Lab 1
The Defect Structure of cubic $Bi_2O_3 \bullet Nb_2O_5$ Solid Solutions
27-202
Fall 2002

Objective

The objective of this lab is to identify the defect structure and charge compensation mechanism in $Bi_2O_3 \bullet Nb_2O_5$ solid solutions. We will accomplish this by comparing pycnometrically determined densities with those computed on the basis of hypothetical solution models.

Introduction

The dissolution of aliovalent solutes requires charge compensation in the solvent phase. For example, consider the dissolution of Al_2O_3 in MgO:

$$Al_2O_3 \rightarrow 2Al_{Mg}^{\bullet} + V_{Mg}^{''} + 3O_O^{*}$$
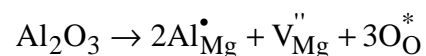
Because Al is trivalent and Mg is divalent, the excess charge associated with the dissolved Al must be compensated by the formation of oppositely charged Mg vacancies. This is an energetically costly process and, therefore, very little alumina will dissolve in magnesia. In fact, it is generally the case that the aliovalent impurities have low solubilities in ceramics. There are, however, interesting and noteworthy exceptions including $CaO \bullet ZrO_2$ and $Bi_2O_3 \bullet Nb_2O_5$. In the latter case, Bi_2O_3 dissolves 22.5 m/o Nb_2O_5. The goal of this experiment is determine how the excess charge associated with the pentavalent Nb is compensated in Bi_2O_3. This problem was originally solved experimentally by Takahashi et al.; the original account of their work can be found at: T. Takahashi, H. Iwahara, and T. Esaka, "High Oxide Ion Conduction in Sintered Oxide of the System Bi2O3-M2O5" J. Electrochem. Soc. 124 [10] (1977) 1563-1569.

Background

As an example of how the charge compensating defect mechanism can be identified, we consider the well- known example of the dissolution of CaO in ZrO_2. This system has some parallels with the $Bi_2O_3 \bullet Nb_2O_5$ system. For example, small amounts of CaO stabilize the cubic fluorite structure. The fluorite structure, illustrated in Fig. 1, takes space group $Fm\overline{3}m$ (no. 225), has four CaF_2 formula units per cell, and situates that Ca in 4a positions (0,0,0 +F) and the O in 8c positions (1/4,1/4,1/4; 1/4,1/4,3/4 +F).
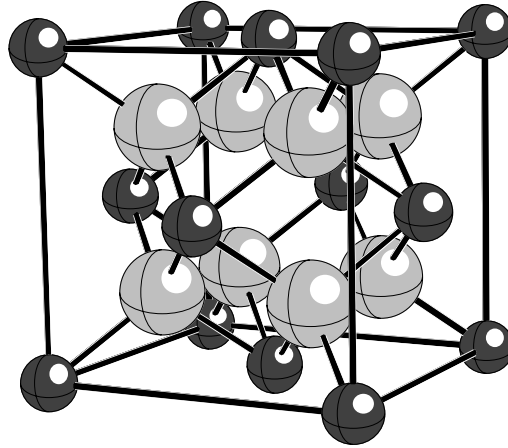
Figure 1. In the fluorite structure, the cations (smaller, darker atoms) occupy the ccp positions and the oxygen ions occupy the tetrahedral sites. In the δ-Bi_2O_3 structure, one quarter of the tetrahedral sites in each cell are vacant.

