Short Communications

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Acta Cryst. (1952). **5**, 841

Reactions between metal oxides and fluorides: some new double-fluoride structures of type ABF_3.

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(*Received* 7 *June* 1952)

In the course of a programme of fundamental research on reactions between solids, reactions between each of the commoner alkali-metal fluorides (LiF, NaF, KF, RbF and CsF) and the oxides of magnesium, calcium, strontium, barium and zinc have been examined. The reactions occur readily in dry powder mixtures at temperatures in the range 500–800° C. With the reactant pairs LiF–MgO, –CaO, –SrO, –ZnO; NaF–CaO, –SrO, –BaO; KF–SrO, –BaO; RbF–SrO, –BaO; CsF–SrO and –BaO, complete anion exchange occurs to give mixtures of alkali-metal oxide and bivalent fluoride (e.g. $2LiF+MgO \rightarrow Li_2O+MgF_2$). In the remaining pairs the reactions give double fluorides of type ABF_3 (e.g. $3NaF+MgO \rightarrow Na_2O+NaMgF_3$).

The double fluorides formed in these reactions have also been synthesized from the component fluorides, and their structures examined by conventional X-ray powder techniques; copper radiation was employed with standard 19 cm. cameras. The results are summarized below; for further details, see Ludekens (1950).

Cubic structures

$RbCaF_3$ $a = 4{\cdot}443$ kX.
$CsCaF_3$ $a = 4{\cdot}514$ kX.
$LiBaF_3$ $a = 3{\cdot}988$ kX.

Tetragonal structures

$NaMgF_3$ $a = 7{\cdot}65,\ c = 7{\cdot}30$ kX.
$CsMgF_3$ $a = 9{\cdot}37,\ c = 8{\cdot}70$ kX.
$NaZnF_3$ $a = 7{\cdot}74,\ c = 8{\cdot}13$ kX.
$KZnF_3$ $a = 8{\cdot}49,\ c = 8{\cdot}09$ kX.
$RbZnF_3$ $a = 8{\cdot}69,\ c = 8{\cdot}01$ kX.
$CsZnF_3$ $a = 9{\cdot}88,\ c = 9{\cdot}03$ kX.

Monoclinic structures

$KMgF_3$ $a = b = c = 8{\cdot}00$ kX., $\beta = 91^\circ\ 18'$.
$RbMgF_3$ $a = b = c = 8{\cdot}17$ kX., $\beta = 98^\circ\ 30'$.
$KCaF_3$ $a = b = c = 8{\cdot}80$ kX., $\beta = 92^\circ\ 36'$.

The lattice constants given were all measured at ordinary ambient temperatures; it is now intended to investigate changes in the parameters with temperature.

Several of the compounds have been detected previously by thermal analysis of binary fluoride systems, and Náray-Szabó (1947) has recorded lattice constants for $KMgF_3$ and $KZnF_3$, both of which he considers to be monoclinic.

All the structures appear to belong to the various modifications of the perovskite type (Megaw, 1946; Náray-Szabó, 1947). Evaluation of the 'tolerance factor', i.e. $(r_A+r_F)/\sqrt{2}.(r_A+r_F)$, for each structure (Goldschmidt, 1928) gives values greater than 0·8 in every case except $LiBaF_3$ (0·53); a normal value is obtained for this compound if the cations are assumed to be interchanged, lithium occupying the six-coordinated cation sites. The existence of an 'inverted' perovskite arrangement, $BaLiF_3$, in this case is in full accord with the X-ray data; similar inversion is known among oxides with perovskite structures. The apparent tolerance factor for $CsMgF_3$ is 1·13, an unusually high value, but the effective radius of the caesium ion may be modified to an unknown extent by polarization effects.

The absence of 'normal' perovskite structures containing strontium or barium is not unexpected, because strontium and barium ions are too large for normal six-coordination with fluoride ions. The formation of 'inverted' structures in cases other than $BaLiF_3$ would evidently involve unduly low tolerance-factor values. The cation pairs LiMg, LiCa, NaCa and LiZn, for which compounds have not been obtained, give unacceptable tolerance factors for both normal and inverted cation arrangements. The behaviour of all twenty-five systems is therefore in accord with the known general principles governing formation of perovskite structures. Discussion of the tetragonal and monoclinic modifications of the ideal cubic lattice is deferred until more data are available.

Double fluorides of other types (e.g. A_2BF_4) have not been observed in the systems examined.

Grateful acknowledgment is made to the Royal Society and to the University of London Central Research Funds for provision of the X-ray equipment used in this research. A brief survey of the results recorded in this paper was presented at the Twelfth International Congress of Pure and Applied Chemistry, New York, 10–13 September 1951.

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