BRIEF COMMUNICATION

Radius Ratio Tolerance Factors and the Stability of Hollandites

S. E. KESSON*

*Research School of Earth Sciences, Australian National University,
GPO Box 4, Canberra ACT 2600, Australia*

AND T. J. WHITE

*Materials Division, Lucas Heights Research Laboratories,
Australian Atomic Energy Commission, Private Mail Bag,
Sutherland NSW 2232, Australia*

The hollandite family of crystal structures conforms to the general formula $[A_x][B_y C_{8-y}]O_{16}$, $x \le 2$ (*1*). The comparatively large A cations may be monovalent or divalent (Na, Ag, K, Rb, Tl, Cs, Sr, Ba, Ra, Pb), while the smaller cations making up the octahedral $[B,C]_8 O_{16}$ framework include di-, tri-, tetra-, and pentavalent species such as Mg, Cu, Zn, Co, Ni, Al, Ga, Fe, In, Cr, Si, Ge, Ti, Mn, Sn, and Sb. The B cations are usually less abundant and of lower valence than C cations. The hollandite structure consists of paired chains of edge-linked $(B,C)O_6$ octahedra that are connected at their corners to form a framework of tunnels either (2×2) or (1×1) octahedra in cross-sectional dimensions (*1*). The large A cations are located within the (2×2) tunnels typically in eightfold coordination to oxygen (e.g., (*2*)) although in exceptional cases tunnel cation coordination may be as low as six or as high as ten. Titanate

hollandites with comparatively large $(B,C)O_6$ octahedra are readily synthesized at ambient pressures (*3, 4*). On the other hand, silicate and germanate hollandites with their smaller octahedra require stabilization by high pressures where sixfold coordination of Ge^{4+} and Si^{4+} to oxygen is preferred (*5*). Hollandites have attracted considerable interest as supposed superionic conductors (e.g., (*6*)), and as crystalline hosts for high level radioactive waste elements (*7*). Accordingly it would be useful to have an easy means of predicting the stability of hollandites containing a variety of tunnel and framework cation combinations.

Two papers which make use of radius ratio considerations have appeared on this subject. In the first, Kinomura (*8*) obtained a narrow range of Goldschmidt tolerance factors (*t*) (*9*) for a series of titanate, germanate and stannate hollandites. The same approach was followed by Pentinghaus (*10, 11*), who concluded that cesium was too
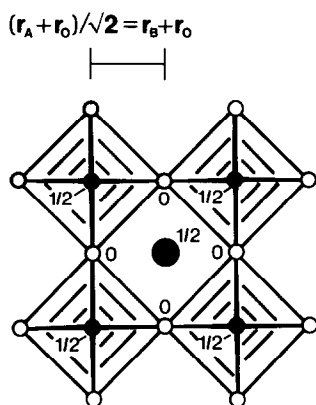
$$(r_A + r_O)/\sqrt{2} = r_B + r_O$$

FIG. 1. BO_6 octahedral motif of cubic perovskite projected along the x axis. The equation describes the condition for a large A cation to fit exactly into the cavity within the BO_6 motif. Oxygens occur at $x = 0$ (small open circles) and $x = \frac{1}{2}$ (small filled circles). The larger A cation is placed at $x = \frac{1}{4}$. For clarity, the B cations of the BO_6 octahedra have not been shown.

large to be accommodated in the titanate hollandite "$Cs_2Al_2Ti_6O_{16}$." However, the tolerance factor used by the above authors was formulated to predict, in a general way, the stability of ABO_3 perovskites and its derivation is linked to the topology of their BO_6 octahedral array. The tolerance factor for perovskite (t_p) defines the size constraints for large A cations to fit exactly into cavities in the BO_6 octahedral framework, as illustrated in Fig. 1. Thus

$$t_p = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} . \qquad (1)$$

Providing $t_p \leq 1$, the perovskite structure should be adopted, and t_p has been found empirically to range between 0.73 and 1.0 (12). Despite the extreme simplicity of this approach, calculation of perovskite tolerance factors has proved a useful means of predicting stability in many cases. Nevertheless it is incorrect to employ Eq. (1) to estimate the possible stability of a hollandite because its crystal structure is fundamentally different from perovskite.

