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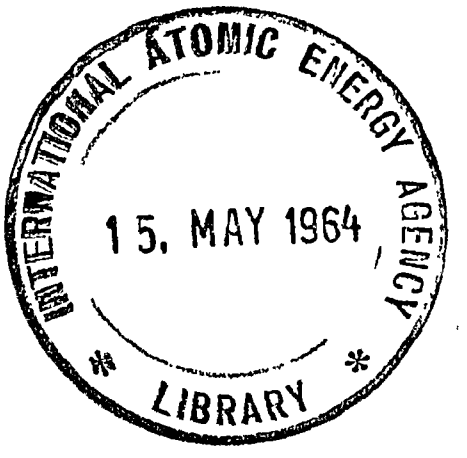

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ABSTRACT

A method is described whereby the density of a single crystal of beryllium oxide can be measured by suspending it in a dense liquid. The method is being used to measure radiation-induced changes in density and is sensitive to 1 part in 10^5. The absolute accuracy has not been established owing to the lack of a suitable standard.

CONTENTS

1. INTRODUCTION

When single crystals of beryllium oxide became available recently, experiments were initiated to establish the precise correlation between the lattice dilatations (detected by X-ray diffraction) and the macroscopic volume changes occurring in beryllium oxide when it is irradiated with fast neutrons.

Lattice parameter changes in small single crystals of beryllium oxide are currently being measured in this laboratory using a modification (Mayer and Walker 1963) of the technique developed by Bond (1960). Calculations of density changes based on the lattice parameter changes indicated the need for a method of macroscopic density determination sensitive to changes of as little as 5 parts in 10^4. Since the beryllium oxide crystals available weighed only 0.01 to 0.03 gram, a density change of 0.05 per cent. in crystals of this size corresponds to a volume change of about 0.00005 cm^3; any method relying on the measurement of the crystal volume would have to be extremely sensitive.

A displacement weighing technique was considered, involving measurement of the weight of about 0.00005 cm^3 of a suitable liquid. Analytical micro-balances appeared to offer adequate sensitivity but the method was discarded in favour of a suspension method in which the density of a large bulk of a dense liquid is measured after having been made equal to that of the specimen. This method has greater simplicity of operation than the hydrostatic weighing technique at sensitivities of 10^{-4} or better, and has virtually no restriction on the specimen size. Furthermore, it offers greater sensitivity than originally sought, at no extra complexity or cost of apparatus.

2. EXPERIMENTAL METHOD

2.1 Establishment of Procedures

The suspension method (Straumanis 1953) relies on a difference in volume expansion between the specimen and the suspension liquid. Straumanis placed his specimen and liquid in a pycnometer whose volume was known accurately over a temperature range of 15°C. The pycnometer was placed in a temperature bath and brought to a temperature at which the specimen remained suspended in the liquid; that is, both liquid and specimen had the same density. Excess liquid was removed, the pycnometer weighed, and the density of the liquid and specimen calculated.

Ideally, suspension of the specimen in the liquid should be done in the pycnometer. However, for accurate adjustment of the liquid level to the reference mark, the pycnometer should have a capillary neck. This places a low upper limit on the specimen size. The beryllium oxide crystals used in this work were generally several millimetres across and it was necessary to effect suspension (that is, temperature adjustment) in a wide-necked suspension tube, then transfer the liquid to the pycnometer, allow its temperature to re-stabilise, and then determine the density of the liquid.

2.2 Apparatus

The suspension tube was simply a Pyrex tube 1 cm in diameter and 12 cm long. A standard 10 mm cone and socket were used as a ground glass mouth and stopper.

The pycnometer is illustrated in Figure 1. Again it was constructed from 1 cm diameter Pyrex glass and had a bulb length of 7.5 cm. A thick-walled neck of about 1 mm bore and 1 cm long separated the bulb from a ground glass socket which took a 7 mm ground glass stopper. The pycnometer was annealed for 30 minutes at 600°C, after which the ground glass stopper was lapped in and a hair line scribed midway along the capillary to serve as the volume reference line.

