Composition of Pulsed-Laser-Deposited Y-Ba-Cu-O and Ba-K-Bi-O Thin Films

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Abstract

The composition of pulsed-laser-deposited Y-Ba-Cu-O and Ba-K-Bi-O thin films is shown to be strongly affected by target conditioning, gas pressure, and target-substrate distance. For both compounds, ablation from a freshly sanded target surface results in films with an excess of the more volatile elements. The concentration of these volatile elements in the films decreases until the system reaches a steady state after sufficient ablation from the target. Y-Ba-Cu-O film composition is also affected by oxygen pressure and target-substrate distance. Increasing pressure or distance results in relative copper and barium depletion in the central region of deposition, presumably due to differences in the efficacy of oxygen in scattering the different elements. This relationship between pressure, distance, and composition is shown to be significant for the growth of optimal superconducting Y-Ba-Cu-O thin films. The composition of Ba-K-Bi-O is also affected strongly by background gas pressure. Ba-K-Bi-O deposited in vacuum is potassium deficient in the film center. A background argon pressure of 1 Torr, however, increases the potassium concentration and results in films with uniform composition over a broad area. We argue that this effect is significant in explaining a successful growth method for superconducting Ba-K-Bi-O films.

1. INTRODUCTION

In spite of numerous studies on the pulsed-laser deposition of Y-Ba-Cu-O and other complex materials systems, the influence of the various deposition parameters on resulting film quality is not well understood. One obviously important factor, affecting both the electrical properties and morphology, is film composition. Due to the complex nature of the laser plasma, however, the film composition resulting from a given set of deposition parameters is difficult to predict. A few studies have addressed this problem.[1-9] A complete understanding, however, has not yet been attained. In a previous study,[9] we analyzed the composition of Y-Ba-Cu-O films deposited with a variety of laser fluences, target conditions, target-substrate distances, oxygen pressures, positions on the substrate, and substrate temperatures. Here we summarize and expand upon the key aspects of this previous work, and present additional data on Ba-K-Bi-O thin films. Target conditioning, gas pressure, and target-substrate distance significantly affect the film composition and are shown to be important in determining superconducting film quality.

II. EXPERIMENT

The equipment and procedure used in this study were previously described in detail.[9] In brief, a 248 nm KrF excimer laser was focused onto a target of Y-Ba-Cu-O or Ba-K-Bi-O with a fluence of roughly 1 J/cm^2. Inductively coupled plasma (ICP) spectroscopy showed the target compositions to be $YBa_{1.96}Cu_{2.85}O_x$ and $Ba_{0.81}K_{0.31}BiO_y$. Fresh target surfaces were prepared by sanding with silicon-carbide paper of 320 or higher grit, The use of Si or MgO substrates simplified the Rutherford backscattering spectroscopy (RBS) analysis. All films were deposited with substrates at ambient temperature except for Y-Ba-Cu-O films used in the target-conditioning study, which were deposited with a substrate temperature of ≈800° C. We showed previously that substrate temperature has no significant effect on Y-Ba-Cu-O film composition, however, we did not carefully investigate temperature effects for Ba-K-Bi-O. Except where noted, substrates were centered in the plume of material ejected from the target, so stated compositions represent the thickest region of the deposited film. The accuracy of the RBS composition data is roughly ±5% except for the potassium data, which are somewhat less accurate due to the small signal. ICP measurements of composition for one Y-Ba-Cu-O and one Ba-K-Bi-O film agree well with the RBS results for films deposited immediately before and after the ICP samples.

III. TARGET CONDITIONING EFFECTS

The composition of films deposited from a freshly sanded target is initially dependent on ablation time. We previously showed[9] that the initial films deposited from a fresh Y-Ba-Cu-O target are copper and barium rich, and these elements decrease in relative concentration in the films until the system reaches a steady state at about 40 shots per site. A similar effect occurs when depositing Ba-K-Bi-O from a freshly sanded target. Figure 1 indicates an initial preferential deposition of potassium and bismuth. Here shots per site represents the total number of laser shots multiplied by the ratio of the laser spot size on the rotating target to the area of the irradiated track on the target. The dashed lines in Fig. 1 represent the target composition.

