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Oxygen determination in materials by $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction

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ABSTRACT

The paper presents a proton induced γ-ray emission method based on $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction to determine bulk oxygen in materials. The determination involves the measurement of 5.27 MeV γ-rays emitted following the de-excitation of ^{15}N nuclei. A description of the energetics of the reaction is given to provide an insight into the origin of 5.27 MeV γ-rays. In addition, thick target γ-ray yields and the limits of detection are measured to ascertain the analytical potential of the reaction. The thick-target γ-ray yields are measured with a high purity germanium detector and a bismuth germanate detector at 0° as well as 90° angles in 3.0–4.2 MeV proton energy region. The best limit of detection of about 1.3 at.% is achieved at 4.2 MeV proton energy for measurements at 0° as well 90° angles with the bismuth germanate detector while the uncertainty in quantitative analysis is <8%. The reaction has a probing depth of several tens of microns. Interferences can arise from fluorine due to the occurrence of $^{19}F(p,\alpha\gamma)^{16}O$ reaction that emits 6–7 MeV γ-rays. The analytical potential of the methodology is demonstrated by determining oxygen in several oxide as well as non-oxide materials.

1. Introduction

The determination of oxygen in materials is a difficult and challenging task. Ion beam analysis (IBA) provides several methodologies for the determination of oxygen in materials. Cohen and Rose published a comprehensive review on the subject in early nineties that remains relevant even to-day [1]. α-Rutherford backscattering spectrometry (α-RBS) and 3.05 MeV $^{16}O(\alpha,\alpha)^{16}O$ resonant scattering are the methods of choice for detecting and depth profiling oxygen in thin films. However, the limitations of these methods in analysing films on heavier substrates and thick targets with high Z constituent(s) are well known [2]. These problems are alleviated by $^{16}O(p,p)^{16}O$ elastic scattering, albeit only to some extent, due to its comparatively better detection sensitivity and higher probing depth [3]. The method has been used for analysing several oxygen bearing compounds including thick Y–Ba–Cu–O superconductors [4].

So far as nuclear reaction analysis (NRA) is concerned, $^{16}O(d,p)^{17}O$, $^{16}O(^3He,p)^{18}F$ and $^{18}O(p,\alpha)^{15}N$ are some of the prominent reactions that are often employed for the determination of oxygen [1]. These reactions are, in fact, useful for probing only thin films or, at the best, the top few microns of thick targets since the measurements entail the detection of particle ejectiles. Particle induced γ-ray emission technique (PIGE), similar to NRA, is sensitive to low Z elements but, in contrast, offers higher (several tens of microns) probing depth. As a result, it has been extensively utilised for the determination of Li, B, F and several other elements in a variety of bulk matrices [5–8]. Oxygen can also be determined by PIGE by means of $^{16}O(p,\gamma)^{17}F$, $^{17}O(p,p\gamma)^{17}O$ or $^{18}O(p,p\gamma)^{18}O$ nuclear reactions that emit 495, 871 and 1982 keV characteristic γ-rays respectively [9]. Use can also be made of $^{16}O(p,p\gamma)^{16}O$ nuclear reaction wherein the measurement is based on the detection of 6–7 MeV γ-rays. However the reaction occurs above 6.8 MeV proton energy which precludes the use of low energy accelerators [10,11]. Furthermore, the presence of fluorine in the specimens can cause severe interference due to the occurrence of $^{19}F(p,\alpha\gamma)^{16}O$ nuclear reaction. Besides the proton induced reactions, deuteron induced reactions, for example, $^{16}O(d,p\gamma)^{17}O$ reaction (E_γ = 871 keV) can also be applied for such an analysis. Vickridge et al. have used this reaction for high precision oxygen determination in high temperature superconductors [12,13].