We will consider two possible defect models for the $CaO \bullet ZrO_2$ system: charge compensation by oxygen vacancies and charge compensation by Zr interstitials.

$$CaO \rightarrow Ca_{Zr}'' + O_O^* + V_O^{\bullet\bullet} \tag{1}$$

$$2CaO + Zr_{Zr}^* \rightarrow 2Ca_{Zr}'' + 2O_O^* + Zr_i^{\bullet\bullet\bullet\bullet} \tag{2}$$

Solid solutions produced by these different reactions will have different densities. To find the density for each one, we imagine a solid solution between the defective structure and ideal structure. So, we have to find the molecular weight of the defective formula unit. For reaction (1), the defective formula unit is made up of one Ca, one O, and one vacancy. For reaction (2), the defective formula unit is made up of one Ca, two O, and one half of a Zr (in an interstitial site. So, the formula weight for each solid solution is:

$$x(M_{CaO}) + (1-x)M_{ZrO_2},$$ vacancy reaction

$$x(M_{CaO2} + \frac{1}{2}M_{Zr}) + (1-x)M_{ZrO_2},$$ interstitial reaction

where M_{CaO}, M_{CaO2}, M_{ZrO2}, and M_{Zr} are the molecular weights of CaO, CaO_2, ZrO_2, and Zr, respectively. To calculate the density, we must note that there are 4 formula units per cell and know the lattice parameter. Thus, we have the equation:

$$\rho = \frac{Z \times (x(M_{defective\ f.u.}) + (1-x)M_{perfect\ f.u.})}{N \times V}$$

Where Z is the number of formula units per unit cell, x is the composition, M is the mass, V is the unit cell volume, and N is Avegadro's number. If you take x = 0.15, Z = 4, and the cubic lattice constant of 5.1535 Å, we calculate densities of 5.52 and 5.92 g/cm^3 for the vacancy an interstitial models, respectively. Thus, the two hypothetical models predict a 8% difference in the density. Assuming that mass and volume measurements can be made with this accuracy, then it is possible to distinguish these models. The results of Diness and Roy [A. Diness and R. Roy, "Experimental confirmation of major change of defect type with temperature an composition in ionic compounds," Solid State Commun. 3 [6] (1965) 123-125.], who originally conducted this experiment, are shown in Fig. 2.
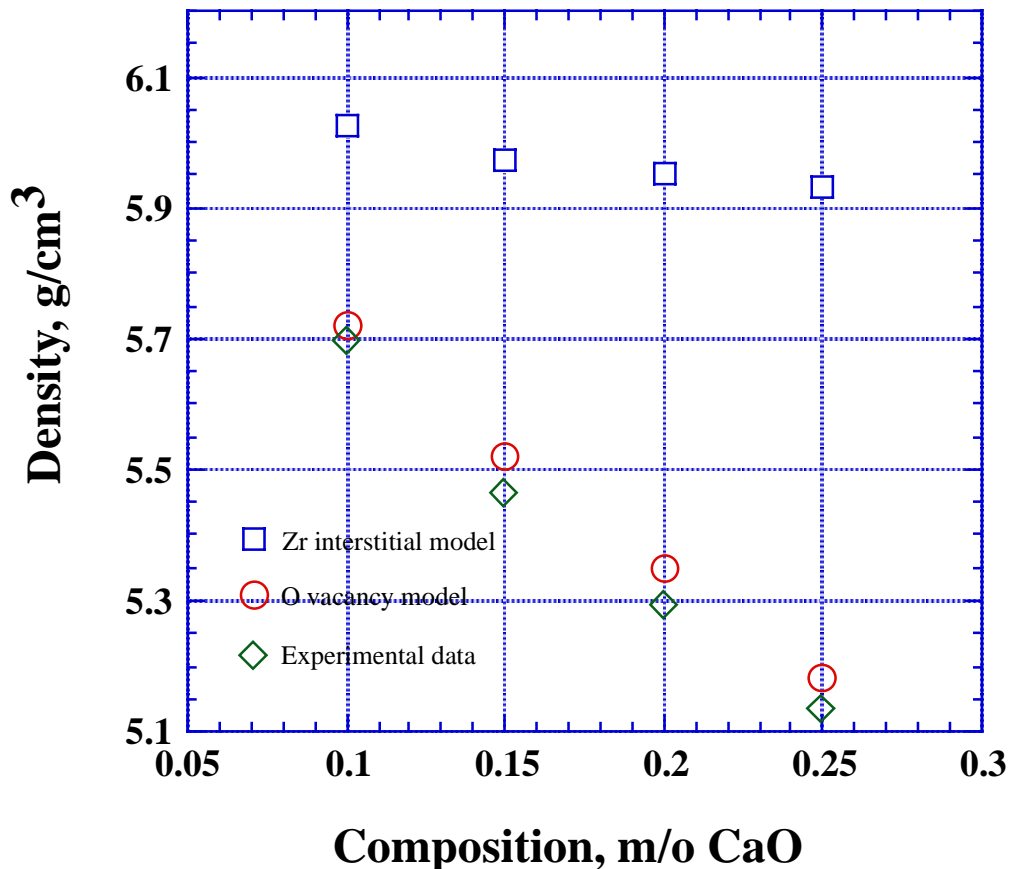