The time dependent composition from fresh target surfaces can be understood in terms of preferential ablation of high-vapor-pressure species. Table 1 shows the melting and boiling points of the target metals and their common oxides. In nearly every case, the metals that are enriched in films made from a fresh target have the lowest melting and boiling temperatures, that is, they are the most volatile. For example, Fig, 1 indicates that potassium is initially deposited preferentially over barium and bismuth, and the phase transitions of potassium and potassium oxide listed in Table 1 are much lower than those of barium, bismuth, and their oxides. A similar effect is well known in sputtering, " where variations in sputtering rates among the target components result in an initial excess flux of the more volatile elements. After an initial time-dependent period, the sputter target surface becomes depleted in the volatile species and a steady state is reached in which the total flux from the target has the same composition as the bulk target. Of course, a comparison such as that in Table 1 oversimplifies the complex target chemistry and laser-target interactions present in the pulsed-laser deposition process, but it provides a strong indication that preferential ablation of the more volatile elements can explain time-dependent film compositions from a fresh target surface.

In all studies described below, the targets were conditioned beyond the regime of time-dependent composition prior to film growth.

IV. Y-Ba-Cu-O FILMS: OXYGEN PRESSURE AND TARGET-SUBSTRATE DISTANCE EFFECTS

Y-Ba-Cu-O films deposited with small target-substrate-distance (3 cm) have compositions which closely reproduce that of the target. Similarly, films deposited in vacuum with target-substrate distances in the range 3-12 cm often have compositions close to that of the target. We should note, however, that the films deposited in vacuum are somewhat copper and barium enriched in the thickest region and large variations between runs are occasionally seen, As oxygen pressure and target-substrate distance are increased, the distribution of each element across the substrate broadens, presumably due to scattering of the ablated species by the oxygen. The copper and barium distributions broaden more than the yttrium distribution, resulting in eventual copper and barium depletion in the central, thick region of film. This effect is shown in Figures 2 and 3, where increases in oxygen pressure and target-substrate distance are seen to dramatically decrease the relative concentrations of copper and barium in the film.

Figure 4 summarizes the effects of oxygen pressure and target-substrate distance on composition. The horizontal bars represent several sets of data at fixed oxygen pressures and a range of target-substrate distances. The extent of the bars shows the range of target-substrate distance for which the film composition in the thickest region has Cu/Y and Ba/Y concentrations within 10°/0 that of the target. Regions of pressure-distance space outside of this graph were not investigated. I-he shaded region schematically shows that region of pressure-distance space where the film metal composition is roughly that of the target (±10%). Note that oxygen stoichiometry is not reflected in this diagram. As can be seen, short target-substrate distance or low pressure are generally good in terms of composition (although some films made in vacuum are highly copper and barium rich). As oxygen pressure and distance are increased, eventually the copper and barium concentrations in the film drop well below those of the target.

The shaded region in Figure 4 represents a fairly wide range in composition (±10%). To reproduce the target composition accurately, closer control of oxygen pressure is required. For the larger target-substrate distances, an oxygen pressure can be found for which the film composition is very close to that of the target. For our setup, 9 cm and 40 mTorr produced stoichiometric films across a 6 cm diameter area.[9] For target-substrate distances near 3 cm, the target composition is reproduced over a broader range in oxygen pressure, however the film thickness distribution is narrow, so uniform, large-area films are difficult to produce. The exact oxygen pressure required for stoichiometric films at a given target-substrate distance may vary with target characteristics or other system parameters, but the qualitative trends shown in Figs. 2-4 are likely to be of a general nature.