An appropriate hollandite tolerance factor, t_H, can be derived from geometrical principles. Figure 2 shows the $(B,C)O_6$ octahedral motif of hollandite. The aperture of a (2×2) tunnel is proportional to the (B,C)–O bond length and its half-width in the appropriate projection is equal to $\sqrt{(\frac{3}{2})}$ $(r_{B,C} + r_O)$. For a large A cation to fit within the tunnel, just touching neighboring oxygen anions,

$$[(r_A + r_O)^2 - (c/2)^2]^{1/2} = \sqrt{(\tfrac{3}{2})}(r_{B,C} + r_O),$$

where c is the short hollandite axis parallel to the tunnel direction. A tolerance factor can accordingly be defined by the expression

$$t_H = \frac{[(r_A + r_O)^2 - (c/2)^2]^{1/2}}{\sqrt{(\tfrac{3}{2})}(r_{B,C} + r_O)}$$
$$= \frac{[(r_A + r_O)^2 - \tfrac{1}{2}(r_{B,C} + r_O)^2]^{1/2}}{\sqrt{(\tfrac{3}{2})}(r_{B,C} + r_O)} . \qquad (2)$$

To illustrate the use of t_H, Table I docu-

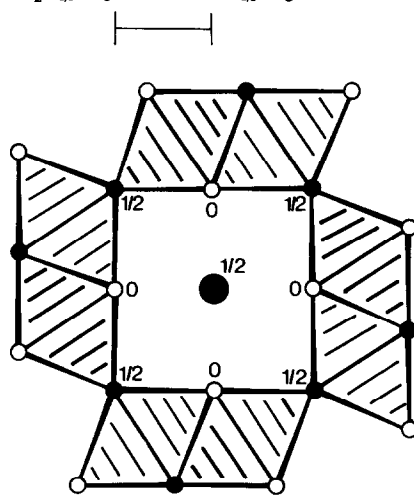$$\{(r_A + r_O)^2 - \tfrac{1}{2}(r_{B,C} + r_O)^2\}^{1/2} = \sqrt{(3/2)}\,(r_{B,C} + r_O)$$

FIG. 2. $(B,C)O_6$ octahedral motif of hollandite projected along the z axis. The equation relates A-cation diameter to tunnel dimensions in the appropriate projection. Oxygens lie at $z = 0$ (small open circles) and $z = \frac{1}{2}$ (small filled circles). The tunnel cation is at a height of $z = \frac{1}{4}$.

TABLE I

TOLERANCE FACTORS t_H FOR SOME $A_xB_yC_{8-y}O_{16}$ PHASES[a]

