Microchemical Journal 130 (2017) 27–32

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Review article

Chemical environment change analysis on *L* X-ray emission spectra of some lanthanide compounds

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ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 29 July 2016
Accepted 29 July 2016
Available online 03 August 2016

Keywords:
Line position
Line width
Chemical shift
Chemical environment changes
Intensity ratio
XRF

ABSTRACT

$L\alpha$, $L\beta_1$ and $L\gamma$ emission line shapes and intensity ratio values have been measured for the elements Nd, Sm, Gd and Tb and for a large number of their compounds. The measurements were done using the EDXRF system, where special attention was given to minimizing the errors in various corrections such as self absorption and detector efficiency. All the lines were excited using a 100 mCi ^{241}Am annular radioactive source. The energy shifts and $L\alpha/L\beta_1$ and $L\alpha/L\gamma$ intensity ratio values of X-rays were examined for chemical effect. The measured $L\alpha/L\beta_1$ and $L\alpha/L\gamma$ intensity ratios were compared with the experimental and theoretical data in literature.

Contents

1. Introduction

It is well known that low-energy X-ray spectra such as *L* X-ray spectra of transition metals and their compounds and *K* X-ray spectra of light elements and their compounds are significantly influenced by the chemical environment [1–5]. In recent years, many publications have dealt with calculations or measurements of the chemical speciation of the elements which can be attributed to the great alterations in the chemical and biological properties of the elements depending on their oxidation state, the type of chemical bonds etc. [6–8]. Brunner et al. [9] reported deviations up to 5% in the $K\beta/K\alpha$ values for compounds of 3d shell elements when compared with the pure elements. In the discussion of chemical effects, they emphasized the screening of 3p electrons by a varying 3d valence charge. They proposed a simple model in which the sensitivity of the $K\beta/K\alpha$ ratio on the construction of the X-ray emitting atom was predicted. Bissinger et al. [10] studied the *K* and *L* X ray spectra of Au bombarded with 12–50 MeV oxygen ions and observed *L* X-ray cross-sections, intensity ratios and centroid energy shifts.

Iihara et al. [11] measured chemical effects on *L* X-ray intensity ratios for some Nb and Mo compounds. When the measured $L\gamma_1/L\beta_1$ ratios were plotted as a function of the effective number of 4d electrons, they found that the experimental data were almost in a straight line. Rao et al. [12] measured the relative intensities of *L* shell X-rays I(Ll)/I($L\alpha$), I($L\beta$)/I($L\alpha$), I($L\gamma$)/I($L\alpha$) for Au and Pb at the excitation energies 36.82, 43.95, 48.60, 50.20 and 53.50 keV with a HP Ge(Li). Earlier studies on $L\alpha/Ll$ ratios were made using different types of excitation and a Si(Li) detector system. Raghavaiah et al. [13] have studied the X-ray emission spectra for 19 elements covering the region 55≤Z≤80 using a 30 mCi

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http://dx.doi.org/10.1016/j.microc.2016.07.025
0026-265X/

^{238}Pu source which emits 14-17 keV X-rays. Öz et al. [14] determined the $L\alpha/L\beta$, $L\alpha/L\gamma$, $L\alpha/Ll$, $Ll/L\gamma$ and $L\beta/L\gamma$ intensity ratios for three different cases. In the first case, the excitation energy (E) is less than the binding energy of the L_2 subshell but sufficient to excite the L_3 subshell. In the second case, E is less than the binding energy of the L_1 subshell but sufficient to excite the L_2 subshell. In the third case, E is less than the binding energy of the K shell but sufficient to excite the L_1 subshell. İsmail and Malhi [15] report the L shell X-ray relative intensities for Sm, Eu, Lu, Hf, Os, Pt, Tl, Pb and Bi using 20.48 keV Rh tube.

The chemical shift of the emission line, similar to asymmetry index and full width is also an important factor in the characterization of the materials. Porikli et al. [16] have used an energy dispersive X-ray spectrometry to study the characteristic quantities such as position of line maxima, full widths at half maximum (FWHM) and intensity ratio values of pure La, Ce, Pr and their compounds. Furthermore, Durdağı et al. [17] studied the X-ray emission lines of the $L\alpha$, $L\beta$, $L\gamma$ and Ll groups in elements La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er to examine the influence of 0.6 T and 1.2 T external magnetic field. They determined the $L\alpha/L\beta$ and $L\alpha/L\gamma$ ratio in 4f elements as a function of the target atomic number.

The chemical environment has a strong effect on the transitions originated in valence band and its influence could clearly be observed in the emission spectrum structure. We presented here results of determination of the $L\alpha$, $L\beta_1$ and $L\gamma$ emission line shapes of the lanthanide metals Neodymium, Samarium, Gadolinium and Terbium. We have been working on the elemental analysis of different kinds of materials using the energy dispersive X-ray fluorescence (EDXRF) system. A commercial ^{241}Am radioactive source was used with an activity 100 mCi. The results were compared with those published before and the possible reason of the chemical shift was discussed as well.