Through this communication we report a PIGE method for the determination of bulk oxygen in materials. The method is based on $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction at 3.2 MeV or higher proton energies and involves the measurement of 5.27 MeV γ-rays, characteristic of the reaction. It is important to note that while $^{18}O(p,\alpha)^{15}N$ nuclear reaction, as stated earlier, is often employed for the analysis, depth profiling in particular, of oxygen by way of α-detection, there is no previous report, to the best of our knowledge, on the

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application of $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction for oxygen determination [14,15]. It prompted us to undertake the present study wherein we describe the origin of 5.27 MeV γ-rays, measure their thick target yields in 3.0–4.2 MeV proton energy region and assess the analytical efficacy of the method by determining the content of oxygen in some oxide and non-oxide materials.

2. Experimental details

The oxide powders were homogeneously mixed with 25 wt.% high purity graphite powder and the resulting mixtures were pressed into 20 mm diameter discs which served as targets. A similarly made disc containing calcium carbonate (75 wt.%) and high purity graphite (25 wt.%) was used for the determination of thick-target yields and also as a standard for quantification. All compounds were of analytical grade and contained oxygen in natural isotopic proportions.

The targets, mounted on a sample manipulator, were irradiated with a well collimated 2.5–4.2 MeV proton beam (diameter: ~5 mm, current: 2–50 nA) obtained from the 3 MV Tandetron (High Voltage Engineering Europa) at NCCCM, Hyderabad in a typical scattering chamber maintained at $\sim 1 \times 10^{-5}$ torr vacuum. A negatively biased (−700 V) ring electrode was used to suppress the secondary electrons. The prompt γ-rays emitted from the nuclear reactions were measured with a high purity Ge detector (HPGe) (Bruker Baltic, diameter: 5.9 cm, depth: 6.4 cm, efficiency: 36%, energy resolution: 1.78 keV at 1332 keV) and also with a 7.6 cm × 7.6 cm bismuth germanate detector (BGO) (Scionix, Holland, energy resolution: ~10% at 1332 keV) placed in air outside the scattering chamber in a 2.5 cm thick cylindrical lead shield. The measurements were carried out at 0° and 90° angles with respect to the direction of the beam. The experimental conditions were identical for the samples and the standard. The spectra were acquired in 4K channels using a 8K MCA and were calibrated using 356 keV ^{133}Ba, 661.7 keV ^{137}Cs, 1332.5 keV ^{60}Co and 2614.5 keV ^{208}Tl γ-rays, and 4.44 MeV and 6.13 MeV γ-rays from $^{15}N(p,\alpha\gamma)^{12}C$ and $^{19}F(p,\alpha\gamma)^{16}O$ nuclear reactions respectively. The data were acquired for integrated beam charges sufficient to produce statistically significant counts-per-channel.

3. Results and discussion

3.1. Origin of 5.27 MeV γ-rays

A high energy segment of the prompt γ-ray spectrum recorded by HPGe detector while bombarding the $CaCO_3$ target (standard) with 4.0 MeV proton beam is shown in Fig. 1(a). It consists of a prominent peak at 5.27 MeV which is a full energy peak and two other strong peaks at about 4.7 and 4.2 MeV which are the single and double escape peaks respectively. Similar spectra were recorded on irradiating the target with 3.0–4.2 MeV proton beam but the one obtained using 2.5 MeV proton was devoid of these peaks. The peak at 5.27 MeV is attributed to the γ-rays emitted from $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction and as is evident from the energy level scheme of ^{15}N nucleus depicted in Fig. 2, it corresponds to the transition from the first excited state ($J = 5/2^+$) to the ground state ($J = 1/2^-$) of the nucleus [16]. The excitation to various energy levels, in general, depends on the excitation energy of the products which is determined largely by the Q-value of the reaction and incident beam energy. The diagram in Fig. 3 summaries the energetics of the present reaction that proceeds with the formation of ^{19}F compound nucleus. It clearly shows that at 4.0 MeV proton energy, the energetics of the reaction is favourable for populating the first excited state of ^{15}N nucleus.