Tunnel cation	r_A (Å)	Framework					
		Aluminosilicates	t_H	Aluminogermanates	t_H	Aluminotitanates	t_H
Ca^{2+}	1.12	$(Ca_{1.5}Al_3Si_5O_{16})$	(0.95)	$(Ca_{1.5}Al_3Ge_5O_{16})$	(0.89)	$(Ca_{1.5}Al_{3.0}Ti_5O_{16})$	(0.86)
Na^+	1.18	$Na_2Al_2Si_6O_{16}$	0.99	$Na_2Al_2Ge_6O_{16}$	0.93	$(Na_2Al_2Ti_6O_{16})$	(0.88)
Sr^{2+}	1.26	$Sr_{1.5}Al_3Si_5O_{16}$	1.02	?	0.96	$(Sr_{1.2}Al_{2.4}Ti_{5.6}O_{16})$	(0.93)
Ag^+	1.28	?	1.04	$Ag_2Al_2Ge_6O_{16}$	0.97	?	0.94
Ba^{2+}	1.42	$Ba_{1.5}Al_3Si_5O_{16}$	1.11	?	1.04	$Ba_{1.2}Al_{2.4}Ti_{5.6}O_{16}$	1.01
Ra^{2+}	1.48	?	1.13	?	1.07	$Ra_{1.1}Al_{2.2}Ti_{5.8}O_{16}$	1.03
K^+	1.51	$K_2Al_2Si_6O_{16}$	1.16	$K_2Al_2Ge_6O_{16}$	1.09	$K_2Al_2Ti_6O_{16}$	1.05
Tl^+	1.59	?	1.20	$Tl_2Al_2Ge_6O_{16}$	1.12	?	1.08
Rb^+	1.61	$(Rb_2Al_2Si_6O_{16})$	(1.22)	$Rb_2Al_2Ge_6O_{16}$	1.13	$Rb_2Al_2Ti_6O_{16}$	1.09
Cs^+	1.74	$(Cs_{1.5}Al_{1.5}Si_{6.5}O_{16})$	(1.28)	$(Cs_{1.5}Al_{1.5}Ge_{6.5}O_{16})$	(1.20)	$Cs_{1.4}Al_{1.3}Ti^{3+}_{0.1}Ti^{4+}_{6.6}O_{16}$	1.15
Range of t_H values in hollandites		0.99–1.16		0.93–1.13		1.01–1.15	

[a] Those known to adopt hollandite structures are unbracketed; those confirmed as unable to adopt the hollandite structure are bracketed. Unknown behavior is indicated by ?. Success or failure of synthesis as reported by (3–5, 13–18).

ments some aluminosilicates, aluminogermanates, and aluminotitanates known to adopt the hollandite structure. Monovalent cations under consideration range from $Na^+(r_A = 1.18$ Å) to $Cs^+(r_A = 1.74$ Å) while divalent cations encompass $Ca^{2+}(1.12$ Å) to $Ra^{2+} = 1.48$ Å). Ionic radii for eightfold coordination are taken from Shannon (19) and mean $r_{B,C}$ values calculated according to the stoichiometries given in the table. The t_H values for phases which either fail to adopt the hollandite structure or whose behavior is unknown are calculated using stoichiometries which might reasonably be expected. Thus if A is monovalent (excluding Cs^+, which is prone to steric interference (3)) a stoichiometry of $A_2Al_2C_6O_{16}$ is assumed. On the other hand, if A is divalent then $A_{1.5}Al_3C_5O_{16}$ is a better approximation because hollandites with divalent tunnel cations (and Cs^+) do not have all of these sites fully occupied i.e., $x < 2$. Table I shows that among all three types of

hollandites, t_H values increase as tunnel cations become larger. Moreover there is a systematic relationship between tunnel cation size and tunnel dimensions. The narrow tunnels of silicate hollandites accommodate Na^+, K^+, Sr^{2+}, and Ba^{2+} but cannot accept cations larger than K^+. Failure to synthesize a calcium aluminosilicate hollandite may reflect the high-pressure disproportionation of this composition to a stable phase assemblage which is more dense than hollandite (5). Germanate hollandites, with tunnels of intermediate dimensions, can accept slightly larger cations, e.g., Tl^+ and Rb^+. (The tolerance factor for sodium aluminogermanate hollandite seems low compared to the range of t_H values for all other hollandites; however, the original experimental data have been reaffirmed by us and its synthesis is unequivocal.) Titanate hollandites with somewhat larger tunnel cross sections are unable to accommodate the smaller cations (Ca^{2+} and Na^+), and

are stabilized only by bigger cations Ba^{2+}, Ra^{2+}, K^+, Rb^+, and Cs^+. Our unpublished experimental studies have demonstrated that strontium aluminotitanate hollandites are unstable ($t_H = 0.93$); thus it is noteworthy that a strontium chromotitanate hollandite $Sr_{1.3}Cr_{2.6}Ti_{5.4}O_{16}$ ($t_H = 0.92$) can be synthesized (4).