The constant temperature bath was a Townson and Mercer X-27 model. Familiarity with this unit enabled the temperature to be adjusted in steps of about 0.01°C and no difficulty was encountered in achieving and maintaining suspension of crystals. All weighings were done on a Mettler B6 semi-micro-balance and bath temperatures were read with a thermometer graduated in tenths of a degree Centigrade.

No pure liquid was available with a density sufficiently close to that of unirradiated beryllium oxide (3.01 g cm^{-3}). The liquid of nearest density was sym-tetrabromoethane (2.95 g cm^{-3}) from which higher density mixtures were prepared by adding either methylene iodide (3.32 g cm^{-3}) or carbon tetrabromide (3.42 g cm^{-3}). The carbon tetrabromide mixture was preferred as it was more stable, remained colourless for long periods, and gave more consistent results. Either mixture could be adjusted readily to a density very close to that of any given crystal.

The volume of the pycnometer was determined at 25, 30, 35, 40, and 45°C, using boiled demineralised water, which was assumed to have the same density as boiled distilled water. The techniques for adjusting the liquid level were the same as used in actual density determinations (see Section 2.3). Calibration volumes are given in Table 1.

2.3 Experimental Procedure

When the pycnometer and suspension tube were first received they were thoroughly cleaned in chromic acid solution followed by concentrated nitric acid. Because of the difficulty of getting strongly-acidic cleaning agents through the capillary, the pycnometer was cleaned with them only when absolutely necessary. Routine cleaning was done with acetone (which readily dissolved the suspension liquids) and the pycnometer was handled and stored with extreme care to minimise the chance of contaminating the inside surface.

Density determinations were made as follows. The crystal was thoroughly cleaned by boiling for 30 minutes in concentrated nitric acid, and all subsequent handling was done with tweezers.

The suspension tube was part-filled with tetrabromoethane and placed in a beaker of water at approximately the required suspension temperature. The crystal was placed in the tube and the liquid density increased, until suspension occurred, by adding methylene iodide or a concentrated solution of carbon tetrabromide in tetrabromoethane.

After the tube was shaken to ensure complete mixing, the liquid was outgassed at a pressure of 10^{-2}mmHg and the tube placed in the constant temperature bath. Frequent tapping during evacuation accelerated outgassing and helped remove traces of acetone which sometimes appeared to contaminate the liquid. The temperature was adjusted until the crystal remained suspended without rising or falling.

During this period, the crystal was observed through a cathetometer; temperature adjustment was considered satisfactory when the crystal remained stationary for about 10 minutes. Using a hypodermic syringe the liquid was then transferred to the pycnometer, to fill it to a level slightly above the reference mark. The liquid and pycnometer were again outgassed at 10^{-2}mmHg and placed in the constant temperature bath and left to stand for about 10 minutes. The liquid level was then accurately adjusted to the reference mark with filter paper needles and 0.020 or 0.005 inch diameter nickel wires. The level was observed and adjusted at further intervals of 5 minutes until no change occurred. During this stabilization period the pycnometer was kept stoppered and after each adjustment of level the inside surface above the reference line was carefully wiped dry with tissues.

When adjustment was completed the pycnometer was withdrawn from the bath, dried with tissues, and dusted with a squirrel-hair brush. It was then weighed and the density of the liquid and specimen (at suspension temperature) calculated. All beryllium oxide crystal densities were normalized to a temperature of 22°C using a coefficient of volume expansion of 16.2×10^{-6} °C^{-1} (Whatham 1962, private communication with General Electric Co. Evendale).

3. ACCURACY OF RESULTS

The known sources of error in the procedure described are as follows:

(i) Adjustment of the bath temperature to give true suspension of the specimen.

(ii) Adjustment of the liquid level in the capillary.

(iii) Reading of the bath temperature.

(iv) Weighing.

The overall error in a density value can be estimated from the accuracy of each of these operations. Operations (i), (ii), and (iii) directly affect the volume of liquid and the volume of the pycnometer itself. Operation (iv) leads to an error in the weight of the liquid, which directly affects the value for the liquid density.

