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Cationic Radius Ratio and Formation of K_2NiF_4-Type Compounds

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A survey of known compounds which can assume K_2NiF_4-type structure at least over a certain P, T range was made. The cationic radius ratios r_A/r_B of this family of compounds were found to vary over a relatively narrow range of values around 2.00, in contrast to the much wider ranges known for other important A_2BX_4 structure groups, e.g., β-K_2SO_4, thenardite, olivine, etc., providing thereby a constraint on the crystal chemical variabilities in this group of compounds. Usefulness of the simple size parameter $r_A(\mathrm{IX})/r_B(\mathrm{VI})$ in predicting formation of new K_2NiF_4-type compounds is discussed.

Introduction

The compound K_2NiF_4 crystallizes in the tetragonal space group $I4/mmm$ (*1*) in which octahedrally coordinated Ni^{2+} ions form extended sheets along (001), interspersed with two layers of much larger K^+ ions in ninefold coordination with fluorine. A large number of isotypes of this compound are known. Current interest in these layer-type compounds stems from the reported two-dimensional antiferromagnetic behavior of K_2NiF_4 (*2*). A survey of the known K_2NiF_4-type compounds was undertaken in search of some characteristic parameters governing formation of this structure among A_2BX_4 compounds. The results show that the size ratio of the cations, $r_A(\mathrm{IX})/r_B(\mathrm{VI})$, serves this purpose to a reasonably good extent.

Cationic Radius Ratios and Their Ranges

The major stoichiometries with known A- and B-site occupants are shown in Table I. It must be pointed out, however, that only about 45% of the total number of possible A–B combinations in Table I lead to the formation of K_2NiF_4-type compounds. Among the rest, there are several forbidden A–B combinations which give rise to non-K_2NiF_4-type structures, e.g., Ba_2TiO_4, Ba_2CrO_4, Ba_2FeO_4, Sr_2PbO_4, Ca_2PbO_4, Ca_2IrO_4, and Ca_2SnO_4 (*4, 5*) in group 2, and Cs_2MgCl_4 (*19*) in group 7; crystallographic information about some others (e.g., $BaLnB^{3+}O_4$, where $B = Al^{3+}$, Cr^{3+}, Fe^{3+}, etc.) is apparently unavailable. Additional compounds not considered in Table I include some oxyfluorides, chlorobromides, and chloroiodides (*5, 6, 18, 21*). Oxygen and fluorine, however, remain by far the most dominant occupants of the X-site.

Effective ionic radius values of Shannon (*7*) were used for computing $r_A(\mathrm{IX})/r_B(\mathrm{VI})$ values of known K_2NiF_4-type compounds (*5, 6, 16, 21, 23–27*). In the case of transition metals, high-spin and low-spin radii were used for divalent and trivalent B-ions, respectively, because (i) published information (*8–10*) suggests such a generalization for the trivalent ions except Fe^{3+} (*3*), and (ii) preliminary plottings of r_A/r_B vs c/a showed relative self-consistencies, especially for the fluorides, when such spin states were

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TABLE I

MAJOR A_2BX_4 STOICHIOMETRIES FOR K_2NiF_4-TYPE STRUCTURES WITH POSSIBLE OCCUPANTS OF A AND B SITES[a]