Figure 2. Summary of results from the CaO•ZrO$_2$ system. The data support the oxygen vacancy model given by reaction 1. From: A. Diness and R. Roy, "Experimental confirmation of major change of defect type with temperature an composition in ionic compounds," Solid State Commun. 3 [6] (1965) 123-125.

Pychnometric density measurements can be made in a number of ways. Perhaps the easiest way is to use Archimedes principle: that a body wholly or partly immersed in a fluid is bouyed up with a force equal to the weight of the fluid displaced by the body. So, if w_i is the weight of the specimen immersed in fluid, then w_i is the difference between the true specimen weight ($w_s = \rho_s V_s g$) and the weight of the displaced fluid ($w_f = \rho_f V_f g$):

$$w_i = \rho_s V_s g - \rho_f V_f g.$$

If we also consider the weight of the specimen in air:

$$w_a = \rho_s V_s g - \rho_a V_a g.$$

Noting that all of the volumes are the same and that the true specimen weight and the weight in air are about the same,

$$V = \frac{w_a}{\rho_s g} = \frac{w_i}{(\rho_s - \rho_f)g},$$

$$\frac{w_a}{w_i} = \frac{\rho_s}{\rho_s - \rho_f}.$$

So, if you measure the weight in air and in a fluid of known density, it is possible to calculate the density of the specimen.

A pychnometer works by using two chambers of known volume. The reference volumn (V_r) is filled to a known pressure (P_1) above ambient. The ideal gas law then relates the pressure and volume to the ambient temperature (T_a) and the moles of gas (n_1) in the volume.

$$P_1 V_R = n_1 R T_a$$

Similary, the volume of gas in the test cell is the cell volume (V_c) minus the volume of the powder (V_p). At ambient presure (P_a) we have:

$$P_a(V_c - V_p) = n_a R T_a,$$

Where n_a are the moles of gas in the test cell. When the valve connecting the two chambers is open, the reference pressure decreases and the pressure in the test cell increase to P_2:

$$P_2(V_c - V_p + V_R) = n_a R T_a + n_1 R T_a$$

Substituting the right hand sides of the two previous equations, you have:

$$V_c - V_p = \frac{P_1 - P_2}{P_2 - P_a} V_R$$

Since the instrument is zeroed so that the ambient pressure is 0,

$$V_p = V_c - V_R\left[(P_1 / P_2) - 1\right]$$

So, by knowing the test cell volume and the reference volume, and by measuring the pressure before and after the valve between them is open, the volume of the power cen be measured. By weighing the sample, one can then determine the density.

Procedure

A. Reaction models

To determine the charge compensation mechanism, we need to begin by considering plausible defect reactions. The dissolution of Nb_2O_5 occurs at elevated temperatures and under these conditions, the cubic fluorite-like δ-Bi_2O_3 structure is stable. The structure of this phase is illustrated in Fig. 1 (background section). The addition of Nb stabilizes this phase and all of the materials we examine will have this structure. For our purposes, we can visualize this structure as a cubic close packed (ccp) arrangement of Bi with O in the tetrahedral interstices. There are two formula units of Bi_2O_3 per unit cell; the four Bi occupy the ccp sites and the six O occupy six of the eight tetrahedral interstices. When we create our model of the defect structure we will assume that the two empty tetrahedral sites in each cell are oxygen vacancies.

