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BRIEF COMMUNICATION

A New 2+/3+ Perovskite: The Synthesis and Structure of $BaScO_2F$

R. L. Needs and M. T. Weller[1]

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom

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$BaScO_2F$ has been synthesized and shown, by refinement of powder X-ray diffraction data, to adopt the simple cubic perovskite structure, the first example with the stoichiometry $A^{2+}B^{3+}[X^{2-}]_2[Y]^-$. The structure analysis and ^{19}F MASNMR data show the anions are disordered.

INTRODUCTION

The perovskite structure is probably one of the most important in complex oxide chemistry in view of its common occurrence and the range of useful properties exhibited by phases adopting it (1). The perovskite structure is found for some hydrides and fluorides, and more recently, a nitride perovskite has been described (2). Perovskites containing mixtures of anions give increased flexibility in terms of compound composition, for example, the oxide nitride $SrMo(O,N)_3$ (3) and the oxide fluoride $Tl^+Tl^{3+}OF_2$ (4). A wide range of perovskites of the stoichiometry ABX_3, where $X_3 = O_3$ and F_3, are known but no material with A divalent and B trivalent giving the stoichiometry ABO_2F has yet been synthesized. The only materials described as having an ABO_2F-type stoichiometry are $KNbO_2F$ (5), where potential variations in the niobium oxidation state mean the exact 2:1 oxygen:fluorine ratio is unproven, and $KTiO_2F$ (6), which is synthesized at 1000°C and 65 kbar. In this paper we report for the first time a perovskite phase ABX_3 containing $A = 2+$ and $B = 3+$.

EXPERIMENTAL

$BaScO_2F$ was synthesized by reaction of barium fluoride and scandium oxide at 1000°C for 72 h with several intermediate regrinds. The sample was characterized using powder X-ray diffraction and confirmed as monophasic except for a very small amount of residual BaF_2. High-quality data were collected on a Siemens D5000 diffractometer operating with $CuK\alpha_1$ radiation in the angular range 20–120° (18 reflections) with a step size of 0.02° over a period of 15 h.

Analysis of this powder X-ray diffraction data showed that it could be indexed using a simple cubic perovskite structure type such as that found for $BaSnO_3$ (7). Refinement of the structure was undertaken using the GSAS package (8) in the normal $Pm3m$ space group. All anions were assigned as oxide for the refinement due to the similar scattering of the oxide and fluoride ions. The refinement proceeded smoothly with the inclusion of all normal atomic parameters; no evidence was found for any lowering of the symmetry. The very small amount of BaF_2 present as an impurity was modeled using the literature structure. The final profile fit to the powder X-ray diffraction data is shown in Fig. 1. The final determined atomic positions and thermal factors, in $Pm3m$, $a = 4.1710(4)$ Å, $R_{wp} = 10.7\%$, $\chi^2 = 11.6$, were Ba (1b) U_{iso} 1.90(6) Å^2, Sc (1a) 1.7(1) Å^2, and O/F (3c) 1.1(2) Å^2. Derived bond lengths were $12 \times$ Ba–O/F 2.9847(2) and $6 \times$ Sc–O/F 2.0850(2) Å.

^{19}F MASNMR data were collected on a Chemagnetics CMX-200 spectrometer operating at 188.288 MHz for fluorine nuclei as described previously (9). Chemical shifts were referenced by replacement to the signal of $CFCl_3$ or C_6F_6. The spectrum consisted of one peak at $\delta = -93$ pm with spinning side bands visible and is shown in Fig. 2. This ^{19}F MASNMR spectrum of $BaScO_2F$ supports the proposed structure, suggesting there is only one fluoride site, as shown by the Rietveld refinement.

RESULTS AND DISCUSSION

$BaScO_2F$, the first example of an oxide fluoride perovskite with $A^{2+}B^{3+}$, has the ideal cubic structure, with one anion site containing disordered oxide and fluoride. The lattice parameter $a = 4.171$ Å is as expected for a cubic perovskite where the scandium sixfold ionic radius equals 0.73 Å. There is no other oxide fluoride perovskite oxide of

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[1] To whom correspondence should be addressed.

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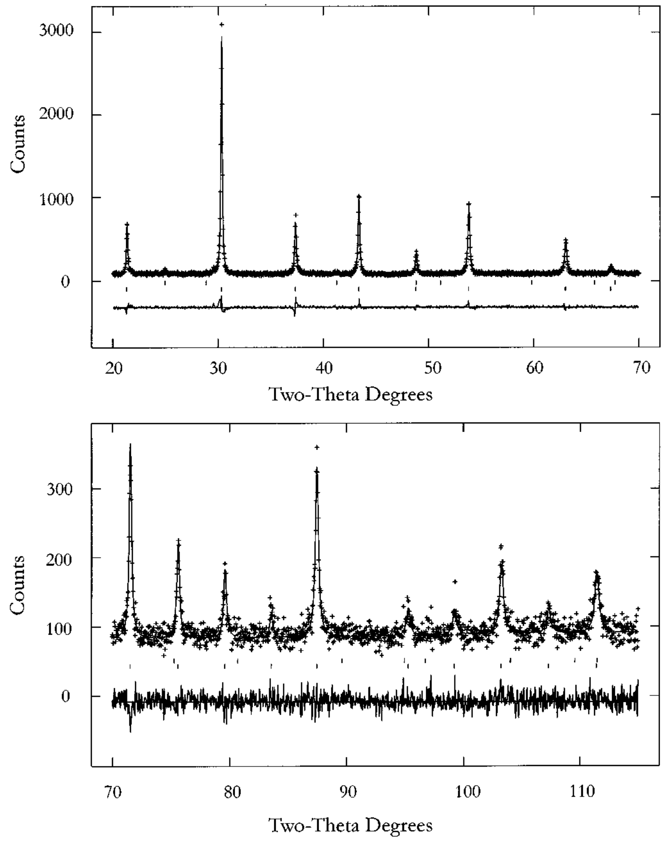

