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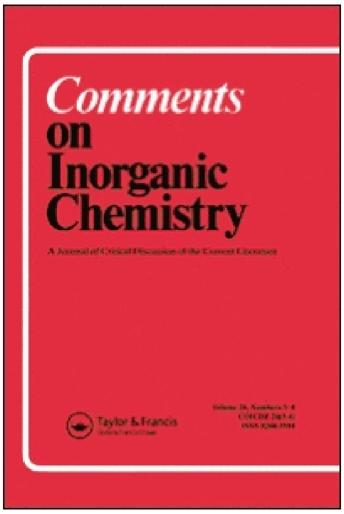

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Alkali-Metal Substitution into Solid-State Chalcogenides: Effects on Dimensionality

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Alkali-Metal Substitution into Solid-State Chalcogenides: Effects on Dimensionality

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The structures of many binary solid-state chalcogenides (chalcogen = S, Se, Te) are known along with the structures of the related ternaries formed by addition of an alkali metal. Similarly, the structures of many ternary solid-state chalcogenides are known along with the structures of the related quaternaries formed by addition of an alkali metal. The dimensionality of such compounds has been examined through a review of the literature. It is found in general that addition of the alkali metal lowers the dimensionality of the resultant structure. This trend, which appears to be general, is illustrated and discussed.

Key Words: *binary chalcogenide, ternary chalcogenide, quaternary chalcogenide, solid state, structure, dimensionality*

INTRODUCTION

Beyond doubt, synthesis is the frontier area of research in solid-state chemistry, for it is self-evident that if a material has not been synthesized its physical properties cannot be measured! And often

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the properties that newly synthesized materials possess lead to potentially wide applications.[1-8] The difficulties of predicting the existence, composition, structure, and physical properties of potential solid-state compounds are well known,[9] many (some would say most) new materials are formed serendipitiously.[10] Although some rational approaches to the synthesis of new solid-state materials exist, including the Zintl concept[11-14] and the notion of coordination preferences,[15] these are of limited applicability. Much of solid-state chemistry remains largely empirical, and as part of this empiricism one seeks clues on how to predict structures or physical properties. Solid-state chalcogenides are an attractive area of research,[16-20] with many of their interesting physical properties and applications[1,7,8,18,19,21-23] related to their propensity to form low-dimensional networks.[1,8,16,17,24-27] But do we understand why some solid-state chalcogenides have low-dimensional structures? Can we predict from known structures the dimensionality to be expected in derivative structures of hypothetical composition? In general, "no" is the answer to these and related questions.

Although dimensionality is a generally understood qualitative concept, we return to a more thorough discussion of it below. Our interest in this matter was triggered by the synthesis of a series of mixed-metal chalcogenides[28-32] with the use of the reactive flux method.[33,34] In the series Cu_3NbSe_4[32,35] to KCu_2NbSe_4[29] to $K_2CuNbSe_4$[28] to K_3NbSe_4[36] we go from three-dimensional to two-dimensional to one-dimensional structures and finally to a structure that contains isolated K^{1+} cations and $NbSe_4^{3-}$ anions. In this series niobium is most conveniently considered to be Nb^{5+}, while copper and potassium are Cu^{1+} and K^{1+}, respectively. Conceptually, then, the series represents the progressive substitution of K^{1+} for Cu^{1+}, and as this occurs the dimensionality of the compound decreases. Is this a general trend? The answer appears to be "yes." This Comment examines the literature of solid-state chalcogenides to conclude that in general the dimensionality of binary compounds is lowered by the progressive addition of alkali metal to form ternaries, and that the dimensionality of mixed-metal ternaries is lowered by the progressive addition of alkali metals to form quaternaries. This general trend, derived empirically, may represent another small step in the direction of predicting the composition, structures, and physical properties of solid-state materials.