We can envision several compensation mechanisms for the Nb_2O_5 dissolution. For example, it is possible to compensate the charge on the Nb by eliminating oxygen vacancies:

$$2V_O^{\bullet\bullet} + Nb_2O_5 \rightarrow 2Nb_{Bi}^{\bullet\bullet} + 5O_O^{*}. \tag{1}$$
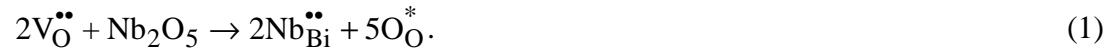
Here, all of the Nb goes to Bi sites and all of the oxygen goes to O sites. There is a one to one ratio of Nb added to Bi replaced. Also, there is one additional O added for every Nb that is added to the crystal. So, the new formula, as a function of x is:

$$(Bi_{(1-x)}Nb_x)_2O_{3+2x}$$

It is also possible to compensate the charge on the Nb by creating the appropriate number of vacancies on Bi sites:

$$3Nb_2O_5 \rightarrow 6Nb_{Bi}^{\bullet\bullet} + 15O_O^* + 4V_{Bi}'''. \tag{2}$$

In this case, every Nb that substitutes in the structure replaces one Bi and creates 2/3 of a Bi vacancy. In other words, each Nb replaces 5/3 Bi. Therefore, the formula unit is:

$$(Bi_{(1-5/3x)}Nb_x)_2O_3$$
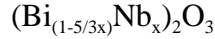
If vacant O sites are consumed, it is possible to compensate charge with fewer Bi vacancies:

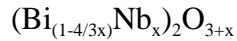$$3V_O^{\bullet\bullet} + 3Nb_2O_5 \rightarrow 6Nb_{Bi}^{\bullet\bullet} + 15O_O^* + 2V_{Bi}''' \tag{3}$$
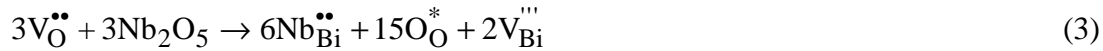
In this case, every Nb that substitutes in the structure replaces one Bi and creates 1/3 of a Bi vacancy. In other words, each Nb replaces 4/3 Bi. In addition, since three oxygen vacancies are eliminated by the addition of six Nb, we can say that for each added Nb, 1/2 of an extra O is added to the crystal. Therefore, the formula unit is:

$$(Bi_{(1-4/3x)}Nb_x)_2O_{3+x}$$

Finally, we must also consider the possibility that the Nb dissolves interstitially:

$$5V_O^{\bullet\bullet} + Nb_2O_5 \rightarrow 2Nb_i^{5\bullet} + 5O_O^* \tag{4}$$

Here, for every two Nb that enter the crystal, 5 oxygen vacancies are consumed. The Nb do not displace any Bi, but, in the solution, the Nb/Bi ratio is constrained to be $x/(1-x)$ and this has to be accounted for in the formula unit:

$$(BiNb(i)_{(x/(1-x))})_2O_{3+5(x/(1-x))}$$
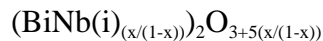
So, we have four different models for the defect structure. Note that each model produces a substance with a different formula weight per unit cell. If we know the cubic lattice parameter (which we can measure using powder X-ray diffraction), then for any given composition, we can compute a hypothetical density based on each of the four models above. If we measure the actual density pychnometrically (by measuring both the volume and the weight) then by comparing the actual density to the five hypothetical densities, we can determine which model matches most closely with observation. Rather than relying on a single composition, we will make our measurements at a range of compositions.

