Pramāṇa - J. Phys., Vol. 34, No. 4, April 1990, pp. L377–L381. © Printed in India.

Detection limits of high temperature superconducting materials on various substrates by energy dispersive X-ray fluorescence and proton induced X-ray emission methods

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MS received 22 November 1989; revised 3 February 1990

Abstract. Application of energy dispersive X-ray fluorescence (EDXRF) and proton induced X-ray emission (PIXE) methods has been demonstrated for determining the elemental composition of thin film superconducting materials. The results of analysis carried out by EDXRF method have been compared with those obtained by PIXE method. Thin films of $YBa_2Cu_3O_7$ superconducting material were deposited on various substrates such as thin mylar sheet and thick substrates of $SrTiO_3$, MgO and Al_2O_3. In thin backing the minimum detection limits obtained for Cu, Y, Ba by the PIXE method are 20 ng, 70 ng and 800 ng respectively and the corresponding values by the EDXRF method are 3000 ng, 600 ng and 1000 ng. Detection limits for samples on thick backings deteriorated to a large extent by both methods.

Keywords. High temperature superconductivity; $YBa_2Cu_3O_7$; thin film deposition; substrates: EDXRF analysis; PIXE analysis; minimum detection limits.

PACS No. 73·60

The development of high temperature superconducting materials in recent years evoked interest in the formation of thin film superconductors for a variety of applications. To optimize various parameters involved in the evaporation method to obtain the composition of the original material with superconducting properties it becomes necessary to choose a method for rapid characterization of the composition of the thin film deposited on any given substrate. A number of methods such as Rutherford backscattering (Dijjkamp *et al* 1987) and X-ray photoelectron spectroscopy (Jin *et al* 1987) have been employed to characterize thin films of the deposited superconducting materials. EDXRF method has been widely employed (Gianelos 1974; Stine and Leidl 1974; Laguitton 1977; Huang and Parush 1979 and Lal and Choudhury 1987) for a rapid non-destructive determination of the elemental composition of any material. This method is particularly suitable for analysis of thin films down to elemental thickness of the level of a few angstroms. Earlier we have reported (Lal and Choudhury 1988) the application of the EDXRF method for monitoring the composition of the films of $YBa_2Cu_3O_7$ superconducting material deposited by laser evaporation. In the present work we have made use of both EDXRF and PIXE methods for monitoring of the thin film composition of $YBa_2Cu_3O_7$ using various substrates and evaluated application of these methods with regard to the level of detection of the elements present in thin films using both

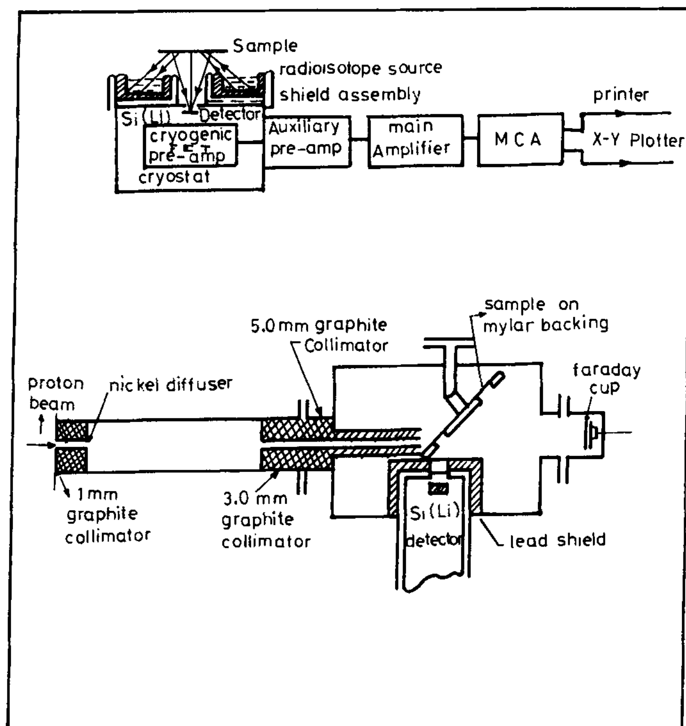

Figure 1. Schematic arrangement of Si (Li) detector X-ray system employing (a) photon excitation from radioisotope sources. (b) proton beam from Van de Graaff accelerator.

thin and thick substrates. The thick substrates used were $SrTiO_3$, MgO and Al_2O_3 in the form of 5 mm thick disks and the thin substrate used was 6 μm mylar sheet.