THE DIMENSIONALITY OF A SOLID-STATE CHALCOGENIDE

We choose to describe solid-state structures in terms of linking of polyhedra to form extended assemblies. This description is particularly useful for chalcogenides[15] and also emphasizes their structural relationships with physical properties.[37]

The concept of dimensionality of solid-state chalcogenides has been discussed often.[24,37-39] While decreasing dimensionality can be associated with increasing anisotropy of structure and properties,[24] we find it more convenient to define dimensionality in essentially an intuitive way. Let us illustrate this with the compounds discussed above. The compound Cu_3NbSe_4[32,35] comprises the edge- and corner-sharing of tetrahedral $CuSe_4$ and $NbSe_4$ units to form a structure in which there are Cu–Se and Nb–Se bonding distances (Fig. 1). We describe such a structure as *three-dimensional*. Conversely, the structure of K_3NbSe_4[36] comprises $NbSe_4^{3-}$ tetrahedra isolated from one another by K^{1+} ions (Fig. 2). We describe such a structure as *isolated*. Intermediate between these two extremes are KCu_2NbSe_4 and $K_2CuNbSe_4$. In the structure of KCu_2NbSe_4[29] edge-sharing and corner-sharing tetrahedra form layers that are separated by K^{1+} ions (Fig. 3). This structure we describe as *two dimensional*. In the structure of $K_2CuNbSe_4$[28] infinite chains of edge-sharing, alternating $CuSe_4$ and $NbSe_4$ tetrahedra are separated from one another by K^{1+} ions (Fig. 4). We describe this

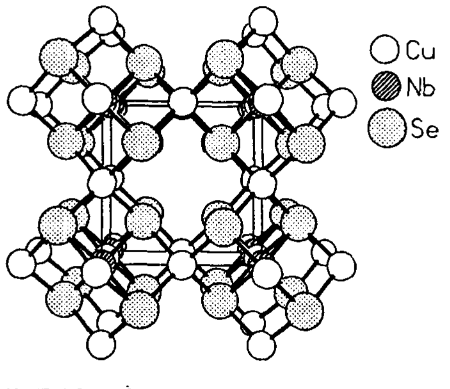

FIGURE 1 The Cu_3NbSe_4 structure (Refs. 32 and 35).

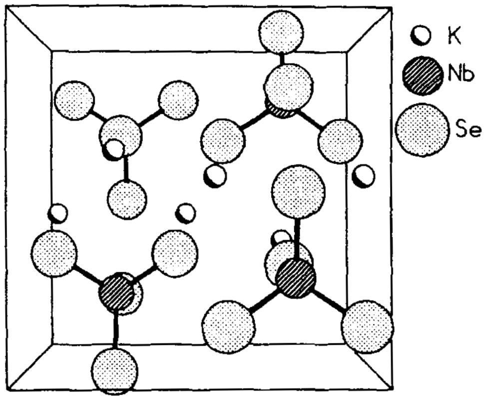

FIGURE 2 The K_3NbSe_4 structure (Ref. 36).

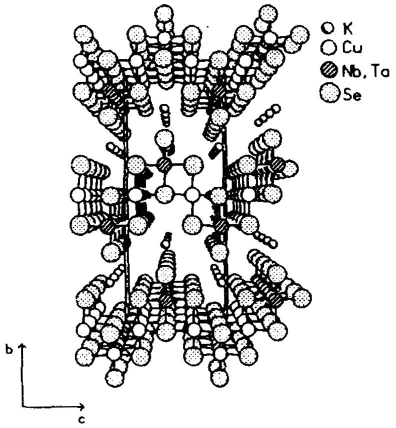

FIGURE 3 The KCu_2MSe_4 (M = Nb, Ta) structure (Refs. 29 and 32).

structure as *one dimensional*. One sees that in describing the decreasing dimensionality from three to two to one to isolated we have focused our attention on the non-alkali metal portion of the structures.

Since this approach to dimensionality depends upon the perception of bonding interactions, there clearly are structures whose dimensionality is ambiguous. $TiSe_2$[40] is a two-dimensional structure made up of infinite two-dimensional slabs interacting with one

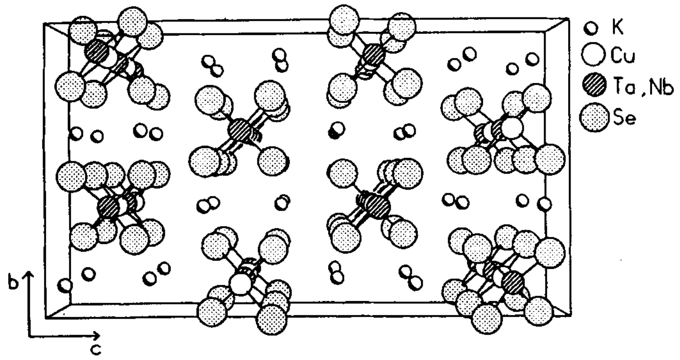

FIGURE 4 The K_2CuMSe_4 (M = Nb, Ta) structure (Refs. 28 and 31).