B. Sample preparation

1. We wish to make $(Bi_2O_3)_{1-x}(Nb_2O_5)_x$ solid solutions with x = 0.05, 0.10, 0.15, 0.2, and 0.225. Begin by calculating the mass ratios (Bi_2O_3/Nb_2O_5) that you will need for each composition.

2. Weigh out appropriate amounts of the two starting materials, Bi_2O_3 (Alfa Aesar 99%) and Nb_2O_5 (Alfa Aesar 99.5%). The total mass of your sample should be approximately 50 g.

3. Mix and grind each composition in a mortar and pestle for 10 min. If you use the same mortar and pestle for more than one composition, clean it between grindings.

4. Using a uniaxial press, consolidate the powder in a die. (Reserve some powder for step 5.)

5. Place the compacted powder in an alumina crucible or dish. Put the loose reserve powder on the bottom of the crucible and the compacted pellet on top of the powder (this creates a marginal contamination barrier between the specimen and the crucible).

6. Fire the sample at 800 or 900 °C in air for 10 hours. (The x = 0.05 composition should be heated at 800°C, the others can be heated at 900 °C).

7. Remove the pellet, regrind in a mortar and pestle, and use the uniaxial press to make a new pellet. Place in crucible as in step 5.

8. Fire the sample for at least 10 hours in air. This second grinding and firing is to complete the homogenization.

9. Cool to 800 °C, and quench to room temperature. The "quench" step can be performed by removing the crucible directly form the furnace and blowing air over the specimen using a fan or hair dryer on the "cool" setting. This quench is need to stabilize the high temperature fluorite phase.

10. Break up the pellets into chunks. Grind about 1/5 of the specimen for powder X-ray diffraction. Reserve the remainder of the chunks for the density measurement. Be sure to keep the chunks from each pellet in separate, clearly labeled containers.

C. Determining lattice parameters

1. Use a mesh sieve should be used to remove any large particles from the sample. (The presence a few large particles can have drastic effects on the relative intensities.)

2. The powdered sample should then be placed in the sample holder (see Fig 3). If the powder particles are platy, packing the powder into the well will result in an undesirable preferred orientation that will influence the relative intensities of the peaks. To minimize this effect, add excess powder to the well so that the level of the powder rises higher than the top surface of the sample holder. By scraping a straight edge along the top surface of the sample holder, the excess is removed and the surface of the powder is level with the reference plane of the sample holder and diffractometer. The sample can then be mounted in the diffractometer.
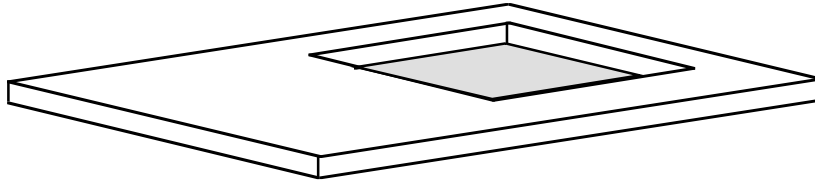
Figure 3. The powder sample holder is a flat plate with a well to hold the powder. The surface of the plate defines the diffractometer reference plane.

3. The scan is controlled entirely by the computer. You will scan from 10 to 90° in 2Θ using increments of 0.05° per step. At each angular position, you should count (measure the intensity) for 2 s. After setting these scan parameters (and recording them in your notebook), the generator can be turned on and the scan can be started. Record the operating current and voltage of the generator. (35 kV, 20 mA is suggested)

4. The scan will take approximately 3/4 of an hour, depending on exactly which parameters you choose. The computer records the data in a text file. Each line of the file contains an ordered pair of numbers, separated by a tab. The first number on each line is the angular position of the incident and diffracted beam (with respect to the diffractometer reference plane) and the second is the intensity measured by the detector. While waiting for the completion of your scans, you should examine the diffraction patterns recorded earlier.