The closed circles in Fig. 4 are data of Kim and Kwok.[12] These points represent, at each distance, the oxygen pressure that the authors found optimized Y-Ba-Cu-O film electrical properties on MgO substrates for a substrate temperature of 680° C. They note that at higher temperature or on $SrTiO_3$ substrates the deposition process is more forgiving, yielding good quality superconducting films over a broader pressure range. They argue that the quality of film growth strongly depends on the energy of impinging species, which is a function of oxygen pressure. The optimal oxygen pressure therefore may be the pressure that produces some optimal impingement energy. While this effect is probably important, the close relationship between their data and the border of the shaded 'stoichiometric' region defined in this work and shown in Fig. 4 suggests that a composition effect may also play a role. Perhaps their points represent a constant composition curve for their experimental setup and target, or, since higher oxygen pressures may assist film grown by providing more oxygen for incorporation, each point may represent the highest oxygen pressure which gives roughly the correct metal stoichiometry. In any case, the relative importance of film composition compared to other factors determining film quality deserves further examination.

V. Ba-K-Bi-O: GAS PRESSURE EFFECTS

Figure 5 shows the composition across a substrate for Ba-K-Bi-O deposited in vacuum, indicating dips in the potassium and barium concentrations in the center region. These dips result from differing widths of the sharply peaked elemental distributions. The bismuth distribution is peaked most sharply and the potassium distribution is the broadest, resulting in less relative potassium and barium near the film center. Such a result is inconsistent with current theories describing pulsed-laser-deposition[5,6,8] which predict narrow distributions for light elements and broad distributions for heavy elements, However, several factors may complicate this analysis. Because of potassium's high vapor pressure, a significant amount of this element may leave the target through simple thermal evaporation, which produces a broad angular distribution. That thermal evaporation processes may contribute in pulsed-laser-deposition has been suggested previously by Venkatesan et all We should note, however, that for deposition both in vacuum and in 1 Torr argon gas the distribution of potassium is much narrower than would be seen in a purely evaporative process from a flat target surface. An additional complicating factor is that current theories of pulsed-laser-deposition assume that the species leaving the target are atomic or single-element oxides. While the results of Chrisey et al.[13] suggest that this assumption is valid for Y-Ba-Cu-O under condition relevant for pulsed-laser deposition, such data is not yet available for Ba-K-Bi-O. It is possible, for instance, that potassium is ejected mostly as heavy cluster molecules.

A successful method of depositing superconducting Ba-K-Bi-O thin films with pulsed-laser deposition involves the use of 1 Torr argon as a background gas.[14] In order to understand the benefit of this gas, the composition of a film deposited in 1 Torr argon at room temperature was analyzed. Figure 6 shows that the resulting film has a much more uniform composition distribution than the film deposited in vacuum, and additionally the relative potassium concentration is increased significantly over vacuum-deposited films. The explanation for this effect is not clear. With 1 Torr argon the bismuth and barium distributions broaden to match that of potassium, but the potassium distribution does not broaden significantly. This result is surprising since potassium is significantly lighter than barium and bismuth, and thus would be expected to be affected more by scattering from argon atoms than the other elements. Again we could argue that potassium is ejected predominantly as heavy cluster molecules, but only additional experiments can show whether this suggestion has any validity. In any case, our results indicate that an increase in relative potassium concentration may contribute significantly to the improvement of Ba-K-Bi-O films deposited with high argon background pressure. Investigation of film composition in 100 mT oxygen showed that oxygen has the same qualitative effect on composition, but a detailed analysis was not carried out.

If a true steady state is reached during target conditioning, the sum of material ejected over all angles should have the same composition as the bulk target. Our data for Y-Ba-Cu-O are consistent with this condition.[9] In particular, at a 9 cm target-substrate distance and 40 mTorr oxygen background, the Y-Ba-Cu-O film composition duplicates that of the target over all angles investigated. For the case of Ba-K-Bi-O, however, the potassium concentration falls well below that of the target. This effect is not well understood, but may be a sticking-coefficient effect, particularly considering the high vapor pressure of potassium. The barium to bismuth concentration is also low in these films, but to a proportionally smaller extent.

