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STRUCTURAL AND MAGNETIC STUDIES ON NEW CESIUM AND BARIUM FLUOROMETALLATES OF 3d TRANSITION ELEMENTS

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Looking for compounds Cs_2MF_4 the cesium richest composition we found at M(II) = Co, Ni was $Cs_7M_4F_{15}$. X-ray single crystal work revealed a layer structure (P2₁/c, Z=2), built up from face-sharing double octahedra M_2F_9 which are mutually connected via three of their vertices. Some interatomic distances are given in Table I, along with data of six novel compounds $Ba_2AM_2F_9$ (R $\overline{3}$ m, Z=3). The puckered layer structure of the latter consists of single octahedra, sharing three corners in a fac-position. It derives from the hexagonal perovskite structure of $CsCoF_3$ by omitting the central cations within the groups of three face-sharing octahedra.

The occurence of three structure types at quaternary fluorides ${\tt BaM}^{II}{\tt M}^{III}{\tt F}_7 \mbox{ is discussed as dependent on r^{II}/r^{III} and r^{II}/r_F radius ratios.}$ The magnetic properties of some nickel(II), manganese(II) and iron(III) compounds exhibiting one of the structures mentioned are reported.

Table I:

	a(pm)	b(pm)	c(pm)	β(⁰)	octahedral M-F (pm)		
					term.	bridg.	mean
Ba ₂ RbFe ₂ F ₉	594.9		2083.7		199.4	213.2	206.3
Ba ₂ CsCo ₂ F ₉	593.1		2131.8		198.8	211.4	205.1
Cs ₇ Co ₄ F ₁₅	788.3	1096.6	1164.9	92.59	197.7	209.4	206.5
Ba ₂ KNi ₂ F ₉	577.5		2075.6		196.1	206.4	201.3
Ba ₂ RbNi ₂ F ₉	58o.1		2099.4		196.0	206.4	201.2
Ba ₂ CsNi ₂ F ₉	585.5		2120.9		196.9	207.1	202.0
Cs ₇ Ni ₄ F ₁₅	787.2	1089.7	1149.5	92.74	196.3	206.1	203.7
${\sf Ba_2CsZn_2F_9}$	590.5		2127.9		195.8	212.7	204.3