in favor of a wurtzite alloy phase. Thus, non-isostructural phase separation is even more likely in $\text{Sc}_{1-x}\text{Ga}_x\text{N}$ and $\text{Sc}_{1-x}\text{In}_x\text{N}$ as compared to the previously studied system $\text{Sc}_{1-x}\text{Al}_x\text{N}$.

E. $\text{Sc}_{1-x}\text{La}_x\text{N}$, $\text{Sc}_{1-x}\text{Gd}_x\text{N}$, and $\text{Sc}_{1-x}\text{Lu}_x\text{N}$

As representative examples of rare-earth-metal alloying, we have chosen La, Gd, and Lu with non-occupied $4f$ states, half-filled $4f$ states, and fully occupied $4f$ states, respectively. Figure 6(a) shows the calculated mixing enthalpies of the $\text{Sc}_{1-x}\text{La}_x\text{N}$, $\text{Sc}_{1-x}\text{Gd}_x\text{N}$, and $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ solid solution. $\text{Sc}_{1-x}\text{La}_x\text{N}$ shows a large positive mixing enthalpy with a maximum value of about 0.39 eV/f.u. due to the very large lattice mismatch between ScN and LaN (Table I). $\text{Sc}_{1-x}\text{Gd}_x\text{N}$ exhibits lower positive mixing enthalpy than $\text{Sc}_{1-x}\text{La}_x\text{N}$ with a maximum value of 0.12 eV/f.u. because GdN has a lattice parameter with a smaller difference to ScN (Table I). Thus, $\text{Sc}_{1-x}\text{La}_x\text{N}$ and $\text{Sc}_{1-x}\text{Gd}_x\text{N}$ have a tendency to phase separate due to an energetic driving force originating in volume mismatch. On the other hand, the mixing

enthalpy of the solid solution in the $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ system shows small and negative mixing enthalpy which is understandable due to the small lattice mismatch between ScN and LuN allowing them to form a stable solid solution. The ordered B1 $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ phases at $x = 0.5$ are very close to the disordered solid solution and at temperatures of 800 °C disordered solid solution is clearly favored as can be seen from the estimated free energy curve. ScLaN and ScGdN, on the other hand, show negligible solubility in equilibrium even at that temperature. Their calculated lattice parameters with respect to composition in Figure 6(b) show that $\text{Sc}_{1-x}\text{La}_x\text{N}$ and $\text{Sc}_{1-x}\text{Gd}_x\text{N}$ have positive deviation from linear Vegard's rule. Especially $\text{Sc}_{1-x}\text{La}_x\text{N}$ has strong deviation, while $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ has a small negative deviation correlating with the mixing enthalpy behavior.

F. $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$

To give large impact on acoustic phonon scattering by solid solution effect, a large mass difference between host and alloy element is required.^{61,62} Considering ScN, it would be highly beneficial if we can alloy by substituting on the N sublattice giving large mass difference. Elements intuitively suitable to choose as substitutes for N would be P, As, and Sb, as they have the same number of valence electrons as N. Moreover, the group-13 pnictides such as InN, InP, InAs, InSb, etc., are known semiconductors and one could expect similar behavior in a compound with Sc.

However, we need to know if it is reasonable to believe that they can form a solid solution with ScN. Figure 7(a) shows the mixing enthalpies of $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$ solid solution. The results show very large positive mixing enthalpies that are increasing following P, As, or Sb substitute into ScN. Therefore, the $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$ systems would prefer to phase

FIG. 6. (a) Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, B1- $L1_0$ and B1- $L1_1$ ordered solid solution and ScTa N_2 -type structure of $\text{Sc}_{1-x}\text{M}_x\text{N}$, as a function of MN content where $\text{M} = \text{La}$, Gd , and Lu , respectively. (b) Calculated equilibrium lattice parameter for rocksalt (B1) $\text{Sc}_{1-x}\text{M}_x\text{N}$ solid solution as a function of MN content where $\text{M} = \text{La}$, Gd , and Lu , respectively. The black line indicates Vegard's rule.