2. Sample preparation and experimental set up

Thirty elements (Nd, $NdBr_3$, $Nd_2(CO_3)_3.XH_2O$, $NdCl_3$, $Nd(NO_3)_3.6H_2O$, $Nd_2(C_2O_4)_3.XH_2O$, Nd_2O_3, $Nd_2(SO_4)_3$, Sm, $SmBr_3$, $Sm_2(CO_3)_3.XH_2O$, $SmCl_3$, SmF_3, SmI_3, Sm_2O_3, $Sm_2(SO_4)_3$, Gd, $GdBr_3$, $Gd_2(CO_3)_3.XH_2O$, $GdCl_3.6H_2O$, GdF_3, GdI_3, $Gd(NO_3)_3.6H_2O$, Gd_2O_3, $Gd_2(SO_4)_3$, Tb, $TbBr_3$, $TbCl_3$, TbF_3, Tb_4O_7) with purity better than 99% were selected and small amounts of the pure element powders were compressed into solid thin pellets of 13 mm diameter by using a 10 ton manual hydraulic press. The surface density (thickness of the target) of the prepared samples ranged between 10 and 20 mgcm^{-2}.

Gama rays of 59.54 keV from 100 mCi ^{241}Am point source were used to ionize the target atoms and the emitted X-rays were detected by a 12.5 mm^2 × 3mm thick Canberra Si(Li) detector having a 0.025 mm thick beryllium window. The resolution of the Si(Li) detector was 155 eV (full width at half maximum) for 5.9 keV X-ray peak. The experimental system consisted of a Si(Li) detector with a low-noise FET-type cooled preamplifier, multichannel analyzer and computer. The structure in computer enabled data acquisition, data storage, peak stripping, background subtraction and determination of the net intensities of each X-ray line with the help of suitable software programs. Data collections were done in a long time period in each case in order to ensure good statistical accuracies.

The experimental arrangement and the geometry used in the present study are shown in Fig. 1. The aim of obtaining accurate results suggested the choice of simple geometrical arrangement, i.e., both the source and the detector equipped with collimators. The axes of these collimators, i.e., the axes of the incident and observed beams made the same angle with the normal to the scattering sample. Moreover, the distance between the scatterer and the detector was equal in practice and very large in comparison with the dimension of the scattering surface seen by the detector and thus this surface practically belonged to a constant scattering angle surface. The present system considerably reduced the scattering and background effects and improved the monochromaticity. Details of the experimental arrangement can be found in the earlier study by Porikli et al. [18].

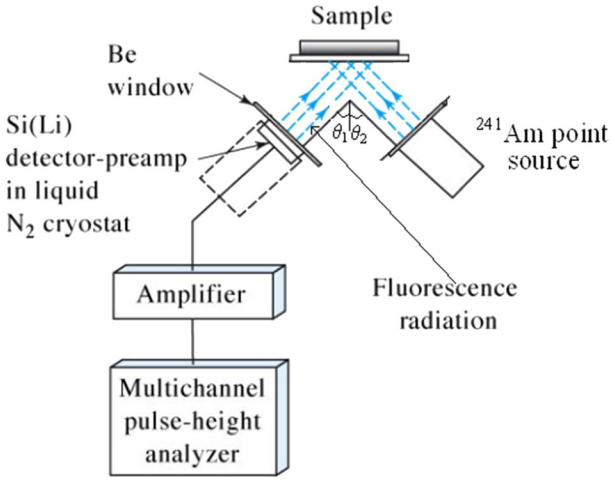

Fig. 1. The experimental arrangement and the geometry.

The spectra were analyzed by using Origin software program with least-squares fit method. A Gaussian representation was selected. The net peak areas were separated by fitting the measured spectra with multi-Gaussian function, linear background and the uncertainty in the area of the Li X-ray peak was evaluated by weighted method. The peaks due to $L\alpha$, $L\beta$ and $L\gamma$ group of lines were well separated and two examples of the fitted spectra are shown in Fig. 2. Measured numbers of counts are shown as solid black circles.

3. Data analysis

The experimental Li (i=l, α, β and γ) X-ray production cross-sections σ_{Li} were evaluated using the following relation:

$$\sigma_{Li} = \frac{N_{Li}}{I_0 G \varepsilon_{Li} \beta t} \quad (1)$$

where N_{Li} is the number of counts per unit time under the photo-peak corresponding to L_i X-ray of the element, the product I_0G is the intensity of the exciting radiation falling on the area of the target sample visible to the detector, ε_{Li} is the efficiency of the detector at the average L X-ray energy of the element, t is the mass per unit area of the element in

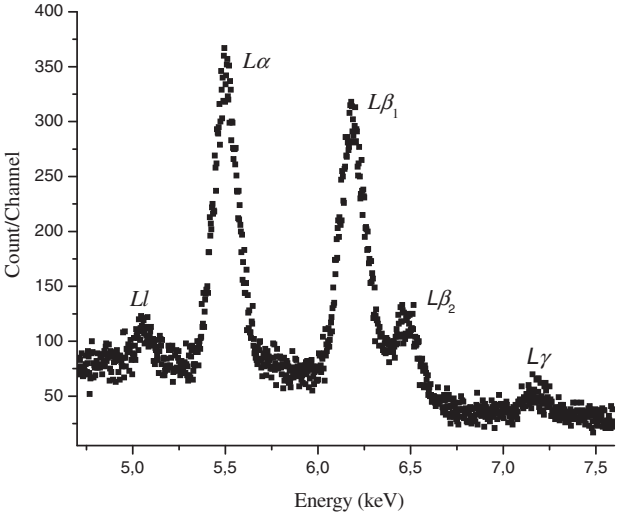

Fig. 2. Measured $L\alpha$, $L\beta_{1,2}$ and $L\gamma$ emission lines of Sm.