The EDXRF set up employed for monitoring these thin film deposits comprises of a high resolution lithium drifted silicon, Si (Li) detector along with radioisotope sources of ^{109}Cd (2·0 mc) and ^{241}Am (100 mc) for excitation of characteristic X-rays. The sources are mounted in an annular geometry as shown in figure 1(a). The signals of the X-rays detected by Si (Li) detector are amplified by high resolution electronics and the spectrum is stored in the multi-channel analyzer. Figure 1(b) shows the PIXE set up (Lal *et al* 1989) at the 5·5 MeV Van de Graaff accelerator, Trombay. The beam from the accelerator is diffused by passing through a thin Ni foil located 0·5 m from the sample target. The diffused beam passes through a set of collimators before striking the sample over a well-defined area. The X-rays from the sample are detected at 90° with respect to the beam by a Si (Li) detector which is shielded against the proton induced γ-ray background from all sides except the Be window which interfaces the sample and the detector.

Figures 2 and 3 show the X-ray spectra of the high T_c superconducting material deposited on thin mylar backing obtained with the EDXRF and PIXE methods. In EDXRF method both ^{109}Cd and ^{241}Am were used to excite the samples. In PIXE method, proton beam of 2·5 MeV was used from the Van de Graaff accelerator. The sample of 500 μg/cm^2 thickness was deposited by micropippeting the $YBa_2Cu_3O_7$ solution. From the observed intensities of the K X-rays of all the elements, the minimum detection limits (MDL) were evaluated. The MDL of an element was

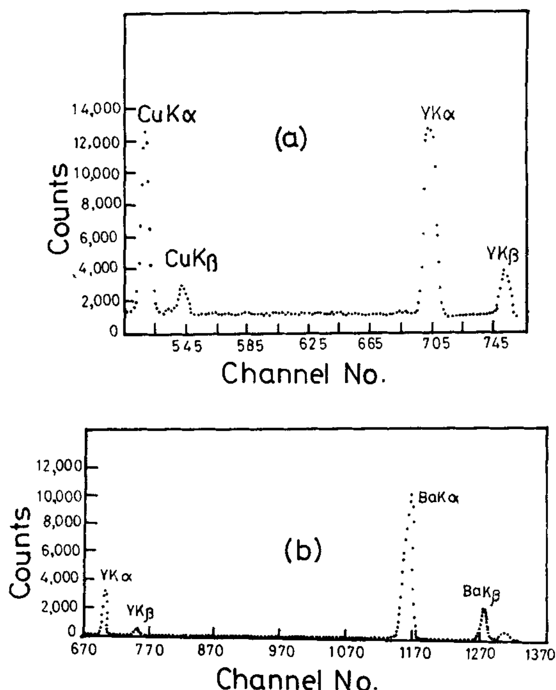

Figure 2. EDXRF spectra of thin superconducting material $YBa_2Cu_3O_7$ on mylar backing excited by (a) ^{109}Cd (b) ^{241}Am.

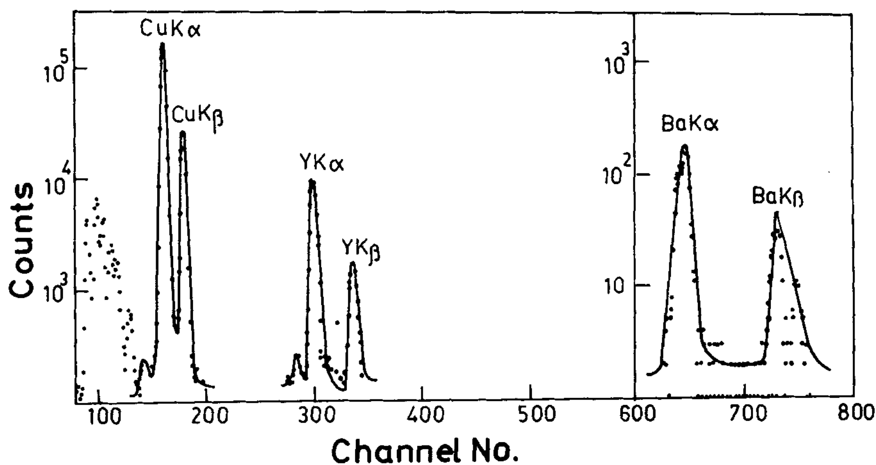

Figure 3. PIXE spectrum of thin superconducting materials $YBa_2Cu_3O_7$ on mylar backing.

calculated as the equivalent of the element concentration corresponding to the total counts of $2\sqrt{N_B}$, where N_B is the background counts under the X-ray peak. Similar analysis was carried out for samples deposited on thick substrates. The detection limits deteriorated to a large extent for the thick substrates. However in $SrTiO_3$ substrate, the K X-rays of Sr were found to heavily interfere with the Y K X-rays (figure 4). The results on detection limits for substrates of mylar, MgO, Al_2O_3 are discussed below.

