Journal of Fluorine Chemistry, 8 (1976) 527 – 530

Received: July 13, 1976

PREPARATION AND UNIT CELL DIMENSIONS OF NEW-PEROVSKITE MATERIALS OF THE FORMULA $K(MM')F_3$ (M=Mn,Fe,Co,Zn,M'=Mn,Co,Ni,Zn)

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SUMMARY

Materials of the type $K(MM')F_3$ are prepared by a simple solution method. The simple replacement of one M^{2+} ion with another without distortion of the cubic unit cell is demonstrated from X-ray powder diffraction data. Unit cell dimensions are reported.

INTRODUCTION

The parent compound (M=Mn,Fe,Co,Ni and Zn) are well documented materials; they have the cubic perovskite structure [1]. Infra-red studies on the $CsSnCl_3$-$CsSnBr_3$ cubic perovskite system led to an understanding of the halide vibrations in the lattices [2,3].

The materials reported here were prepared to investigate if they were cubic; if the M^{2+} ions were random throughout the structure or ordered in discrete domains, and to see if the model used for the infra-red studies could be applied to these materials.

EXPERIMENTAL

The materials are all prepared by the same method. A solution of 5.7 g of potassium fluoride dihydrate in 10 mls of water is boiled, 5 drops of hydrofluoric acid is added and then a solution of 0.02 moles of the appropriate transition-metal

mixture (e.g. $MnSO_4.4H_2O$+$FeSO_4 7H_2O$). The resulting solution or suspension is heated on a water bath for fifteen minutes, then filtered, washed with cold water followed by 5 mls of acetone then ether. The products are dried under vacuum. The yields are highly dependent on concentration but average 2.5 - 3.0 g.

X-ray powder diffraction data of the products were obtained using Philips 11.64 cm powder cameras and Cu-Kα Ni filtered radiation. The unit-cell dimensions are refined from the X-ray powder diffraction data by simple least squares methods.

RESULTS AND DISCUSSION

The X-ray powder data for the new materials and those of the parent materials are in Tables 1 and 2. All the materials are cubic; those that contain two transition metals have unit cell parameters between those of the parent compounds.

The materials reported in Table 1 give diffraction patterns in which the lines are no wider than those obtained from the parent materials indicating no distortion; showing that they contain the transition-metal ions are randomly distributed throughout the lattices.

Unfortunately the infra-red spectra for the $K(MM')F_3$ materials were identical to the KMF_3 parent compounds and are therefore not reported. There is not enough difference in the vibrations of the parent compounds to see the sort of effect found in the $CsSnCl_3$-$CsSnBr_3$ system [2,3].

The 'tolerance' of the cubic perovskite lattice for the different ionic radii of the M^{2+} ions is apparent indicating that the 'sigma' bonding M-F,M'-F bonds are the same length and different to those in the parent compounds. This suggests that the overall packing is decided by the total electro-negativity (resultant from the positions of both the K^+ and M^{2+} ions; the F^- ions balance this) of the lattice, and is not just resultant from the M-F (M=transition-metal) bonding and the packing of the K^+ ions in the holes. This conclusion is in agreement with the ionic nature of these cubic perovskites.

Table 1

X-ray powder diffraction data for the $K(MM')F_3$ (M=Mn,Fe,Zn,M'=Mn,Co,Ni,Zn) materials

Intensity	(FeMn) d/Å	(FeCo) d/Å	(FeNi) d/Å	(FeZn) d/Å	(MnZn) d/Å	(ZnCo) d/Å	hkl
m	4.14	4.10	4.06	4.08	4.11	4.06	(100)
vs	2.93	2.90	2.87	2.89	2.91	2.87	(110)
vw	2.37	2.37	2.34	2.36	2.37	2.34	(111)
s	2.07	2.05	2.03	2.04	2.06	2.03	(200)
w	1.851	1.834	1.816	1.824	1.838	1.816	(210)
m	1.690	1.673	1.657	1.665	1.678	1.657	(211)
m	1.464	1.450	1.435	1.442	1.453	1.435	(220)
vw	1.380	1.366	1.353	1.360	1.370	1.353	(300)(221)
w	1.309	1.296	1.284	1.290	1.300	1.284	(310)

Table 2

Unit cell data for all the cubic fluoride perovskites

Phase	colour	a/Å (this work)	literature	ref.
$KMnF_3$	off white	4.19	4.19	1
$KFeF_3$	fawn	4.12	4.11	1
$KCoF_3$	pink	4.08	4.07	1
$KNiF_3$	yellow green	4.02	4.01	1
$KZnF_3$	white	4.05	4.05	1
$K(FeMn)F_3$	fawn	4.14		
$K(FeCo)F_3$	pink	4.10		
$K(FeNi)F_3$	yellow green	4.06		
$K(FeZn)F_3$	fawn	4.08		
$K(MnZn)F_3$	off white	4.11		
$K(ZnCo)F_3$	pink	4.06		

REFERENCES

1 R. L. Martin, R. S. Nyholm and N. C. Stephenson, Chemistry and Indistry, (1956) 83.

2 J. D. Donaldson, D. Laughlin, S. D. Ross and J. Silver, JC.S. Dalton, (1973), 1985.

3 J. D. Donaldson, S. D. Ross and J. Silver, Spectrochimica Acta, (1975), 31A, 239.