V1. SUMMARY

We have shown that target conditioning, gas pressure, and target-substrate distance have significant effects on film composition in pulsed-laser deposition of complex oxides. Further work in this area is needed, both to clarify the processes affecting composition in these films and to understand the effects of film composition on electrical properties and morphology. Nonetheless, it is hoped that the present results will aid in the optimization of superconducting oxide thin films.

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FIGURE CAPTIONS

1. Ratios of elements in film versus degree of target conditioning for Ba-K-Bi-O deposited in vacuum at ambient temperature with 1,1 J/cm^2 and a target-substrate distance of 5.5 cm. 0: Ba/Bi, ■: K/Ba, A: K/Bi. Dashed lines represent the target composition.
2. Ratios of elements in film versus oxygen pressure for Y-Ba-Cu-O deposited at ambient temperature at a target-substrate distance of 6 cm with fluence = 1.1 J/cm^2. O: Cu/Y, A: Ba/Y, ❑ : Cu/Ba. Dashed lines represent the target composition.
3. Ratios of elements in film versus target-substrate distance for Y-Ba-Cu-O deposited at ambient temperature in 200 mTorr oxygen with fluence = 1.1 J/cm^2. O: Cu/Y, **A:** Ba/Y, ❑ I: Cu/Ba. Dashed lines represent the target composition.
4. Bars and shaded area show region of pressure-distance space where Y-Ba-Cu-O film metal composition in thickest region of film is within **10°/0** that of the target. Oxygen stoichiometry is not reflected in this diagram. With high oxygen pressures and large distances, films are copper and barium depleted. Data points (0) are from Ref. 12, and indicate points of optimal film electrical characteristics for films on MgO substrates deposited at 680° C.
5. Ratios of elements in film vs. horizontal position on substrate (parallel to long axis of laser spot) for Ba-K-Bi-O deposited at ambient temperature in vacuum with fluence = 1 J/cm^2 and a target-substrate distance of 6 cm. O: Ba/Bi, ■ : K/Ba, A: K/Eli. Dashed lines represent the target composition. The position origin is defined by the peak in the thickness distribution.
6. Ratios of elements in film vs. horizontal position on substrate (parallel to long axis of laser spot) for Ba-K-Bi-O deposited at ambient temperature in 1 Torr argon with fluence = 1 J/cm^2 and a target-substrate distance of 6 cm. ●: Ba/Bi, D: K/Ba, A: K/Bi. Dashed lines represent the target composition. The position origin is defined by the peak in the thickness distribution.

