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Growth of Rare Earth Scheelites by the Flux Method[1a]

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Single crystals of scheelites having the formulas $Sr_{0.9}Gd_{0.1}MoO_4$, $Sr_{0.9}Eu_{0.1}MoO_4$, $Na_{0.5}Pr_{0.5}MoO_4$, $Na_{0.5}Tm_{0.5}MoO_4$, $Na_{0.5}Dy_{0.5}TeO_4$, $Li_{0.5}Dy_{0.5}TeO_4$, and $Li_{0.5}Dy_{0.5}MoO_4$ were grown and their unit cell dimensions reported. Rare earth tellurides with scheelite structure are mentioned for the first time in this note.

The natural mineral "scheelite" has a chemical formula $CaWO_4$. Isomorphous with it is $SrMoO_4$, which crystallizes with the $C_{4h}^{6}\text{-}I4_1/a$ symmetry having four formula units per unit cell.[2] To a certain extent a trivalent rare earth ion can substitute for the divalent alkaline earth ion without charge compensation *via* a univalent ion. In that case charge compensation is achieved through either ion vacancies or a corresponding lowering of the valence of the hexavalent ion.

Single crystals of scheelite molybdates or tungstates containing rare earth ion dopings were recently reported by Van Uitert.[3] The crystals were grown by a modified Czochralsky method and were used for the study of the emission spectra of rare earth ions excited by ultraviolet excitation. Other scheelite crystals with a formula $MGe_{0.5}Mo_{0.5}O_4$ (M = rare earth ion) were also recently reported.[4] In that case charge compensation is achieved by substituting part of the Mo^{6+} by Ge^{4+}.

The present paper will describe the conditions of growth for scheelite crystals containing rare earth ions showing two different types of charge compensation. These crystals were grown using the flux method, *i.e.*, crystallization by slow cooling of a multicomponent solution.

Experimental

Crystal growth by the flux method involves the knowledge of the composition limits of the equilibrium primary phase fields of scheelite in various systems. However, such phase fields are often so varied in composition–temperature relationships that larger crystals can be grown only within a restricted area of the field. The more restricted composition field satisfies a favorable supersaturation ratio of crystallizing phase *vs.* solvent which restricts the rate of nucleation and favors the growth of larger crystals. Both the wider and the narrower composition limits were studied by the present author and published[5] for the system Na_2O–MoO_3–Gd_2O_3. Using these data, in addition to $Na_{0.5}Gd_{0.5}MoO_4$ the following crystals could be grown: $Na_{0.5}M_{0.5}MoO_4$ with M = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb, $Li_{0.5}Dy_{0.5}MoO_4$, $Li_{0.5}Dy_{0.5}TeO_4$, and $Na_{0.5}Dy_{0.5}TeO_4$. In addition, the phase relationships in the ternary system MoO_3–SrO–Eu_2O_3 were also determined.

All the crystals mentioned above were grown in 50-cc. covered platinum crucibles filled to about four-fifths of their capacity with molten material. The annealing time was 6 hr. at the higher indicated temperature and the rate of cooling was about 1.2°/hr. The amount of volatilization in these particular systems was very low (below 3%) as compared with other crystals grown by the flux method.[6] No temperature gradient existed across the crucibles during the crystallization process.

The unit cell dimensions of all the grown crystals were determined using a least-square programmer on the IBM 7090 Harvard computer for the X-ray powder diffraction. The results are shown in Table I. Some of the crystals were also chemically analyzed in order to prove their composition. *Anal.* Calcd. for $Na_{0.5}Gd_{0.5}MoO_4$: Na, 4.6; Gd, 31.44; Mo, 38.36. Found: Na, 4.7; Gd, 31.1; Mo, 38.5. Calcd. for $Li_{0.5}Dy_{0.5}MoO_4$: Dy, 33.30; Mo, 39.1. Found: Dy, 33.2; Mo, 39.3. Calcd. for $Na_{0.5}Dy_{0.5}TeO_4$: Na, 4.04; Dy, 28.55; Te, 44.89. Found: Na, 4.2; Dy, 28.2; Te, 44.8. Calcd. for $Sr_{0.9}Eu_{0.1}MoO_4$: Sr, 30.96; Eu, 6.04; Mo, 37.80. Found: Sr, 30.7; Eu, 6.2; Mo, 37.9. Calcd. for $Sr_{0.9}Gd_{0.1}MoO_4$: Sr, 30.9; Gd, 6.19; Mo, 37.73. Found: Sr, 30.7; Gd, 6.3; Mo, 37.8.

