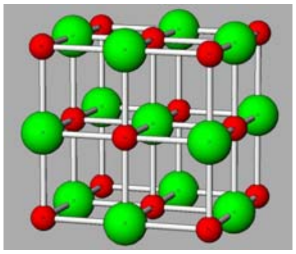
Synthetic Alkali Halides

Notes for Instructors



References

This exercise was originally developed by John Brady (in Brady, Mogk and Perkins, Teaching Mineralogy, Mineralogical Society of America, 1997, pp 91-96).

Two good references, in addition to Brady's are:

- Barrett, W.T., and Wallace, W.E. (1954) Studies of NaCl-KCl solid solutions. J. Am. Chem. Soc. 76, 366-69.
- Levin, E.M., Robbins, C.R., and McMurdie, H.F. (1964) Phase Diagrams for Ceramists. Am. Ceramic Soc., Columbus, 601 p.

These are Experiments!

This is an experimental investigation. Like "real" experiments, there are lots of problems to overcome. Students will have varying degrees of success and many results will be bogus. Why? There are lots of things that can go wrong, but weighing errors and getting samples mixed up seem to be the most common mistakes made. Part of the goal of the exercise is for students to critically analyzed the results and to separate what is valid from what is not.

Lots of Choices

There are many ways to do this project. The write-up describes what we did in 2005 at UND, but you can do more or do less. You may opt to do more or fewer compositions. You may opt to skip the low-temperature annealing. You may opt to have students calculate unit cell parameters from d_{111}, and then use the results to calculate effective ionic radii. See Brady's original write-up for more ideas and discussion.

Duration

This project cannot be completed in one afternoon – or two or three. Depending on the number of students you have, there will be lines waiting to weigh, to put stuff in the oven, to collect diffraction patterns, etc. I suggest introducing the project n class but having students work on their own time to do the various parts.

Results

Following are two pages from Brady's original article - they will give you an idea of the sorts of results your students may get.

NOTES TO THE INSTRUCTOR

These experiments are quite easy and satisfying to perform. The kinetics of crystallization, nucleation and growth, exsolution, and diffusion are quite rapid in the NaCl-KCl system, so quite a few experiments can be performed during one lab session. Because x-ray diffraction data is needed only for a 6° range in 2θ, characterization of the run products also can be completed quickly. The first part of the exercise as I have described it is very structured. Part II is less structured and more open-ended. Alternatively, you can design an exercise that gives the students less guidance and lets them discover for themselves the details of the NaCl-KCl phase diagram. However, because alkali halide crystals of intermediate composition are notoriously unstable at room temperature, I suggest that you at least warn students of this fact and give them guidance in preparing their samples for x-ray diffraction. When I first tried these experiments, I had some puzzling results due to grinding and also due to getting the sample damp while trying for a more rapid quench (hot ceramic crucibles crack if you set them in a pan of water!). Then I read that some of the chemists trying similar experiments (e.g. Barrett and Wallace, 1954) worked in a dry box to get consistent results! The following figures are the results of experiments with two different classes. The data are surprisingly good with minimal effort and care.