Values for t_H range from 0.93 to 1.16. Since all phases whose behavior is unknown have t_H values within this range, it is likely that they too will be able to adopt the hollandite structure under favorable synthesis conditions. It is evident that hollandite structures are permitted even when t_H is greater than unity and as high as 1.16. This situation arises because shared octahedral edges are shortened with respect to unshared edges, leading to dilation of the (2 × 2) tunnels (21). In contrast, t_p values do not exceed 1.00 (12) because the perovskite structure does not contain edge-sharing octahedra.

It should be emphasized that t_H (like t_p) does not take into account either distortions of the $(B,C)O_6$ octahedral or subtle changes in symmetry as displayed by tetragonal and monoclinic (pseudotetragonal) hollandites (20, 21). Moreover, if t_H is used to predict whether $A_x(B,C)_8O_{16}$ phases may adopt the hollandite structure, then certain assumptions regarding both the coordination number of tunnel cations and the most appropriate stoichiometry for the phase become necessary. Conversely, anomalously low tolerance factors for a stable hollandite may indicate that in reality, its tunnel cation coordination is higher than presupposed. Hollandite tolerance factors nevertheless constitute a useful predictive method, and demonstrate that it is the size compatibility between (2 × 2) tunnel dimensions and large-cation diameter which determines whether the hollandite structure is stabilized.

Acknowledgments

References

1. A. BYSTROM AND A. M. BYSTROM, Acta Crystallogr. 3, 146 (1950).
2. W. SINCLAIR, G. M. MCLAUGHLIN, AND A. E. RINGWOOD, Acta Crystallogr. Sect. B 36, 2913 (1980).
3. G. BAYER AND W. HOFFMANN, Am. Mineral. 51, 511 (1966).
4. F. C. MIJLHOFF, D. J. W. IJDO, AND H. W. ZANDBERGEN, Acta Crystallogr. Sect. B 36, 98 (1985).
5. A. F. REID AND A. E. RINGWOOD, J. Solid State Chem. 1, 6 (1969).
6. H. U. BEYELER, Phys. Rev. Lett. 37, 1557 (1976).
7. A. E. RINGWOOD, S. E. KESSON, N. G. WARE, W. HIBBERSON, AND A. MAJOR, Geochem. J. 13, 141 (1979).
8. N. KINOMURA, J. Am. Ceram. Soc. 56, 344 (1973).
9. V. M. GOLDSCHMIDT, Skrifter Norske Videnskapes—Akad. Mat. Naturvid. Kl. No. 4, 1928.
10. H. PENTINGHAUS, Phys. Chem. Minerals 3, 85 (1978).
11. H. PENTINGHAUS, Juel Conf—42, Proc. Int. Semin. Chem. Process Eng. High Level Liquid Waste Solidification, p. 713 (1981).
12. R. S. ROTH, J. Res. Natl. Bur. Stand. 58, (1957).
13. S. KUME, T. MATSUMOTO, AND M. KOIZUMI, J. Geophys. Res. 71, 4999 (1966).
14. A. E. RINGWOOD, A. F. REID, AND A. O. WADSLEY, Earth Planet. Sci. Lett. 3, 38 (1967).
15. J. LIU, Earth Planet. Sci. Lett. 37, 438 (1978).
16. R. S. ROTH, NBSIR 81-2441, p. 42, 1981.
17. A. G. SOLOMAH, personal communication.
18. S. E. KESSON AND T. J. WHITE, Proc. R. Soc. London (1986), in press.
19. R. D. SHANNON, Acta Crystallogr. Sect. A 32, 751 (1976).
20. J. E. POST, R. B. VON DREEL, AND P. R. BUSECK, Acta Crystallogr. Sec. B 38, 1050 (1982).
21. R. W. CHEARY (1986), Acta Crystallogr., Sect. B 42, in press.