another through weak van der Waals' forces. Contrast this with transition-metal ditellurides where the basic structure is the same but where the interactions between layers can be interpreted[38,39] as being somewhat stronger than van der Waals' forces. Nevertheless, such forces are still weak compared with intraslab forces, and for our purposes we consider such ditellurides as being two dimensional.

INFLUENCE OF ALKALI METALS ON DIMENSIONALITY

The structures of more than four hundred alkali-metal containing and related solid-state chalcogenides have been determined. This number does not include the numerous structures known where there is intercalation of alkali metals into the van der Waals' gaps of layered binary chalcogenides. The intercalation chemistry of two-dimensional layered compounds has received extensive attention.[1,18,41–43] Since intercalation is generally reversible through appropriate chemical or thermal treatment and does not involve a structural transformation, such compounds are excluded from the following discussion. We also exclude the comparison of structures where a change of oxidation state of metal and chalcogen occurs upon addition of an alkali metal. Such an example would be FeS_2 (Fe^{2+}, S_2^{2-}) to $KFeS_2$ (Fe^{3+}, K^{1+}, S^{2-}). With these exclusions,

TABLE I

Selected examples of alkali-metal content vs. dimensionality in solid-state chalcogenides.

Element	Oxidation State	Compound	M/A	Dim.[a]	Ref.
Sc	3+	Sc_2S_3		3-D	(60)
	3+	$NaScS_2$	1.0	2-D	(61)
Ln[b]	3+	Ln_2S_3		3-D	(62)
	3+	$NaLnS_2$	1.0	2-D	(63)
Ti	4+	$TiSe_2$		2-D	(40)
	4+	$Na_2Ti_2Se_8$	1.0	1-D	(64)
Nb	5+	Cu_3NbQ_4 (Q = S, Se, Te)		3-D	(32, 35)
	5+	KCu_2NbQ_4 (Q = S, Se)	3.0	2-D	(29)
	5+	$K_3Cu_3Nb_2Q_8$ (Q = S, Se)	1.7	1-D	(30)
	5+	$K_2CuNbSe_4$	1.0	1-D	(28)
	5+	$K_3CuNb_2Se_{12}$	1.0	1-D	(28)
	5+	K_3NbQ_4 (Q = S, Se)	0.33	Iso.	(36)
	5+	Nb_2Q_5 (Q = S, Se) unstable			(32)
Ta	5+	Cu_3TaQ_4 (Q = S, Se)		3-D	(35)
	5+	KCu_2TaSe_4	3.0	2-D	(32)
	5+	$K_3Cu_3Ta_2Q_8$ (Q = S, Se)	1.7	1-D	(30)
	5+	$K_2CuTaSe_4$	1.0	1-D	(31)
	5+	K_3TaQ_4 (Q = S, Se)	0.33	Iso.	(36)
	5+	Ta_2Q_5 (Q = S, Se) unstable			(32)
Cr	3+	Cr_2S_3		3-D	(65)
	3+	ACr_5S_8 (A = K, Rb, Cs)	5.0	3-D[c]	(66)
	3+	$KCrS_2$	1.0	2-D	(67)
Mn	2+	MnS		3-D	(44)
	2+	$A_2Mn_3S_4$ (A = K, Rb, Cs)	1.5	2-D	(45, 46)
	2+	A_2MnQ_2 (A = K, Rb, Cs; Q = S, Se, Te)	0.5	1-D	(47)
	2+	A_6MnQ_4 (A = Na, K; Q = S, Se, Te)	0.17	Iso.	(48)
Fe	3+	Fe_2S_3 unstable			(61)
	3+	$AFeS_2$ (A = K, Rb, Cs)	1.0	1-D	(68)
	3+	Na_5FeS_4	0.2	Iso.	(69)
Co	2+, 3+	Co_3S_4		3-D	(70)
	2+, 3+	$Na_5Co_2S_5$	0.4	1-D	(71)
	2+	$Cs_2Co_3S_4$	1.5	2-D	(46)
	2+	Na_6CoS_4	0.17	Iso.	(71)
Pd	2+	PdS		3-D	(49, 50)
	2+	$A_2Pd_3Q_4$ (A = K, Rb, Cs; Q = S, Se)	1.5	2-D	(51, 72)
	2+	A_2PdQ_2 (A = Na, K, Rb; Q = S, Se)	0.5	1-D	(52, 53)
Ag	1+	Ag_2S		3-D	(73)
	1+	$A_2Ag_4S_3$ (A = K, Rb)	2.0	2-D	(74)
	1+	Na_3AgS_2	0.33	1-D	(75)