FIG. 1. Final profile fit to PXD data for $BaScO_2F$; upper tick marks are the BaF_2 and lower tick marks the $BaScO_2F$ allowed reflections; crosses, the observed data; upper continuous line, the calculated profile; and lower continuous line, the difference.

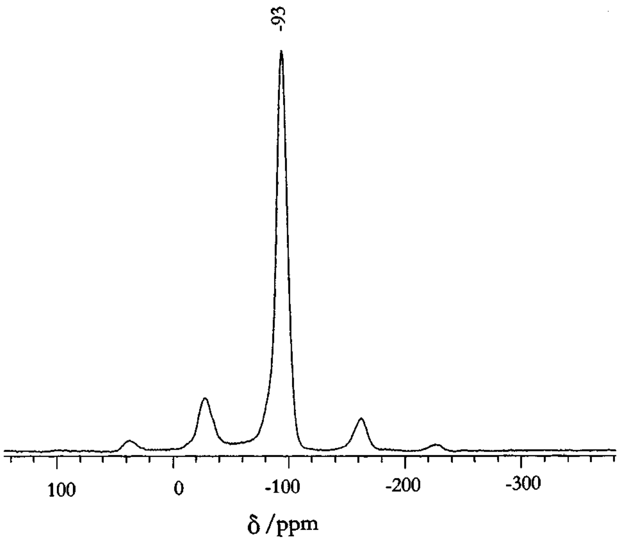

FIG. 2. ^{19}F MAS NMR spectrum of $BaScO_2F$.

this type so comparison can be drawn only by reference to pure oxide perovskites $BaB^{4+}O_3$. In $BaSnO_3$ $a = 4.12$ Å and in $BaHfO_3$ $a = 4.17$ Å the tin and hafnium six-coordinate ionic radii are 0.69 and 0.71 Å, respectively. From these lattice parameters it is clear that the presence of fluoride substituting for one third of the oxide has little effect on the cell size, in agreement with the similar sizes of F^- and O^{2-} in solids. The structure of $Ba_2Sc_2O_5$ ($BaScO_{2.5}$) has been reported (10) as a tetragonally distorted oxygen-deficient perovskite, possibly similar to $BaTiO_3$, with the lattice constants $a = 4.15$ and $c = 3.99$ Å. Such a distortion is not seen in the oxide fluoride and is therefore probably due to ordering of the oxide vacancies in $BaScO_{2.5}$. The complex scandium oxide perovskite $LaScO_3$ (11) adopts the $GdFeO_3$-type structure as expected for a $A^{3+}B^{3+}O_3$ perovskite and as such contains scandium in a distorted octahedral environment. The calculated bond valences, scandium 2.93 and barium 1.85, are close to the expected values (12). Attempts to synthesize the strontium-containing analogues, $Ba_{2-x}Sr_xScO_2F$, were unsuccessful, as were all efforts at compositionally equivalent indates.

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REFERENCES

1. F. S. Galasso, "Perovskites and High Tc Superconductors." Gordon & Breach, New York, 1990.
2. N. E. Brese and F. J. Disalvo, *J. Solid State Chem.* **120,** 378 (1995).
3. G. Liu, X. Zhao, and H. A. Eick, *J. Alloys Compds.* **187,** 145 (1992).
4. G. Demazeau, J. Grannec, A. Marbeuf, J. Portier, and P. Hagenmuller, *C.R. Hebd. Seanc. Acad. Sci. Ser. C* **269,** 987 (1969).
5. W. Rüdorff and D. Krug, *Z. Anorg. Allg. Chem.* **329,** 211 (1964).
6. B. L. Chamberland, *Mater. Res. Bull.* **6,** 311 (1971).
7. A. J. Smith and A. J. E. Welch, *Acta Crystallogr.* **13,** 653 (1960)
8. A. C. Larson and R. B. Von Dreele, "Generalized Structure Analysis System," MS-H805, Los Alamos, NM, 1990.
9. R. L. Needs, M. T. Weller, U. Scheller, and R. K. Harris, *J. Mater. Chem.* **6,** 1219 (1996).
10. W. Kwestroo, H. A. M. van Hal, and C. Langereis, *Mater. Res. Bull.* **9,** 1623 (1974).
11. S. Geller, *Acta Crystallogr.* **10,** 243 (1957).
12. I. D. Brown and D. Aldermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).