TABLE I

UNIT CELL DIMENSIONS (Å.), VOLUME (Å.³), AND COLOR FOR SOME TETRAGONAL SCHEELITE CRYSTALS

Formula	*a*, Å.	*c*, Å.	*V*, Å.³	Color	Reference
$SrMoO_4$	5.36	11.94	343.031	. . .	2
$Sr_{0.9}Gd_{0.1}MoO_4$	5.315	11.791	333.086	Yellow shade	Present work
$Sr_{0.9}Eu_{0.1}MoO_4$	5.310	11.783	332.234	Dark purple	Present work
$Na_{0.5}Pr_{0.5}MoO_4$	5.303	11.575	325.509	Deep green	Present work
$Na_{0.5}Tm_{0.5}MoO_4$	5.179	11.311	303.399	Yellow shade	Present work
$Na_{0.5}Dy_{0.5}MoO_4$	5.207	11.339	307.455	Light green	*a*
$Na_{0.5}Dy_{0.5}TeO_4$	5.251	11.595	319.811	Yellow-green	Present work
$Li_{0.5}Dy_{0.5}TeO_4$	5.204	11.442	309.372	Yellow-green	Present work
$Li_{0.5}Dy_{0.5}MoO_4$	5.182	11.168	299.915	Green shade	Present work

[a] M. Schieber and L. Holmes, *J. Appl. Phys.*, **35**, 1004 (1964).

With the experimental errors, the chemical composition of all the crystals analyzed corresponds to the nominal formula. The size of the crystals varied from 100 to 1500 mg. They were transparent and apparently free from flux inclusions.

Discussion

Table I summarizes the unit cell dimensions of the grown crystals. It can be seen that the unit cell volume decreases slightly with the partial substitution of Gd^{3+} or Eu^{3+} for the slightly larger ionic size of Sr^{2+}. A similar effect is found by substituting the smaller Li^+ for Na^+ ions. The unit cell volume of the lithium scheelites is smaller than that of the sodium scheelites. However, in the case of Te^{6+} and Mo^{6+}

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(2) R. W. G. Wykoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 8, p. 96.

(3) L. G. Van Uitert, *J. Chem. Phys.*, **37**, 981 (1963), and references in that paper.

(4) C. B. Finch, L. A. Harris, and G. W. Clark, Proceedings of the Fourth Rare Earth Research Conference, Phoenix, Ariz., 1964, to be published.

(5) M. Schieber, *J. Inorg. Nucl. Chem.*, in press.

(6) M. Schieber, *J. Am. Ceram. Soc.*, **47**, 537 (1964).

the unit cell volume of the tellurium scheelites is larger than that of the molybdenum scheelites, suggesting a larger ionic size of Te^{6+} than Mo^{6+}. From chemical analysis evidence which yields stoichiometric formulas, it seems that the charge compensation in $Sr_{0.9}Gd_{0.1}MoO_4$ and $Sr_{0.9}Eu_{0.1}MoO_4$ is achieved through the presence of some lower valent molybdenum. However, more physical measurements would be needed to ascertain this assumption. Table I also reports the unit cell dimensions of $Na_{0.5}Tm_{0.5}MoO_4$, whose growth conditions were apparently different from the other scheelites with similar composition. In the composition diagram Na_2O–Gd_2O_3–MoO_3 two fields are indicated[5] to produce large crystals. One field requires a higher and the other a lower heating temperature. Apparently, the Tm scheelite seems to prefer the higher temperature composition rather than the lower temperature mixtures. Figure 1 represents the unit cell volume of the different sodium rare earth scheelites *vs.* the empirical Goldschmidt radius of the rare earth ions. As expected one can see the volume contraction of the scheelite crystal with the increase of the atomic number of the rare earth ion.