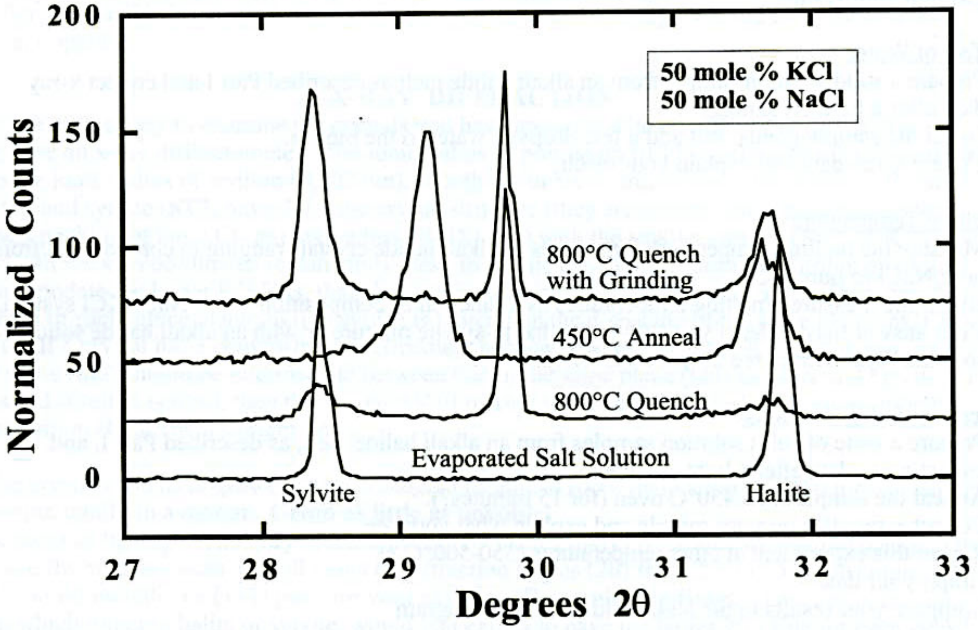


Figure 1. Class x-ray diffraction data for four experiments with a 50:50 KCl-NaCl mix. All peaks are for the (111) plane of sylvite, halite, or an alkali halide solid solution. The bottom line, which shows the location of the (111) peak for halite and sylvite, was obtained from a sample preciptated from an aqueous solution upon evaporation. The second line is for a nearly homogeneou solid solution sample quenched from an 800°C molten salt solution. The third line is for a sample that was first quenched from a melt and then held at 450°C for 24 hours. The two peaks show that both a potassium-rich and a sodium-rich alkali halide phase are present. The top line is for the quench sample of the second line that has been ground a short time in a mortar. Sylvite and halite peaks have appeared due to recrystallization during grinding.

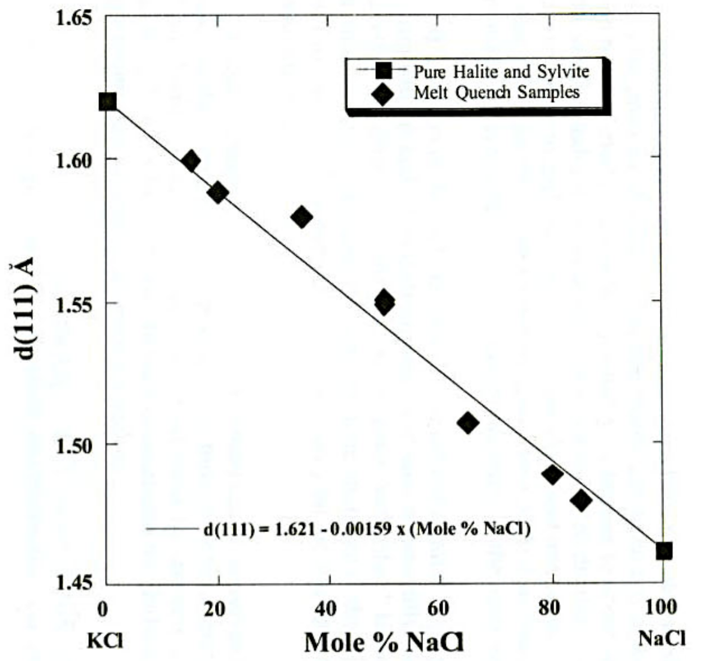


Figure 2. Class x-ray diffraction data for alkali halide solid solution samples quenched from alkali halide melts. The chemical composition of the melt mixture is given on the horizontal axis. The measured $d_{(111)}$ of the quenched products is given on the vertical axis. The line connects the observed $d_{(111)}$ values for sylvite and halite.

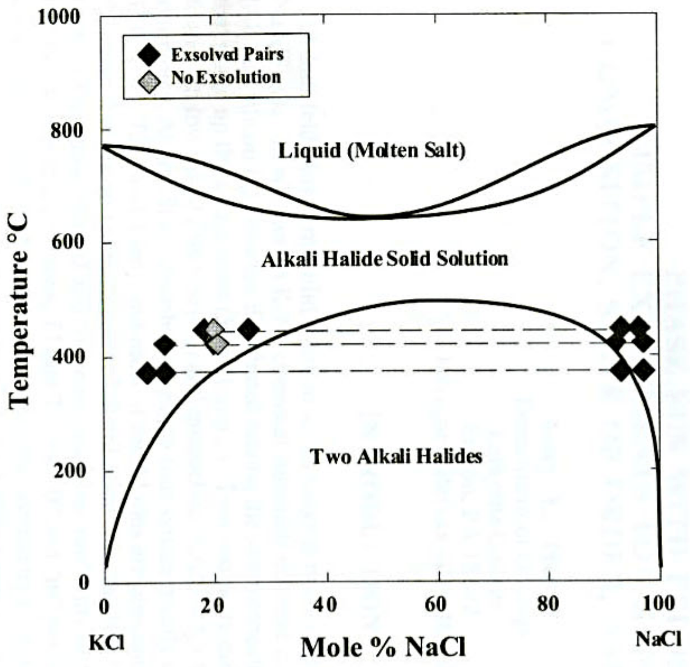


Figure 3. Class exsolution data for annealing of samples quenched from alkali halide melts. The dashed lines connects the observed alkali halide pairs. Two samples that did not exsolve are also shown. Compositions are based on measured $d_{(111)}$ values and the line in Figure 2. The solvus is from Barrett and Wallace (1954). The liquidus and solidus are schematic, but are based on the melting points of sylvite and halite and Figure 1258 in Levin et al. (1964).