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NEUTRON - ACTIVATION DETERMINATION OF MICRO- AND MACROCOMPOSITION OF FERRITE AND SPINEL

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The instrumental neutron activation analysis for the determination of the macrocomponent of aluminium and magnesium in magnesium aluminium spinel is used. The elements of impurities in the natural and synthetic spinel are determined.. The techniques of the simultaneous determination of the main components Fe, Zn, Ni and Co in ferrite are elaborated.

1. INTRODUCTION

There is a large number of compounds that can be classified as spinel. Ceramics based on the magnesium-aluminium spinel are possible materials for fission reactors in order to take advantage of their special properties[1]. Spinel single crystals are used in integrated electronics[2]. Magnesium-aluminium spinel is known as a laser material during a long time[3-5]. Ferrite is the magnetic composition with general formula $xMe_aO_b \cdot yFe_2O_3$, when x and y denote relative abundance of metal oxides Me_aO_b (Me-metal ions) and Fe_2O_3. Depending on Me_aO_b and Fe_2O_3 ratio and Me-ion the ferrite has spinel, garnet , perovskite and magnetoplumbite structure. The electromagnetic characteristics of ferrite are connected with their chemical composition. Changing the percentage contents of the separate components in the process of manufacturing puts forward a question of the quantitative analysis of the mixture and finished products with the given accuracy. One of the methods satisfying these requirements is neutron-activation analysis. Present high γ-resolution gamma-spectrometers provide the instrumental version for the activation analysis, and thereby the accuracy and rate of analysis are improved. The method give a possibility to use after the analysis the same samples for the study of the radiation effects on the physical properties.

The aim of the present work is the development of: 1) the rapid method for the quantitative determination of the macrocomponent of aluminium and magnesium in the magnesium-aluminium spinel, 2) the determination of the elements of impurieties that influence the optical parameters of the spinel, as well as the simultaneous determination of Fe, Zn, Ni and Co and their unhomogeneity in ferrite with the different composition.

2. EXPERIMENTAL

2.1. ANALYSIS OF MAGNESIUM-ALUMINIUM SPINEL

2.1.1. Macrocomponents.

The synthetic spinel were grown by help of the Verneuil method, the manganese having been added to the mixture in the $MnCO_3$ salt form. Natural spinel crystals descent from the Ural and the Pamir mountains.

The samples of spinel with the mass of 15-25 mg are packed hermetically in the polyethylene envelopes. As standards specifically cleaned magnesium oxide (20 mg) and metallic aluminium (2-3 mg) are used. The samples and the standards are placed in the special polyethylene containers for irradiation.

The irradiation of the specimen was carried out in the horizontal experimental channel of the nuclear reactor of Salaspils, Latvia, by employing the pneumatic tube. The transport time to the reactor core is 2 s. The time of irradiation of the samples and standards - 30 s ($\Phi_{th} = 1.6 \times 10^{13}$ neutrons /cm^2. s). The time of cooling is - 15 min.

The γ-spectra were measured using the γ-spectrometer with Ge(Li) detector (35 cm^3) energy resolution of γ-lines 1333.5 keV ^{60}Co is 2.5 keV. For quantitative aluminium and magnesium determination is used γ- lines 1778 and 1014 keV.

2.1.2 MICROIMPURITIES

The spinel samples with the mass 100-400 mg are packed in high purity aluminum foil. As standards were used the synthetic multi-elements standards SSB-1, SSB-2, GSP-1 produced in the Institute of Physics, Tbilisi (Georgia). The samples have been put in the special aluminium container.

For the determination of the impurities the specimen were irradiated in the vertical experimental channel ($\Phi_{th} = 3.1 \times 10^{13}$ neutrons /cm^2 s) for 70 hours. After irradiation the samples were re-packed in the polyethylene envelopes for the measurement.

The proposed method permits to determine impurities with the detection limit (ppb): Cr-2, Sc-0.1, Mn-100, Fe-1000, Co-0.2, Ni-60, Eu-1 and Hf-4.

The γ- spectra were measured using the Ge detector (80.3 cm^3). The statistical accuracy is less than 2%, the reproducibility of results -- 5-7%.

2.2. FERRITE ANALYSIS

The investigated ferrite contain mainly iron, manganese, magnesium, zinc, calcium, nickel, cobalt and copper oxides in several combinations with the contents of different percentage. Before the irradiating the mixture is dried at temperature 120±5 °C., where if necessary the ferrite products are cut up. The experiments were conducted in three variants, for each of them choosing the corresponding method of analysis. The determination was made using:

1. The short-lived radionuclides ($T_{1/2}$<10min), t_{irr} =1 min;
2. The medium-lived radionuclides (2h<$T_{1/2}$<16h), t_{irr}=0,5 h;
3. The long-lived radionuclides ($T_{1/2}$>27 day) at t_{irr}=150 hours, depending on the properties of the nuclei and the total radioactivity of the analyzed samples.

3. RESULTS OF MEASUREMENTS.

The table 1 presents the results of the determination of the macrocomponent in the magnesium- aluminium spinels. The contents of impurities in the natural and the synthetic spinel are given in the table 2. The quantitative contents of main components in ferrite are presented in the table 3.