TABLE I (*Continued*)

Element	Oxidation State	Compound	M/A	Dim.[a]	Ref.
Zn	2+	ZnS		3-D	(76)
	2+	$Na_2Zn_3S_4$	1.5	2-D	(46)
	2+	Na_2ZnS_2	0.5	1-D	(71)
	2+	Na_6ZnS_4	0.17	Iso.	(71)
Hg	2+	HgS		3-D	(54)
	2+	$A_2Hg_6Q_7$ (A = K, Cs; Q = S, Se)	3.0	3-D[c]	(55, 56)
	2+	$A_2Hg_3Q_4$ (A = K, Cs; Q = S, Se)	1.5	1-D	(55, 56)
	2+	A_6HgQ_4 (A = K, Rb; Q = S, Se)	0.17	Iso.	(57)
Al	3+	Al_2S_3		3-D	(77)
	3+	$AAlQ_2$ (A = Na, K; Q = Se, Te)	1.0	1-D	(78)
	3+	Na_3AlS_3	0.33	Iso	(79)
Ga	3+	Ga_2Se_3		3-D	(80)
	3+	$CsGaSe_2$	1.0	1-D	(81)
	3+	$Cs_{10}Ga_6Se_{14}$	0.6	Iso.	(81)
	3+	$Cs_8Ga_4Se_{10}$	0.5	Iso.	(81)
	3+	$Cs_6Ga_2Se_6$	0.33	Iso.	(81)
In	3+	In_2S_3		3-D	(82)
	3+	KIn_5S_8	5.0	3-D[c]	(83)
	3+	$AInS_2$ (A = K, Rb, Cs)	1.0	1-D	(84)
Si	4+	$SiTe_2$		2-D	(85)
	4+	$Cs_2Si_2Te_6$	1.0	1-D	(86)
	4+	SiQ_2 (Q = S, Se)		1-D	(87)
	4+	$Na_4Si_4S_{10}$	1.0	Iso.	(88)
Ge	4+	GeQ_2 (Q = S, Se)		2-D	(89, 90)
	4+	Na_2GeSe_3	0.5	1-D	(91)
	4+	Na_4GeSe_4	0.25	Iso.	(92)
Sn	4+	SnQ_2 (Q = S, Se)		2-D	(25)
	4+	$Na_4Sn_3S_8$	0.75	2-D	(93)
	4+	$Na_6Sn_2S_7$	0.33	Iso.	(94)
	4+	Na_4SnS_4	0.25	Iso.	(95)
P	5+	P_4S_{10}		Iso.	(96)
	5+	K_3PS_4	0.33	Iso.	(97)
	5+	$K_2P_2S_6$	1.0	Iso.	(98)
Sb	3+	Sb_2S_3		2-D	(99)
	3+	A_3SbS_3	0.33	Iso.	(100)

[a] 3-D: three-dimensional; 2-D: two-dimensional; 1-D: one-dimensional; Iso.: Isolated.

[b] Ln = lanthanide.

[c] This structure shows some one-dimensional character.

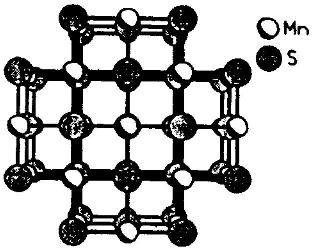

FIGURE 5 Structure of MnS (Ref. 44).