Suspension temperatures can be adjusted to less than 0.01°C and it was found that a change of this magnitude could reverse the direction of motion of a crystal when the correct temperature was almost reached. Use of Stokes' law shows that a movement of 1 mm in ten minutes (a typical suspension condition) gives rise to an error of no more than 5 parts in 10^7 if the specimen is assumed to be a sphere of 1 mm radius. The liquid level can be adjusted to $\pm$ 0.1 mm and the bath temperature can be read to $\pm$ 0.01°C. Differential weighings on the Mettler B6 balance can be reproduced with a precision of 1 in 10^6 at the 20-gram level.

Based on these errors, the overall error in the determination should not be more than 2 in 10^5 (or 0.00006 g cm^{-3} in a density of 3.0 g cm^{-3}), and the sensitivity should be 4 parts in 10^5.

The validity of this figure was checked by a series of six determinations on a single crystal over a period of ten days. The results of these measurements are given in Table 2. Assuming the mean value (3.011787 g cm^{-3}) to be the true density, the observed variations are between +0.000013 and -0.000017 g cm^{-3}. Thus values can be reproduced to within 6 parts in 10^6 and the experimentally determined sensitivity is 1.2 parts in 10^5. This is considerably better than the estimate of 4 parts in 10^5. It should be pointed out, however, that the sensitivity would probably decrease slightly with smaller crystals. A safe estimate for small specimens would be 2 parts in 10^5 which is still quite adequate for the radiation damage studies in hand.

As the method is being used for measuring changes in the density the absolute accuracy of the results is of secondary importance. An attempt was made to determine the absolute accuracy by comparing the measured density of a high purity calcium fluoride crystal with the theoretical density determined from X-ray measurements. These values (shown in Table 3) agree to within 2 parts in 10^4. This agreement is considered to be fairly satisfactory and closer agreement may have been obtained if the atomic weight of calcium (five naturally occurring isotopes) was known more accurately.

4. CONCLUSION

A technique has been developed for measuring the density of small single crystals of beryllium oxide. The method is sensitive to density changes of 1 part in 100,000 and has been used on specimens weighing as little as 10 milligrams.

5. REFERENCES

Bond, W.L. (1960). - Acta Cryst. 13: 814.

Mayer, R.M., and Walker, D.G. (1963). - AAEC/TM211.

Straumanis, M.E. (1953). - American Mineralogist 38: 662.

TABLE 1

VOLUME OF PYCNOMETER

Temperature (^{o}C)	Volume (cm^3)
25	7.291293
30	7.291532
35	7.291773
40	7.291996
45	7.292209

TABLE 2

DENSITY OF BeO SINGLE CRYSTAL

Measurement No.	Density (g cm^{-3})
1	3.01178
2	3.01179
3	3.01179
4	3.01180
5	3.01177
6	3.01179
Mean 3.011787 g cm^{-3} 99% confidence limits 3.011787 $\pm$ .000017 g cm^{-3}	

TABLE 3

DENSITY OF CALCIUM FLUORIDE CRYSTAL

Technique	Density (g cm^{-3}
X.R.D.	3.18119
Suspension	3.18076$\pm$.000017

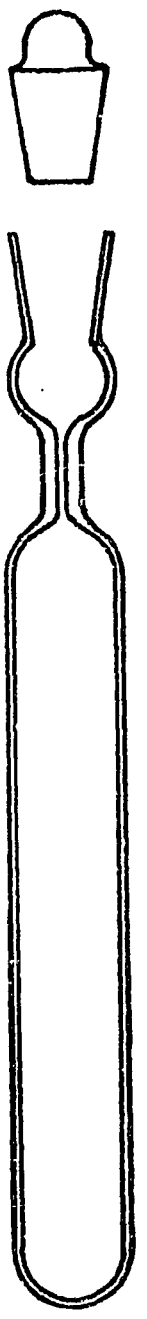

FIGURE 1 THE PYCNOMETER