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The Synthesis and Characterization of Some Fluoride Perovskites

An Undergraduate Experiment in Solid State Chemistry

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In light of the increasing importance of solid state chemistry, an experiment dealing with at least some aspects of this rapidly expanding area should be included in advanced chemistry laboratories. Herein is described one of the experiments that we have developed to meet this need. This experiment was designed for a senior level integrated chemistry lab taken by all our chemistry majors. Normally six to eight hours are needed to complete this experiment.

This experiment deals with the synthesis and characterization of a perovskite. Perovskites were chosen because compounds with this structure are important in solid state technology, and since most of them are cubic, the characterization by X-ray diffraction is simplified. In addition, magnetic ordering may be observed, and the effects of a Jahn-Teller distortion seen.

Background

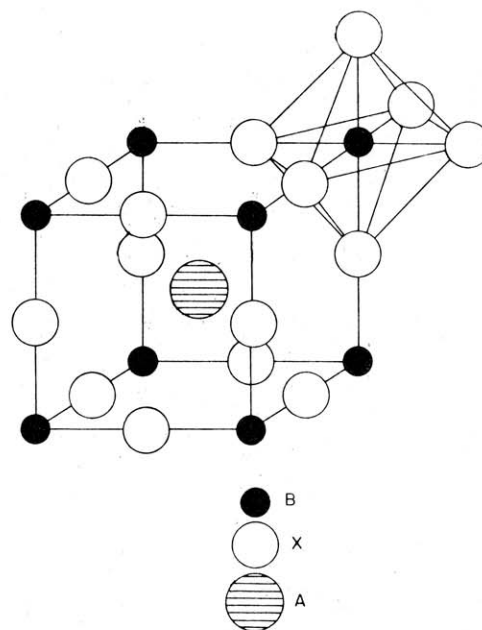
The perovskite (or perovskite) structure is the structure adopted by the mineral with the same name (CaTiO_3). It is a common structure. Wyckoff lists over 180 materials adopting this structure or a distorted structure related to it (1). The idealized perovskite structure belongs to the $\text{Pm}\bar{3}\text{m}$ space group. The structure is illustrated in Figure 1.

Perovskites are known where A is commonly any of a number of large ions (e.g., Ag, Ba, K, . . .); B is normally a relatively small ion (e.g., Zn, Ti, . . .); and X is usually oxygen though perovskites are known where X is fluoride, chloride, bromide, or nitrite (1). In this experiment A is potassium; B is a divalent first row transition metal ion (Mn-Zn); and X is fluoride. Many distorted perovskites are known. The distortion may be small, so that a pseudocubic structure results, or the symmetry may be drastically lowered. The compound KCuF_3 is an example of a distorted perovskite. In this case the distortion is apparently due to a Jahn-Teller distortion of the octahedron of fluorides around the copper(II) ion. This distortion is evidenced in the powder diffraction pattern as a splitting of lines in a pattern perovskites.

Preparation of the Fluoride Perovskites

Caution: Fluorides may yield HF due to hydrolysis. This is not too serious for alkali metal fluorides or insoluble fluorides; however, the possibility does require that precautions be taken to prevent contact with the skin.

All of the compounds to be used in this experiment are prepared by the same general procedure. In a typical synthesis



The perovskite structure. The structure has been extended in the upper right to illustrate the octahedral coordination about the B ions.

0.12 moles of potassium fluoride dihydrate is dissolved in a minimum volume of water containing three drops of concentrated nitric acid. This solution is heated on a hot plate to boiling and kept near boiling while a solution of the divalent metal chloride is added dropwise to it. The divalent metal chloride solutions are made by dissolving 0.04 moles of the appropriate metal (Mn, Fe, Co, Ni, Cu, or Zn) chloride hydrate in a minimum volume of water. A few additional milliliters of water may be used to wash the last of this solution into the fluoride solution. Once all of the chloride solution is added, the beaker is removed from the hot plate, and 30 milliliters of cool water is added. The precipitate is allowed to settle and the supernatant is decanted and discarded. The solid is washed twice with ethanol and twice with acetone with the washings being removed by decantation. The precipitate is then dried. This may be done by transferring it to a fritted glass funnel and drawing air through it; or it may simply be dried on a watch glass.

Two useful modifications may be made in this procedure. First, in the case of zinc, it is easier to begin with zinc oxide.

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The zinc oxide is converted to the chloride by adding concentrated hydrochloric acid to a paste made by mixing ten milliliters of water with the appropriate amount of zinc oxide until dissolution is complete. In this manner it is not necessary to work with the very hygroscopic zinc chloride, thus simplifying the weighing procedure. The second modification is needed in the case of iron. Iron(II) is air oxidized rather readily, and so there is a problem with the purity of the iron(II) chloride tetrahydrate used in this synthesis and with air oxidation during the synthesis. These problems may be alleviated by adding 0.5 M tin(II) chloride solution (in 3 M HCl) dropwise to the iron(II) solution until any traces of yellow color due to iron(III) disappear, leaving a clear green iron(II) solution. Then ten drops of excess tin(II) solution are added. Tin(II) may also be added to the fluoride solution to assure that the iron remains in the reduced form. The iron in solid KFeF_3 may be oxidized if the solid is wet. To minimize this oxidation the washings should be done as rapidly as possible or under an inert atmosphere (e.g., in a glove bag).

Characterization

The densities of the solids were determined with a pycnometer using toluene. Since the densities of these compounds are rather high (3–4 g/cm³), the buoyance method of determining densities is not readily applicable here.

The powder X-ray diffraction patterns of each of the compounds were run using a Debye-Scherrer camera with a copper X-ray target. All of the powders appeared well crystallized and gave a very good pattern. Alternatively a diffractometer could be used to collect the data.