Stoichiometry (1)	Possible A cations (2)	Possible B cations (3)	Reference (4)
1. $A_2^{+}B^{2+}F_4$	K^+, Rb^+, Cs^+, Tl^+, NH_4^+	Mg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}	(*5, 23*)
2. $A_2^{2+}B^{4+}O_4$	Ba^{2+}, Sr^{2+}, Ca^{2+}	Pb^{4+}, Zr^{4+}, Hf^{4+}, Sn^{4+}, Tc^{4+}, Mo^{4+}, Ir^{4+}, Ru^{4+}, Ti^{4+}, Rh^{4+}, Fe^{4+}, Cr^{4+}, Mn^{4+}	(*5, 23*)
3. $A_2^{3+}B^{2+}O_4$	*Ln*(=La–Gd)	Ni^{2+}, Cu^{2+}	(*5*)
4. $A^{2+}A^{3+}B^{3+}O_4$	Sr^{2+}, Ba^{2+}, Ca^{2+}, *Ln*(=La–Er)	Ni^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Al^{3+}, Cr^{3+}	(*5, 24–26*)
5. $A^{+}A^{3+}B^{4+}O_4$	Na^+, *Ln*(=La–Lu)	Ti^{4+}	(*5*)
6. $A^{+}B^{6+}O_4$	K^+, Rb^+, Cs^+	U^{6+}, Np^{6+}	(*5*)
7. $A_2^{+}B^{2+}Cl_4$	K^+, Rb^+, Cs^+	Cr^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}	(*5, 18, 19*)
8. $A^{2+}_{1.5}A^{3+}_{0.5}B^{4+}_{0.5}B^{3+}_{0.5}O_4$	Ca^{2+}, *Ln*(=Pr–Gd)	$Cr^{3+}+Cr^{4+}$	(*16*)

[a] Any given A cation/cation pair of column 2 may not necessarily combine with *every* B cation of column 3 to give a K_2NiF_4-type compound; see text.

assumed. However, the basic observations made here were not dependent on this choice. The cationic radius ratio was found to assume values around 2.00, varying mostly within the narrow range of 1.70 to 2.40. A comparison of this spread (~0.7) of r_A/r_B with those for other A_2BX_4 structural families (*5, 11, 12, 20*), e.g., $r_A(VI)/r_B(IV)$ for olivines, yielded the following approximate values: β-K_2SO_4, 9.5; thenardite, 5; olivine, 4; spinel, 2; phenakite, 1.8. The relatively narrower spread, which is also suggested by the A_2BX_4 structure field maps (*5, 27*), makes the $r_A(IX)/r_B(VI)$ ratio a characteristic parameter for ascertaining if a certain A_2BX_4 ($X = O^{2-}$, F^-; also Cl^-, Br^-, etc.) compound can, under some suitable P, T conditions, crystallize with a K_2NiF_4-type structure.

Discussion

Out of more than 150 compounds assuming the K_2NiF_4 structure, only about 5% have r_A/r_B values lying outside the prescribed range of 1.7–2.4. Most of the exceptions are below the minimum value, i.e., around 1.6–1.7, which should cause a relative decrease of the two-dimensional character. Among these, La_2CoO_4, La_2CuO_4, and Nd_2NiO_4 have the tetragonal structure only at elevated temperatures (*13–15*). This should also be valid for the series $CaLnCrO_4$ (Ln = Pr, Nd, Sm, Eu, Gd) where

r_A/r_B values are much more favorable (*16*). The $r_A(IX)/r_B(VI)$ values for hypothetical K_2NiF_4-type polymorphs of compounds (*6, 20*) belonging to other structure groups (obviously only when the *A* and *B* cations have the capability of going into ninefold and sixfold anion coordination, respectively; this excludes, for example, all the phenakite-type compounds, as well as most of the olivines and spinels) largely fall outside the prescribed range. The same is true for most of the "forbidden" *A*–*B* combinations mentioned earlier, and is probably a cause of their inability to crystallize with a K_2NiF_4-type structure. It is, thus, reasonable to expect that polymorphism involving this structure type will be rare in occurrence. The few known examples (*5, 17, 22*) undergoing temperature/pressure-induced phase inversion, i.e., Sr_2CrO_4, Ca_2GeO_4, and some $CaLnGaO_4$ phases have cationic radius ratios varying in the range 1.79–2.38, which supports our contention. Other potential candidates include the olivines $NaLnGeO_4$ (Ln = Y, Eu–Lu) and Mn_2GeO_4, though ninefold anion coordination of Mn^{2+} is