FIG. 7. (a) Comparison of the calculated mixing enthalpies of substitutionally disordered solid solution, B1-L1₀ and B1-L1₁ ordered solid solution and ScTa₂N₂-type structure of $\text{ScN}_{1-x}\text{A}_x$, as a function of ScA content where A = P, As, and Sb, respectively. (b) Calculated equilibrium lattice parameter for rocksalt (B1) $\text{ScN}_{1-x}\text{A}_x$ solid solution as a function of ScA content where A = P, As, and Sb, respectively. The black line indicates Vegard's rule.

separate rather than to form a solid solution. Since, P, As, and Sb have the valence electron as N the lattice mismatch will be the determining factor in the mixing energetics. When we consider the lattice mismatch between ScN and ScP, ScAs, or ScSb, the lattice mismatch is large in all cases and increasing with respect to change of element from P to Sb (Table I). Also the trend of lattice parameter variation over composition follows in the same manner; large lattice mismatch shows large positive deviation from linear Vegard's rule (See Figure 7(b)). Despite this fact, there are reports on highly mismatched metastable alloys $\text{GaN}_{1-x}\text{As}_x$ or $\text{GaN}_{1-x}\text{Sb}_x$ being possible to grow as solid solution in amorphous structure.^{63–65} Therefore, $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$ system could possibly behave in similar fashion. Furthermore, the effect of temperature at $T = 800^\circ\text{C}$ shows a very small influence to this alloy family, i.e., the result still is a positive symmetric mixing free energy curve. This result indicates that these systems will phase separate also at high temperatures as soon as atomic diffusion is initiated.

G. Summary and discussion

To summarize all the results, Figure 8 shows an overview of the results of 0 K phase stability of $\text{Sc}_{1-x}\text{M}_x\text{N}$ and $\text{ScN}_{1-x}\text{A}_x$ at $x = 0.50$. The results indicate that $\text{Sc}_{1-x}\text{Y}_x\text{N}$, $\text{Sc}_{1-x}\text{La}_x\text{N}$, $\text{Sc}_{1-x}\text{Gd}_x\text{N}$, $\text{Sc}_{1-x}\text{Ga}_x\text{N}$, and $\text{Sc}_{1-x}\text{In}_x\text{N}$ for Sc sublattice and $\text{ScN}_{1-x}\text{P}_x$, $\text{ScN}_{1-x}\text{As}_x$, and $\text{ScN}_{1-x}\text{Sb}_x$ for N sublattice have an energetic driving force for phase separation due to volume mismatch. When the volume mismatch is small, the system shows tendency to form solid solution like $\text{Sc}_{1-x}\text{Lu}_x\text{N}$. On the other hand, $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, and $\text{Sc}_{1-x}\text{Hf}_x\text{N}$ exhibit B1-L1₀ and B1-L1₁ ordered solid solution tendency because of low volume mismatch and the effect of electronic structure due to d shell valence electron,

as well as shown in $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$. Moreover, at $x = 0.50$ of $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$ system can form ScTa₂N₂-type structure as the most competitive phase. However, all these results come from 0 K DFT calculations alone. Our objective of this study is to obtain information about the phase stability of ScN-based solid solution at temperatures where diffusion could be active to select a suitable element and strategy in thermal conductivity reduction for thermoelectric medium to high temperature application of ScN. Therefore, we need to consider these results at elevated temperature.

Figure 9 shows the results of phase stability of $\text{Sc}_{1-x}\text{M}_x\text{N}$ and $\text{ScN}_{1-x}\text{A}_x$ for $x = 0.50$ at estimated temperature effect at $T = 800^\circ\text{C}$ which is a typical temperature where metal sublattice diffusion has been reported to be activated in mixed nitrides. The results show that at $x = 0.50$ and

FIG. 8. Summary of phase stability of ScN-based solid solution at $x = 0.50$ and $T = 0\text{ K}$.

FIG. 9. Summary of phase stability of ScN-based solid solution at $x = 0.50$ and $T = 800^\circ\text{C}$.

$T = 800^\circ\text{C}$, $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, $\text{Sc}_{1-x}\text{Hf}_x\text{N}$, and $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ system have changed their phase from B1-L1₀ and B1-L1₁ ordered solid solution to a disordered solid solution. However, also after inclusion of the effect of temperature the $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$ system still have ScTa₂N₂-type structure stable meaning that ScTa₂N₂-type structure is stable at this considered temperature.