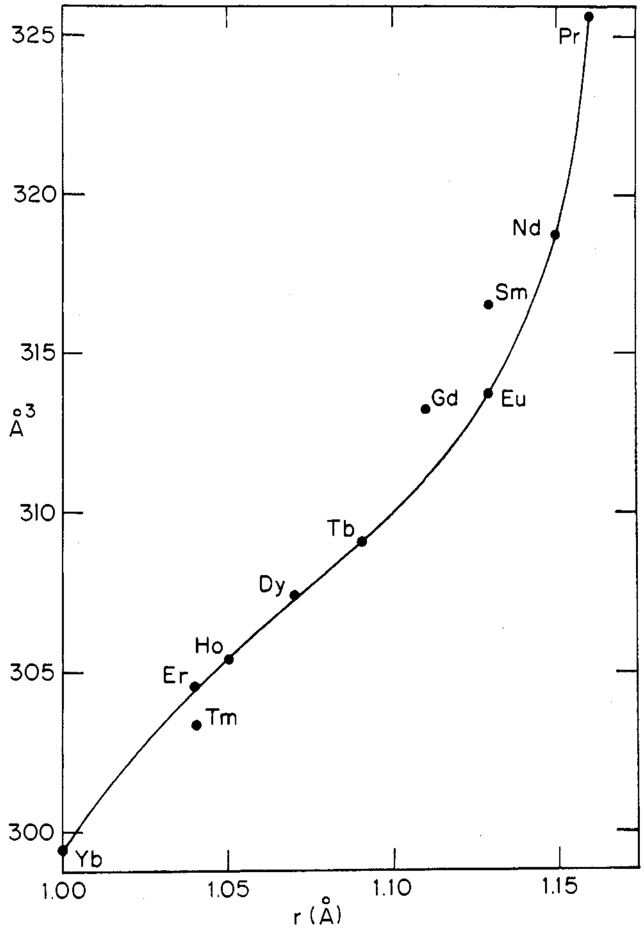

Figure 1.—Variation of the crystal volume in Å.³ with the Goldschmidt ionic radius of the rare earth ion M in the formula $Na_{0.5}M_{0.5}MoO_4$. The unit cell volume was calculated from the data published in ref. 5 except for $Na_{0.5}Pr_{0.5}MoO_4$ and $Na_{0.5}Tm_{0.5}MoO_4$, first reported in this note.

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The Magnetic Moments of Some Tetragonal Nickel Complexes

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Magnetic measurements have for some time been used to distinguish between the nickel ion in a tetrahedral or in an octahedral environment.[1] Octahedral nickel(II) complexes generally have temperature-independent magnetic moments within the range 2.9–3.3 B.M.; tetrahedral derivatives, on the other hand, have magnetic moments, which are temperature dependent, within the range 3.3–4.0 B.M. at 25°. Temperature range measurements are, however, rarely employed and single-temperature studies have been extensively used as a guide to the stereochemical environment of the nickel ion.

It is the purpose of this note to point out the existence of a class of tetragonal nickel complexes which have moments above 3.3 B.M.

Six-coordinate nickel complexes of the form *trans*-NiA_2X_2, where A is an amine and X a halogen, commonly have moments between 3.3 and 3.5 B.M. (Table I). The moments observed are not only outside the range generally associated with octahedral nickel derivatives, but are, in fact, higher than the theoretical maximum obtainable from the simple theory.

Gill and Nyholm[2] have calculated the magnetic moment values to be expected for the nickel ion in a variety of different circumstances (*e.g.*, zero or infinite spin–orbit coupling, very weak or very strong crystal fields, etc.) Although the moment can rise as high as 5.59 B.M. in the absence of an electrical field, they conclude that in an octahedral environment the magnetic moment should be 3.1–3.2 B.M.

Few temperature-range studies have as yet been carried out with the complexes listed in Table I,[3-10] but

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(1) J. Lewis, *Sci. Progr.*, **51**, 452 (1963).

(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(3) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(4) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, in press. The author is indebted to Dr. S. M. Nelson for permission to quote from the manuscript prior to publication.

(5) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 5042 (1963).

(6) D. M. L. Goodgame and M. Goodgame, *ibid.*, 207 (1963).

(7) A. B. P. Lever, *J. Inorg. Nucl. Chem.*, **27**, 149 (1965).

(8) A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, in press.

(9) W. Klemm and W. Schuth, *Z. anorg. allgem. Chem.*, **210**, 33 (1933).

(10) B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2400 (1964).