TABLE CAPTIONS

1. Melting and boiling temperature of target elements and their common oxides.[10]

|

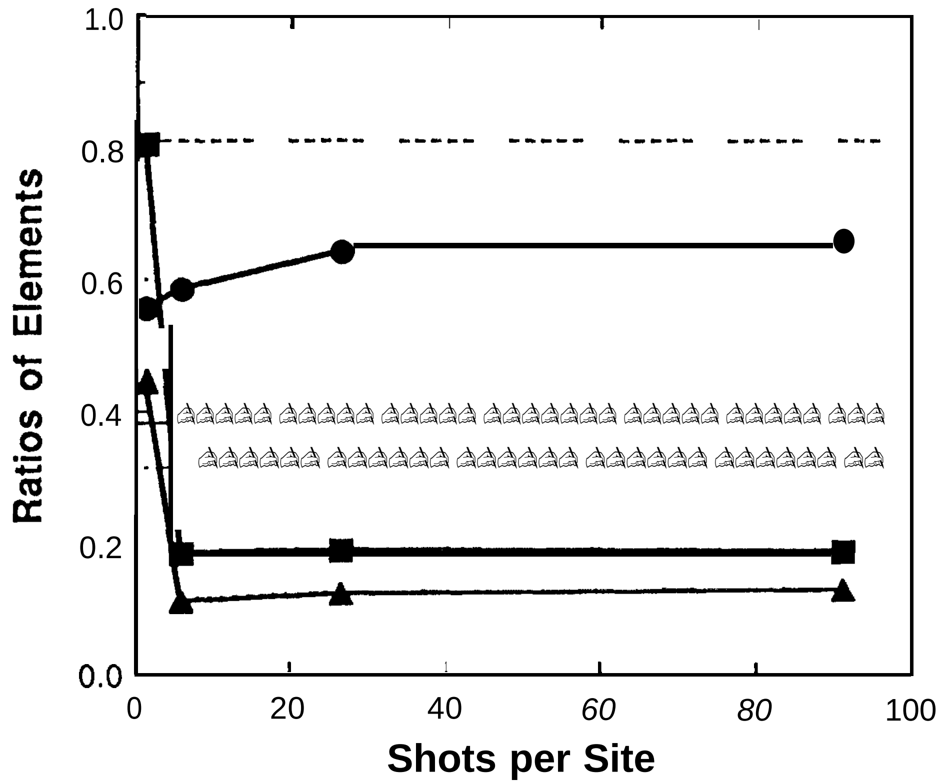

1.0
0.8
0.6
0.4
0.2
0.0