5. The files are easily read and displayed using the applications such as "Kaleidagraph" and "Excel".

6. Use Bragg's law to calculate the d-spacing of each peak. These data can be used to measure the cubic lattice constant for each sample. Either use a program designed for this purpose, such as finax, or follow one of the procedures outlined by Cullity in Chapter 11 (Elements of X-ray Diffraction, Addison Weseley, Reading, Mass).

D. Determining hypothetical densities

1. Four defect models were presented in section A. For each model, determine the contents of a single unit cell, as a function of x. The atomic masses are $M_{Bi} = 209$, $M_{Nb} = 93$, and $M_O = 16$.

2. At each composition ($x = 0.05$, 0.10, 0.15, 0.20, and 0.225), the density is computed by dividing the mass per cell by the cube of the lattice constant.

3. Make a graph, with density on the vertical axis and composition (x) on the horizontal axis that shows the results from each model.

E. Density measurement

1. For the density measurement, we will use the Quantachrome Corp. Multipychnometer.

2. Coarsely grind a portion of your sample to a particle size of about 50 microns. It is important that there is little or no enclosed porosity. It is also important that the powder be coarse enough that it is easy to handle and transfer from the balance to the pychnometer without loosing any material. Alternatively, you can begin with a finely ground material, and coarsen it by heating at 800°C in air for several hours.

3. Weigh approximately 10 grams of your sample.

4. Transfer it to the "micro" cell of the pychnometer.

5. Follow the written instructions for the pychnometer to measure the volume of your specimen.

6. Use the mass and volume of each sample to calculate its density. Compare these densities to the hypothetical densities calculated in part C by plotting the results on the graph.

Report Format.

TITLE

Your name, names of those in your group, date

Abstract

In <u>less than</u> 100 words, describe what you have done as well as the most important data and/or results and/or conclusions. For this lab, you should specify the compositions prepared, state that the pychnometric densities and X-ray densities were compared, and state your conclusions regarding the defect structure of the solid solutions.

 [Note: the abstract can be thought of as a one paragraph report that says what you did and what the result was. Remember, the abstract is <u>not an introduction</u> to the report, it should be capable of standing by itself.]

Introduction

1) What was the objective of your work?

2) What method(s) did you employ?

3) Which hypothetical defect structures did you consider?

4) What range of compositions did you study?

5) What limited the possible range of compositions?

 [Note: the purpose of an introduction is to state the subject and the objective of the work. The introduction may also describe the experimental strategies, the reason that this course of action was chosen, and the range of parameters that were explored.]

Procedure

1) How did you grind and prepare the powder for the density measurement?

2) What instruments were used?

3) What did the powdered samples look like (colors)?

4) For how long were the samples purged with He for the density measurements?

[Note: the procedure describes the details of your method, with sufficient accuracy to be duplicated. Of special interest are novel or original procedures that were developed for your work and elements of the procedure that were identified as critical to the success or failure of the project.]

Results

1) You should make a table that contains the following information for each specimen: composition, cubic lattice parameter, mass, volume, and density. You should also make a graph of composition v. density that includes the hypothetical models.

2) How many trials did you carry out?

3) Estimate the errors in your measurements and their effect on the measured density.

[Note: the results section should specify, in detail (numerically when possible) the results of your work. In addition, it is usually appropriate to qualify the results through comparisons. All figures (images and graphs) must be clearly labeled. In the text, refer to each figure by the number (for example, Fig. 1)]

Discussion

1) Which defect model is most consistent with the experimental results?

2) Were all of the samples phase pure?

3) The phase diagram for this system indicates that the cubic δ-phase is stabilized by Nb additions. Is this consistent with the defect model?

4) If this material is to be used as an ionic conductor, what is the ideal composition?

[Note: in the discussion section you should explain and interpret the results, develop conclusions, and suggest modifications. In the event of unsatisfactory results, this is the place to propose explanations. In addition, it is often appropriate to place the results of your work in context by comparing your results with established knowledge.]

Conclusions

Which defect model provides the best explanations for your observations?

[Note: in this section you make a brief statement of the central conclusions of your work]