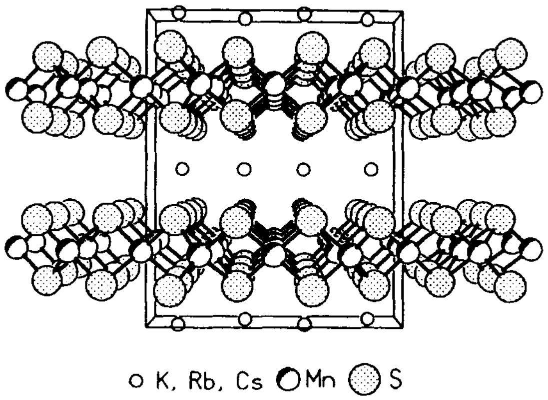

FIGURE 6 Structure of $A_2Mn_3S_4$ (A = K, Rb, Cs) (Refs. 45 and 46).

the trend noted above in the Cu_3NbSe_4 to K_3NbSe_4 series appears to be general. In Table I we have tabulated examples of the changes of dimensionality with alkali-metal substitution across the Periodic Table. The tabulation is not exhaustive, but it is meant to be detailed enough to illustrate the trend of decreasing dimensionality with increasing alkali-metal content.

We now discuss transformations in selected systems. MnS^{44} has a face-centered cubic structure in which Mn atoms are in tetrahedral coordination and the tetrahedra edge- and corner-share in three directions (Fig. 5). The $A_2Mn_3S_4$ (A = K, Rb, Cs)[45,46] compounds, in which a quarter of the Mn atoms in MnS are substituted by alkali metals, have two-dimensional layers formed from the edge- and corner-sharing of Mn-centered tetrahedra. These layers are separated by alkali metals and we describe the structures as

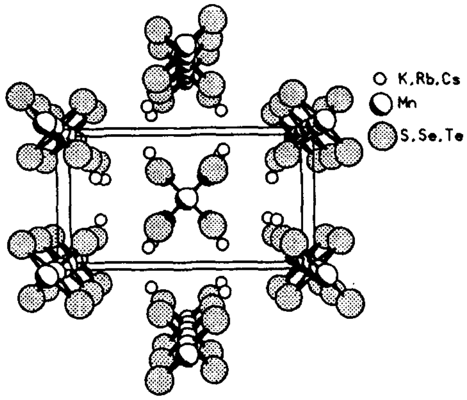

FIGURE 7 The A_2MnQ_2 structure (A = K, Rb, Cs; Q = S, Se, Te) (Ref. 47).

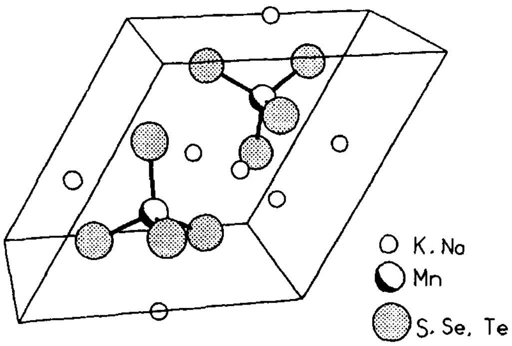

FIGURE 8 The A_6MnQ_4 structure (A = Na, K; Q = S, Se, Te) (Ref. 48).

two-dimensional (Fig. 6). The non-alkali metal to alkali metal ratio (M/A) is 1.5 here. The A_2MnQ_2 (A = K, Rb, Cs; Q = S, Se, Te)[47] compounds, in which one half of the Mn atoms in MnS are substituted by alkali metals, have structures in which infinite tetrahedral, edge-sharing, one-dimensional chains are separated by alkali metals, and we describe these structures as one-dimensional (Fig. 7). The M/A ratio is 0.5. The A_6MnQ_4 (A = Na, K; Q = S, Se, Te)[48] compounds, in which three-fourths of the Mn atoms in MnS are substituted by alkali metals, display structures in which there are discrete MnQ_4^{6-} ions separated by alkali metals (Fig. 8), and we describe these structures as isolated. The M/A ratio is 0.17.

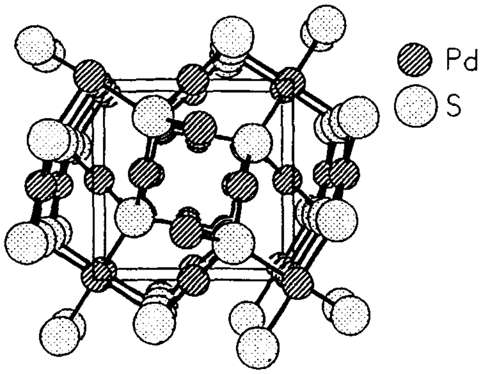

FIGURE 9 The structure of PdS (Refs. 49 and 50).