Ratios of Elements
0
20
40
60
80
100
Shots per Site

Fig. 1

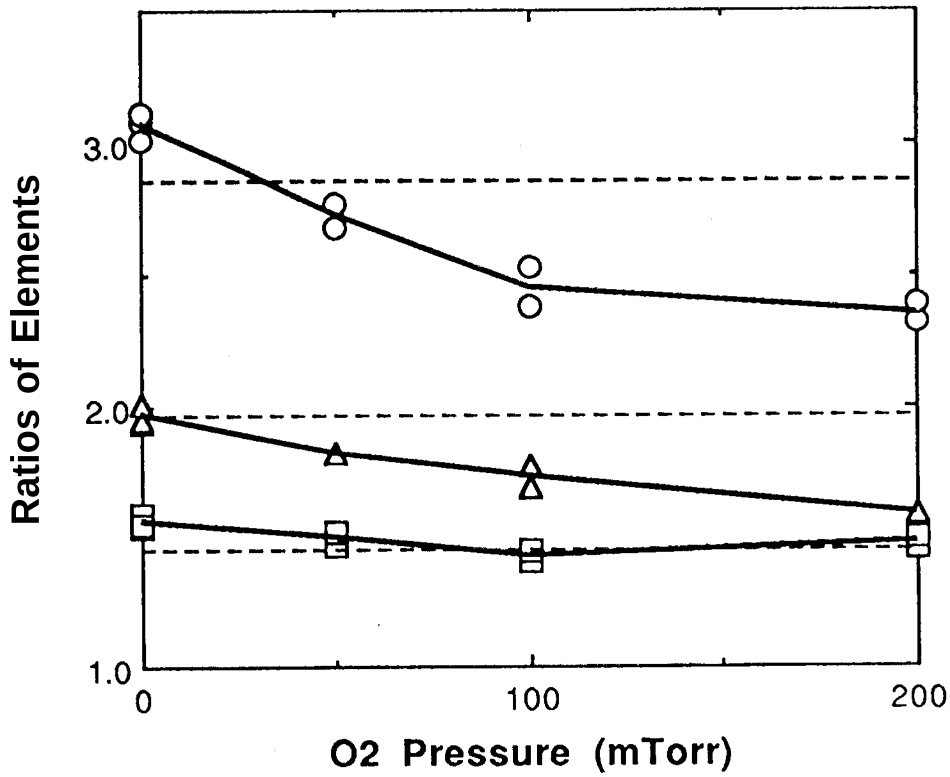
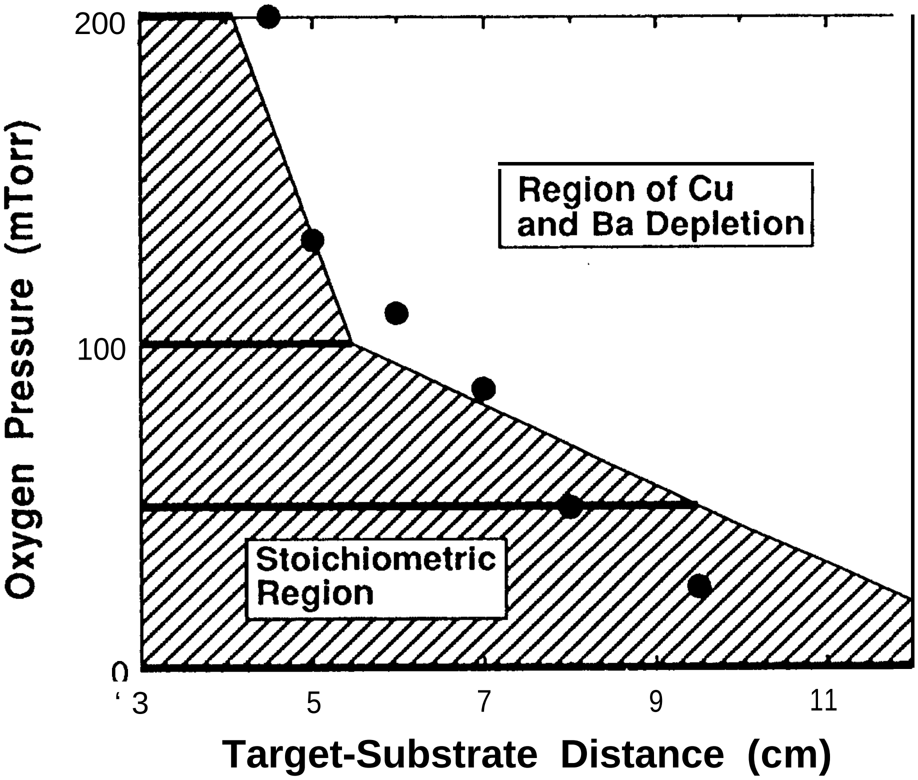
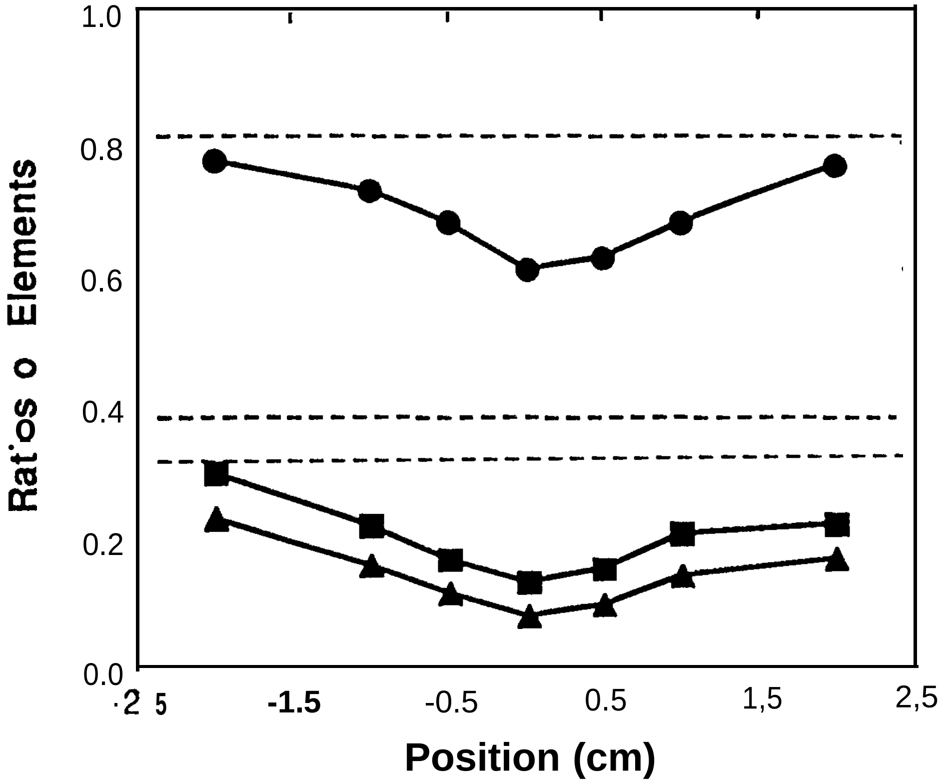


