Some New Weberites

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Structural characteristics of a new type of weberite with the general formula $(A^+A^{3+})B^{5+}{}_2O^{2-}{}_7$ with $A^+ = Na^+$ or K^+, A^{3+} = a rare-earth metal cation or Y^{3+}, and $B^{5+} = V^{5+}$ or Ta^{5+} are reported. The orthorhombic distortion in these compounds and the tolerance factors (t_1,t_2) indicative of the stability of the structures are correlated.

EARLIER reports [1] from this laboratory indicated the formation of pyrochlores of general formula $(A^+A^{3+})B^{5+}{}_2O^{2-}{}_7$ where $A^+ = Li^+$, Na^+, or K^+, A^{3+} = a rare-earth metal cation or Y^{3+}, and $B^{5+} = Ta^{5+}$, Nb^{5+}, or V^{5+}. Further scrutiny of the *X*-ray diffraction pattern in this system showed the presence of compounds of similar formula type with the weberite structure. In this paper, the structural data for these compositions are reported.

EXPERIMENTAL

The compounds were prepared by solid-state reactions of the alkali-metal carbonates, rare-earth metal oxides, and pentaoxides (purity $\geqslant$99.99%). The weighed samples were mixed in stoicheiometric amounts in an agate pestle and mortar under acetone. The dried samples were pre-fired at 800 °C for 10 h and furnace cooled. The primary products were then homogenised again in a pestle and mortar and 12 mm diameter, 1—2 mm thick pellets were pressed at a pressure of 3 000 kgf cm^{-2}. These were then refired at 1 200—1 300 °C for another 12 h. The measured weight losses during the different firing operations were less than 0.1% on a 5 g batch, hence chemical analysis was not considered useful.

Lattice parameters were determined by powder *X*-ray patterns of the products on a Debye–Scherrer camera (diameter 14 cm) using nickel-filtered Cu–K_α radiation. These are accurate to 0.2% and are shown in the Table.

RESULTS AND DISCUSSION

The results in the Table show that the weberite structure is stable for $1.97_2 \leqslant r_A/r_B \leqslant 2.11_1$ in agreement with the results of Aleshin and Roy,[2] who reported the stability of these compounds for larger values of r_A/r_B ($\geqslant$1.52). For example, $Ca_2Sb_2O_7$, reported by these authors, has $r_A/r_B = 1.83_6$. Similar results were obtained by Rooksby and White [3] on rare-earth metal niobates and tantalates in which the weberite structure was shown to be confined to compounds with $1.75 \leqslant r_A/r_B \leqslant 1.84$. The corresponding range of stability for the pyrochlore structure, which is closely related to weberite, is 1.18—1.52 (see ref. 4). The unit-cell volume in the vanadium series decreases with decreasing size of the rare-earth metal cation. Although similar results are observed for the tantalum series, these compounds occupy relatively larger volumes. Another significant result is the increase in the '*b*' parameter with decreasing size of the rare-earth metal cation for both series, implying by comparison with the decrease in unit-cell volume, considerable strain (*b*/*a*) in the lattice. The *c*/*a* value, however, remains constant (*ca.* 0.99) in both the series. Multiplying the '*a*' and '*c*' parameters of the present structures by $2^{\frac{1}{2}}$ yields a unit cell of nearly cubic size with a = 10.8 Å.

The weberite structure can hence be regarded as an orthorhombic distortion of the cubic pyrochlore structure, the limits of stability in terms of the tolerance factors [5] t_1 and t_2, calculated on the basis of the pyrochlore unit cell, being $0.949 \leqslant t_1 \leqslant 1.127$ and $1.131 \leqslant t_2 \leqslant 1.343$, the corresponding values for the *true* pyrochlore being $t_1 = 0.87$ and $t_2 = 0.96$ ($t_1 = 0.885$ and $t_2 = 1.05$ using the effective ionic radii due to Shannon and Prewitt).[6] A high degree of correlation between the orthorhombic strain (*b*/*a*) and tolerance factors (t_1, t_2) thus exists in both series and is consistent with the classification of weberite, fluorite, and pyrochlores structures on the above basis.[7]

Unit-cell parameters of compounds in the $(A^+A^{3+})B^{5+}{}_2O^{2-}{}_7$ series

Compound	r_A/r_B *	t_1	t_2	*a* / Å	*b* / Å	*c* / Å	*b*/*a*	*U*/Å^3
$NaNdV_2O_7$	2.111	1.127	1.343	7.62	10.82	7.50	1.420	618.4
$NaSmV_2O_7$	2.083	1.120	1.335	7.58	10.86	7.48	1.433	615.7
$NaGdV_2O_7$	2.054	1.114	1.327	7.56	10.88	7.46	1.440	612.5
$NaDyV_2O_7$	2.028	1.107	1.320	7.53	10.94	7.44	1.453	612.9
$KSmTa_2O_7$	2.031	0.963	1.148	7.86	10.82	7.76	1.377	660.0
$KGdTa_2O_7$	2.008	0.957	1.141	7.84	10.86	7.72	1.385	660.7
$KDyTa_2O_7$	1.984	0.952	1.135	7.80	10.88	7.70	1.395	653.4
$KYTa_2O_7$	1.972	0.949	1.131	7.78	10.92	7.66	1.404	651.0

* Average values of the A site cations. Ionic radii from ref. 6.

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REFERENCES

[1] V. S. Chincholkar, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2973.
[2] E. Aleshin and R. Roy, *J. Amer. Ceram. Soc.*, 1962, **45**, 18.
[3] H. P. Rooksby and E. A. D. White, *J. Amer. Ceram. Soc.*, 1964, **47**, 94.
[4] O. Knop, F. Brisse, and L. Castelliz, *Canad. J. Chem.*, 1969, **47**, 971.
[5] H. D. Megaw, 'Ferroelectricity in Crystals,' Methuen, London, 1957, p. 148.
[6] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1969, **B25**, 925.
[7] V. S. Chincholkar, unpublished work.

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