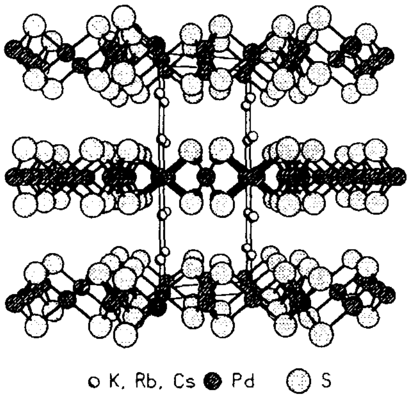

FIGURE 10 The structure of $A_2Pd_3S_4$ (A = K, Rb, Cs) (Ref. 51).

As another example, $PdS^{49,50}$ has a three-dimensional structure (Fig. 9). Partial substitution of Pd by alkali metals affords the two-dimensional layer compounds $A_2Pd_3S_4$ (A = K, Rb, Cs)[51] (M/A = 1.5) (Fig. 10). A further substitution of Pd by alkali metal to the composition A_2MQ_2 (A = K, Rb; M = Pt, Pd; Q = S, Se)[52,53] (M/A = 0.5) results in compounds that contain one-dimensional chains of edge-sharing, square-planar PdQ_4 units (Fig. 11). HgS^{54} displays both zincblende and rock-salt structures. Consider the following progressive substitution of Hg by alkali metal: $A_2Hg_6Q_7$ (A = K, Cs; Q = S, Se)[55,56] (M/A = 3.0), three-dimensional

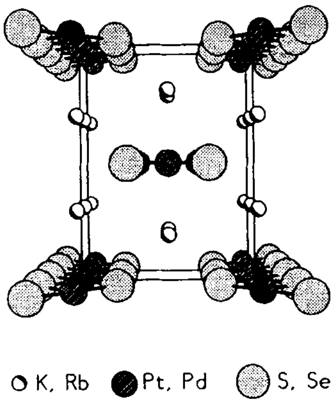

FIGURE 11 The structure of A_2MQ_2 (A = K, Rb; M = Pt, Pd; Q = S, Se) (Refs. 52 and 53).

framework structures; $A_2Hg_3Q_4$ (A = K, Cs; Q = S, Se)[55,56] (M/A = 1.5), infinite one-dimensional chains; A_6HgQ_4 (A = K, Rb; Q = S, Se)[57] (M/A = 0.17), isolated HgQ_4^{6-} tetrahedra. The same trend of decreasing dimensionality with increasing substitution of alkali metal holds for ternaries to quaternaries as well, as the original example of Cu_3NbSe_4 to KCu_2NbSe_4 to $K_2CuNbSe_4$ to K_3NbSe_4 demonstrates.

Although the dimensionality of a given system tends to decrease with decreasing M/A ratio, that ratio should not be interpreted in a quantitative way among systems. Thus both KCuSe[58] and $KCuQ_4$ (Q = S, Se)[56,59] have M/A = 1, but the structure of KCuSe is two-dimensional whereas that of $KCuQ_4$ is one-dimensional. In most solid-state chalcogenides the dimensionality of the structure is independent of the alkali metal, but this is not always so. Thus $NaAuSe_2$[56] has a two-dimensional layer structure, whereas $KAuSe_2$[56] has a one-dimensional structure.

PROBABLE EXPLANATION

Put very simply, the alkali metals are sufficiently electronegative so that they do not enter into chemical bonding with the chalcogens. As a result the addition of alkali metals to a solid-state chalcogenide will tend to break up the original bonding, ultimately leading to lower dimensionality of the system. One would expect the same trend with alkaline earths, but the structural data for such systems are very sparse.

Thus, the trend of decreasing dimensionality of a solid-state chalcogenide with increasing alkali-metal content is not really surprising. What is surprising is that attention has not been called to this trend in the past, for as we noted in the Introduction solid-state chemistry is a sufficiently empirical subject that any trend of even modest generality is a welcome addition.

Acknowledgment

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