Fig 2



200
100
0
3
5
7
9
11
Oxygen Pressure (mTorr)
Target-Substrate Distance (cm)
Region of Cu
and Ba Depletion
Stoichiometric
Region

Fig. 4



F.g. 5

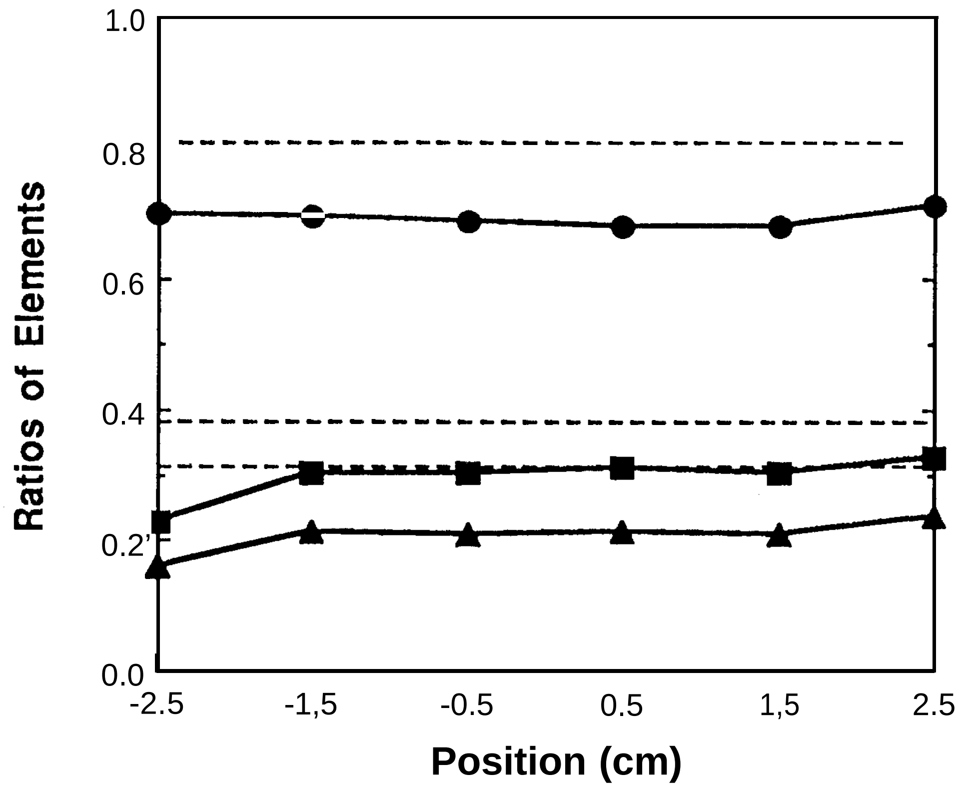

1.0
0.8
0.6
0.4
0.2
0.0
Ratios of Elements
-2.5
-1,5
-0.5
0.5
1,5
2.5
Position (cm)

Fig. 6

Material	Melting Temperature (°C)	Boiling Temperature (“C)
Ba	729	1805
BaO	1918	≈2000
Bi	271	1564
Bi_2O_3	≈825	1890 (?)
Cu	1085	2563
Cu_2O	1235	decomposes at 1800
K	64	759
K_20	decomposes at 350	----
Y	1522	3338
Y_2O_3	2410	----

Table 1