The room temperature magnetic susceptibilities were determined by the Guoy method as reported elsewhere (2). Unfortunately, low temperature measurements were not carried out. These would have been useful since most of the fluoride perovskites synthesized in this study exhibit anti-ferromagnetic behavior. An examination of the temperature dependence of the magnetic susceptibilities would therefore add to the value of this experiment.

Values for the room temperature magnetic susceptibility measurements are given in the table.

Discussion

The procedure employed in the synthesis of the fluoride perovskites is similar to various literature methods (3–7). The main problem is that the products tend to be deficient in potassium and fluoride (8); and in the case of iron, contamination by iron(III) is likely. While it is possible to purify these materials or to synthesize purer materials by other methods, the methods employed are, in general, fairly extreme and not readily applicable to an undergraduate laboratory (e.g., heating the samples to 500°C in anhydrous hydrogen fluoride (8)). The modification of the KFeF_3 synthesis introduced here seems to be very effective in reducing oxidized iron impurities. No contamination by tin was observed.

The compound KCuF_3 is reported to be white (7), but in practice it is normally found to be a pale blue. The species causing the blue color has not been identified, but it is probably the hydrated copper(II) ion. Samples that are pale blue in color do not give results that significantly differ from other samples. The iron compound is very light tan, becoming brown as the iron is oxidized. The other compounds do not seem to vary in color: KMnF_3 , very light pink; KCoF_3 , bright pink; KNiF_3 , greenish-yellow; and KZnF_3 , white.

Problems may arise in the synthesis if the solutions are not saturated, if there is too much acid, or if the boiling is continued very long after the last of the chloride solution has been added (5). The manganese compound is reported to be hydrolyzed (5), but we did not have any problems with it. Oxidation of dry KFeF_3 is very slow, and does not present a problem.

The X-ray data indicated a perovskite structure in all cases.

Properties of Some Fluoride Perovskites

	cell parameters	density ^a	magnetic susceptibility (5)		μ_{eff} (296 K) this work
			μ_{eff} (300K)	T_{Neel}	
KMnF_3	$a = 4.193 \text{ \AA}$	3.402 g/cm ³	4.86	80 K	4.93
KFeF_3	$a = 4.121$	3.605	4.27	112	4.49
KCoF_3	$a = 4.089$	3.766	3.92	135	4.12
KNiF_3	$a = 4.020$	4.085	2.19	280	2.39
KCuF_3	$a = 4.138$	3.936	1.38	215	1.40
	$c = 3.933$				
KZnF_3	$a = 4.094$	3.908

^a As determined from the X-ray data.

In some cases an impurity giving rise to d values of 3.15 to 3.20 and 2.2 was observed in the powder pattern. These two lines may be rather intense. Since only two impurity lines were observed identification of the phase is still uncertain. Other lines appear in the KZnF_3 pattern indicating the presence of KHF_2 . Finally, a severely oxidized KFeF_3 sample gave a very poor X-ray pattern which could not be easily interpreted.

The primitive cubic pattern of these perovskites is relatively easy to index. The only complication is the impurity lines; however, this was never a serious problem. By comparing the various diffraction patterns it may be readily seen that these compounds are indeed isostructural. The fact that isostructural compounds give similar diffraction patterns is not often illustrated in undergraduate laboratories.

The indexing of the non-cubic perovskite, KCuF_3 , is a little more challenging, but again it is not a serious problem as there are no systematic absences. The results of the indexing are very good in showing that the structure is indeed a distortion of the structure of the cubic perovskites. For example, in a cubic perovskite, the diffraction from the 100, 010, and 001 planes are coincident since all axes (a , b , and c) are identical. However, in a tetragonal perovskite one axis (c) is not equal to the other two, so the 100 and 010 planes give coincident diffractions while the 001 diffraction is different. Thus, the tetragonal pattern has two diffraction lines (100 and 001) where the cubic pattern only has one (100). This carries over to other lines (i.e., cubic 110 versus tetragonal 110 and 101). Not all lines will be split (i.e., 111), and so indexing may be simplified. The distortion of the perovskite structure by copper(II) points out its tendency to undergo a Jahn-Teller distortion in an octahedral environment.

The densities as determined with the pycnometer are, as expected, low. However, they may be combined with the X-ray data to show that there is indeed only one formula unit in the unit cell (i.e., primitive). This requires the following equation:

$$\rho = \frac{nM}{VN}$$

where ρ is the density (g/cm³), n is the number of formula units in the unit cell, M is the formula weight, V is the volume of the unit cell (in cm³), and N is Avogadro's number. In practice an approximate density (as determined in this case with a pycnometer) is used to find a value for n . Since n must be an integer it is rounded off to such and then put back into this equation to find a true density.

The magnetic measurements, in some cases, were a little higher than the literature values (probably due to potassium and fluoride deficiencies—i.e., excess transition metal). However, they do lead to a correct prediction of the number of unpaired electrons.

Where lab sections are sufficiently small each student will normally prepare and characterize one of the fluoride perovskites. After the students have interpreted their own data they are encouraged to compare results in their written lab reports. This procedure has the advantage of allowing each

student to examine the data on several compounds and to draw conclusions based on much more data than he/she could gather alone in a reasonable length of time. This gives the student a better overall view.

This experiment illustrates many aspects of solid state chemistry. Modifications could be made to enlarge its scope. For example, other fluoride perovskites could be made (e.g., KCrF_3 (7)). However, these, in general, require a different synthetic procedure. It is also possible to prepare solid solutions (e.g., $\text{KNi}_\alpha\text{Zn}_{1-\alpha}\text{F}_3$ (5)), to see how properties may vary with concentration.

Acknowledgement

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