Expressing more explicitly, $^{18}O(p,\alpha\gamma)^{15}N$ reaction that is characterised by a Q value of +3.98 MeV and Coulomb barrier of 3.18 MeV for the entry channel, can be assumed to take place in two successive steps i.e. (i) the formation the compound nucleus (^{19}F) via $^{1}H + {}^{18}O \rightarrow {}^{19}F$ reaction and (ii) the decay of the compound nucleus into products via $^{19}F \rightarrow {}^{4}He + {}^{15}N$ reaction. The excitation energy (E_x) of a compound nucleus formed in a nuclear reaction is given by the expression

$$E_x = \frac{M_2}{M_1 + M_2} E_0 + Q \quad (1)$$

where E_0 is the incident beam energy and M_1 and M_2 are the masses of the projectile and target nuclei respectively. Accordingly, the E_x of ^{19}F nucleus at $E_0 = 4.0$ MeV is 11.7835 MeV with the Q value of the first step being +7.994 MeV. Meanwhile the Q value of the second step is −4.0138 MeV. Hence the total excitation energy of the products ($^{4}He + {}^{15}N$) is 7.7697 MeV. The emission of α-particles from the compound nucleus may leave the residual ^{15}N nucleus in the ground state or in the first/second excited states. In the former condition, α-particles with about 7.2 MeV will be emitted in the direction of the beam, while the later will cause the emission of 5.27 MeV or higher energy γ-rays accompanied with about 2.0 MeV α-particles. These considerations suggest that the total excitation energy of the products should at least be about 5.27 MeV for populating the first excited state of the ^{15}N nucleus. In other words, the emission of 5.27 MeV γ-ray is possible only above about 1.5 MeV proton energy. But it should not be construed as the minimum proton energy required for initiating $^{18}O(p,\alpha\gamma)^{15}N$ nuclear reaction since the emitted α-particles must have sufficient energy to cross the Coulomb barrier for the exit channel that measures about 5.0 MeV. Simple calculations show that for cases wherein (a) the incident energy is about 1.0 MeV or higher and (b) the residual ^{15}N nucleus is left directly in the ground state, the emitted α-particles have sufficient energies (i.e. $\geqslant$5.0 MeV) to surmount the Coulomb barrier. But for proton energies used presently, the α-particles have $\leqslant$2.5 MeV energy if the residual ^{15}N nucleus is left in the first excited state which is rather inadequate for surmounting the Coulomb barrier of 5 MeV height. Therefore it can be surmised that α-particles accompanying the 5.27 MeV γ-rays penetrate the Coulomb barrier and not surmount it during emission. Similar situation prevails while depth profiling oxygen by the resonance at 163 or 629 keV in $^{18}O(p,\alpha)^{15}N$ reaction.

It is worthwhile mentioning that ^{15}N nucleus can also be formed as a result of $^{16}O(p,2p)^{15}N$ nuclear reaction. The Q value of the reaction is −12.12 MeV and thus it cannot be initiated by the proton beam energies (2.5–4.2 MeV) presently employed. It is equally important to note that 5.27 MeV γ-rays are emitted from the de-excitation of ^{15}O nucleus as well. However, the reaction $^{16}O(p,pn)^{15}O$ that can lead to its formation too has a large negative Q (−15.663 MeV) value. Meanwhile $^{19}F^*$ nucleus, formed as result of $^{18}O(p,\gamma)^{19}F$ reaction, represents yet another possible source of γ-rays of about 5.3 MeV energy and therefore it is instructive to examine its likely contribution within the framework of present experimental conditions. A perusal of the energy level scheme of ^{19}F shows that $^{19}F^*$ nuclei de-excite to ground state through the emission of 2.58, 5.210, 5.28 and 6.3 MeV γ-rays [16]. However, except 5.27 MeV γ-rays, none of these were observed in the spectra recorded using 2.5–4.2 MeV protons. Thus it can be inferred that the 5.27 MeV γ-rays observed presently do not have their origin in $^{18}O(p,\gamma)^{19}F$ reaction. This inference gets credence from the fact that there is no perceptible signal of 5.27 MeV γ-rays in spectra recorded at $E_p = 2.5$ MeV which is unlikely had $^{18}O(p,\gamma)^{19}F$ reaction been contributing considering the fact that its Q value is as high as +7.964 MeV. The absence of 5.27 MeV γ-rays at $E_p = 2.5$ MeV, in fact, points to the non-occurrence of $^{18}O(p,\alpha\gamma)^{15}N$ reaction. This is apparently due to the reason that the α-particles have too less