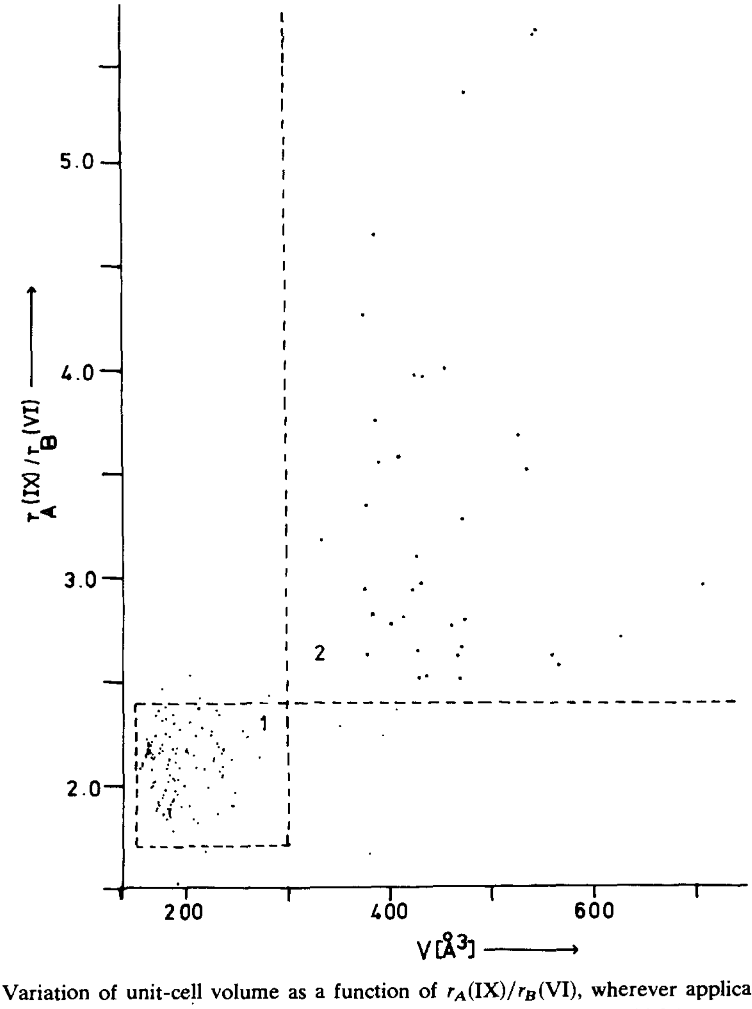

FIG. 1. Variation of unit-cell volume as a function of $r_A(IX)/r_B(VI)$, wherever applicable, among A_2BX_4 compounds (see text); field 1 is for K_2NiF_4-type compounds, while field 2 is a part of the area represented by β-K_2SO_4-type and related structures.

apparently unknown (7). Compounds yielding values less than 1.70 are mostly distorted forms of K_2NiF_4 or isotypes of Sr_2PbO_4 structure; those having higher values are mostly β-K_2SO_4-type or closely related structures. The cationic radius ratio vs cell volume plot clearly demonstrates the very restricted field for K_2NiF_4-type structure, as compared to that of β-K_2SO_4, only a part of which is shown in Fig. 1.

A further use of the r_A/r_B value is in suggesting new compounds which could crystallize with a K_2NiF_4-type structure; various new stoichiometries can be expected to do so, though those for which r_A/r_B lies comfortably within 1.9–2.3 will stand better chances. Some typical examples are: Ca_2BO_4 ($B = Ru^{4+}$, Rh^{4+}, Cr^{4+}); $BaLnAlO_4$ (Ln = Gd–Lu); $SrLnAlO_4$ (Ln = Pm–Lu); A_2UO_3F ($A = K^+$, Rb^+, Cs^+); Ln_2AlO_3F (Ln = La–Ho); Ln_2NiO_3F (Ln = La–Eu); and $Ba_2BO_2F_2$ ($B = Mg^{2+}$, Ni^{2+}, Cu^{2+}).

The reasons for the relatively strict control of r_A/r_B in the formation of K_2NiF_4-type compounds can be manifold. The large difference in coordination number of A and B ions excludes ions of similar size in both the sites, and their interchange, as among the spinels; the high coordination number of A restricts the types of cations acceptable in this site. The crystallographic restrictions put by special positions of the atoms in the lattice disallow, among others, rotation or nonsymmetrical deformation of the octahedra; this could be another controlling factor.

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