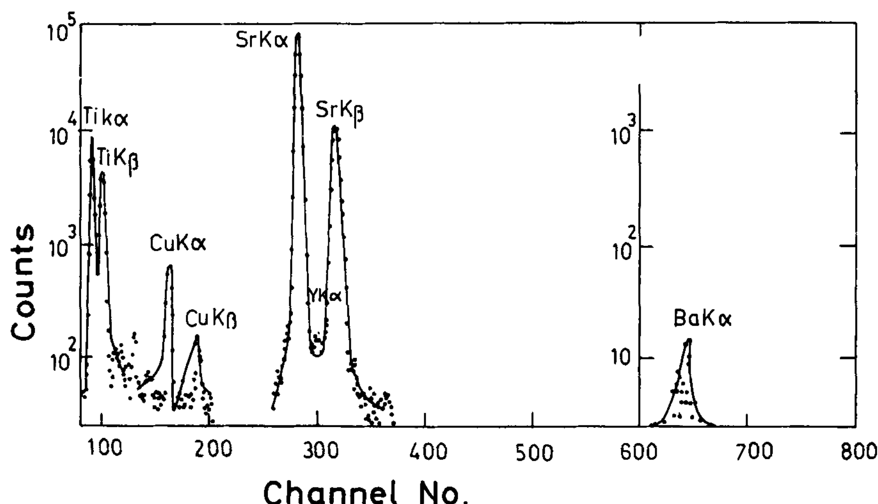

Figure 4. PIXE spectrum of superconducting material $YBa_2Cu_3O_7$ on thick substrate of $SrTiO_3$.

To achieve good detection limits in EDXRF analysis, it is essential to employ suitable exciting source energies for X-ray lines to be excited and also to minimize the background under the X-ray peak of the elements to be measured. Better detection limits are obtained by employing the excitation source energy closer to the absorption edge of the element and for this reason ^{109}Cd is used for Cu and Y and ^{241}Am for Y and Ba. In this way, the Y K_α counts are used to normalize the spectra to determine the relative intensities of Cu and Ba. The background in EDXRF arises mainly due to the tailing of incomplete charge collection of the scattered photons.

PIXE method offers better detection limits for lower atomic number elements because of much higher excitation cross section and easier availability of large flux of proton beam from the accelerator. Even though in the lower energy region the bremsstrahlung background due to electrons emitted in charge particle interaction is predominantly high, the sensitivity of detection by PIXE method is superior to EDXRF method.

Table 1 gives the MDL for Cu, Y, Ba by EDXRF and PIXE methods using thin and thick substrates. For thin substrates, PIXE offers better detection limits for all the three elements. In thick substrates though performance of PIXE method deteriorates by an order of magnitude, it is still better for Cu and Y but not for Ba. The detection limits for thick substrates given in table 1 correspond to MgO and Al_2O_3 substrates. In $SrTiO_3$ there was heavy interference of Sr K X-rays with the Y K X-rays obscuring their proper detection. For an element to be detected, its concentration has to be higher than the MDL as quoted above. The error in the determination of the concentration of an element will however, depend on the counting statistics of the K X-ray peak including the background under it.

In summary we have applied the PIXE and EDXRF methods for characterizing the composition of elements of high T_c superconducting films on various substrates. As a typical case the material of $YBa_2Cu_3O_7$ was used in the present analysis. It was observed that in general PIXE gives better detection limits than EDXRF except for the measurement of Ba on thick substrates. Depending upon the elemental thickness

Table 1.

Substrate	Elements	Minimum detection limits ($\mu g/cm^2$)	
		EDXRF	PIXE
Thin (Mylar)	Cu	3·0	0·02
	Y	0·6	0·07
	Ba	1·0	0·8
Thick (Al_2O_3, MgO)	Cu	10·0	0·2
	Y	7·0	0·5
	Ba	0·7	4·0

required for a particular application both EDXRF and PIXE methods can be employed. The present analysis can also be extended to other high T_c materials.

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