The results that show in Figure 8 suggest the suitable strategies for ScN lattice thermal conductivity reduction for thermoelectric application. First, Lu is a suitable element for lattice thermal conductivity reduction by solid solution. $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ is stable as solid solution at $T = 800^\circ\text{C}$ and Lu is a heavy element compared to Sc and N. Furthermore, Lu has the same number of valence electrons as Sc, therefore, there is no doping effect unlike when ScN form solid solution with Ti, Zr, Hf. The latter should be considered only when intentional electron doping is desired. One should keep in mind that such alloying could give a side effect of Seebeck coefficient reduction yielding no improvement or even decreasing the value of the thermoelectric figure of merit ZT . The tendency of mixing of TiN/ZrN/HfN and ScN should also be kept in mind when designing superlattices between them as the transformation of these superlattices to a metallic solid solution would destroy their thermoelectric performance completely.⁵¹

A second strategy is using inclusions to reduce lattice thermal conductivity. The results indicate that we can use Y, La, Gd, Al, Ga, In, P, As, and Sb, since these systems have phase separation tendency and they tend to have isostructural, possibly semi-coherent, interfaces after the decomposition which should have minor effects on carrier mobility. Moreover, we can use these results to suggest a good nitride material for superlattice to reduce lattice thermal conductivity and enhancing power factor, i.e., using YN, LaN, GdN, ScP, ScAs, or ScSb forming alternating layer with ScN, since all of them prefer to phase separate and have similar crystal structure as ScN. Even at high working temperature, they should thus not intermix and degrade the thermoelectric properties. Finally, the ScTa₂N₂-type inherently nanolaminated structures could potentially be promising structure for thermoelectric application in themselves, since they are

thermodynamically stable and have been reported to have semimetallic character.⁴⁵ Thus, Nb or Ta is a good choice to use for ScTa₂N₂-type structures since both of them have heavy mass difference which give more effect on lattice thermal conductivity reduction as compared to V.

IV. CONCLUSIONS

We have used density functional theory calculations to investigate the effect of mixing thermodynamic in order to determine phase stability of ScN-based solid solutions of relevance for lattice thermal conductivity reduction in thermoelectric applications. Our results demonstrate that at $T = 800^\circ\text{C}$ the free energy of mixing for $\text{Sc}_{1-x}\text{Y}_x\text{N}$, $\text{Sc}_{1-x}\text{La}_x\text{N}$, $\text{Sc}_{1-x}\text{Gd}_x\text{N}$, $\text{Sc}_{1-x}\text{Ga}_x\text{N}$, and $\text{Sc}_{1-x}\text{In}_x\text{N}$ for Sc sublattice and $\text{ScP}_{1-x}\text{N}_x$, $\text{ScAs}_{1-x}\text{N}_x$, and $\text{ScSb}_{1-x}\text{N}_x$ for N sublattice still have phase separation tendency at high temperature. In addition, the ScTa₂N₂-type structure in the $\text{Sc}_{1-x}\text{V}_x\text{N}$, $\text{Sc}_{1-x}\text{Nb}_x\text{N}$, and $\text{Sc}_{1-x}\text{Ta}_x\text{N}$ systems is also stable at high temperature. On the other hand, at 800°C $\text{Sc}_{1-x}\text{Ti}_x\text{N}$, $\text{Sc}_{1-x}\text{Zr}_x\text{N}$, $\text{Sc}_{1-x}\text{Hf}_x\text{N}$, and $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ systems are predicted to be thermodynamically stable in disordered B1 solid solutions rather than in the B1-L1₀ and B1-L1₁ ordered solid solutions stable at 0 K.

From these results, we are able to suggest suitable materials for the different possible strategies for reduction of the lattice thermal conductivity of ScN. Since, Lu has tendency to mix with ScN and Lu does not give doping effect after mixing due to it has the same valence electron as ScN, thus, $\text{Sc}_{1-x}\text{Lu}_x\text{N}$ system can be used for solid solution strategy. Next, Y, La, Gd, Al, Ga, In, P, As, and Sb, have phase separation tendency when they mix with ScN, therefore, they are a good system for a nano-inclusion strategy. YN, LaN, and GdN or ScP, ScAs, and ScSb can be used for making a superlattice with ScN, since, they are not tending to intermixing at high temperature and are isostructural with ScN. The mixing thermodynamics of the considered alloy systems can be understood by considering the effect of the factors of volume mismatch, favoring phase separation, and an electronic structure effect of delocalization of extra *d*-electrons to empty Sc 3*d*-2*g* states, favoring mixing.

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