Table 1. The contents of the macrocomponents of $MgO{\cdot}nAl_2O_3$

Notation	Introduced	Obtained
MA 1:1	1:1	1:0.9
MA 1:1	1:1	1:1.5
MA 1:2	1:2	1:1.7
MA 1:2.8	1:2.8	1:2.5

Table 2. The concentration of the impurities in the spinel, mass %

Notation	Cr	Mn	Fe
Natural			
Black	$1.5x10^{-3}$	23	1.2
Pink	$2x10^{-3}$	2.9	0.31
Dark pink	$8.0x10^{-2}$	0.1	$3x10^{-2}$
Middle pink	$7.0x10^{-2}$	0.1	$6x10^{-2}$
Lilac	$9.8x10^{-5}$	0.02	1.31
Synthetic			
MA 1:1 Mn 0.1	$4.3x10^{-4}$	0.015	$1.2x10^{-2}$
MA 1:2 Mn 0.1	$2x10^{-4}$	0.04	$5.9x10^{-3}$
MA 1:2.5 Mn 0.1	$1x10^{-4}$	0.03	$1.4x10^{-2}$

Table 3. The contents of Fe, Zn, Ni and Co in ferrite, mass %.

Notation	Fe	Zn	Ni	Co	Other components
Mixture 1	41.0±0.5				Mg, Ca. Mn
Mixture 2	44.7±1.4	2.38±0.07			Mg, Mn
Ferrite 2	45.5±0.8	2.55±0.06			Mg, Mn
Ferrite 3	50.1±0.7		1.61±0.03		Mg, Mn, Cu
Ferrite 4	41.8±0.7	11.6±0.2	10.0±0.2	0.25±0.01	Mg, Mn, Cu

4. DISCUSSION

In the analysis of Fe, Zn, Ni and Co in ferrite one should evaluate the contribution of the possible interference: from γ -lines of the other component, and from the interfering activities of the fast neutron reactions with other macrocomponents. The table 4 presents the nuclear properties of the specific elements, the analytical γ- lines, as well as the interfering nuclear reactions. For the quantitative analysis of the iron determination the γ- line 1292 keV of ^{59}Fe should be used. The contribution of the interfering activities from Co and Ni is considered as well.

Table 4. The nuclear properties of the determined elements [6-8].

Elements	Nuclei	Half-life	Activation section σ, barn	Analytical γ-lines, keV	Interfering nuclear reaction	Activation section σ, barn
Fe	^{59}Fe	45.6 days	1.01*	1291	^{59}Co (n, p) ^{59}Fe ^{62}Ni (n,α) ^{59}Fe	$1.42x10^{-3}$ $9x10^{-5}$
Ni	^{65}Ni ^{58}Co	2.56 hours 71.3 days	1.5 0.113	368 810	^{59}Co (n, 2n) ^{58}Co	$4x10^{-4}$
Co	^{60}Co	5.26 years	20	1332	^{63}Cu (n,α) ^{60}Co ^{60}Ni (n, p) ^{60}Co	$5x10^{-4}$ $2.3x10^{-3}$
Zn	^{69m}Zn ^{65}Zn	13.9 hours 245.7days	0.10 0.46	439 1115		

* - for thermal neutrons.

If the contents of Ni, Co and Fe in the sample are equal then in the identical conditions of the irradiation and measurements the contribution of Ni in the content of Fe is 0.1%, the contribution of Co is much more significant - near 40%. In fact the content of Co is two orders below iron and the influence of Co accordingly decreases and it can be ignored.

For the quantitative determination of cobalt it is recommended to use the γ-line 1332 keV, since in this case the contribution from γ-lines of the other nuclei should not

be taken into account. The interference from radioactivity of Cu and Ni are very small: $2x10^{-3}$ and $3x10^{-5}$% accordingly.

Ni contents are determined using the γ-line 810 keV of ^{58}Co. In this case the contribution of the radioactivity from Co, does not exceed 0,5% with similar percentage contents of both components. For the determination of zinc the γ-lines 439 keV of ^{69m}Zn is preferred.

Calcium determination is made using ^{47}Sc. The determination calcium using the γ-lines with the energy of 1297 keV of ^{47}Ca is interfered by the γ-lines of the macrocomponent ^{59}Fe with the energy of 1292 keV. The analysis of calcium using the short-lived nuclei is impossible because the ^{56}Mn has to high radioactivity.

In view of the low magnesium contents comparing with the other main components (Fe, Zn, Mn) and the small activation cross-section of Mg (29 mbarn), as well as nearly full interference of the γ-lines of ^{27}Mg and ^{56}Mn (E_γ =844 and 846 keV) and the short half-life of ^{27}Mg ($T_{1/2}$=9.46 min.) the instrumental analysis of magnesium using the (n, γ) reaction with the reactor neutrons is difficult.

The determination of magnesium is possible using the samples irradiated by the neutrons via the cadmium filter. ^{24}Na forms from ^{24}Mg in the (n, p) reaction. However, the analysis of magnesium is difficult due to the presence in the samples of the sodium admixtures, that in the (n, γ) reactions form the same nuclide ^{24}Na. The calculation of the sodium influence is carried out in the way offered in the paper[9].

The contents of chromium in the spinel were determined using ^{51}Cr ($T_{1/2}$=27,7 day, E_γ = 320 keV).

The analysis has shown that the single crystals of the magnesium-aluminium spinel grown with the Verneuil method have lower actual contents of aluminium than aluminium put in the mixture. The magnesium-aluminium spinel that has the composition corresponding to $MgO{\cdot}Al_2O_3$ is identified as the stoichiometric one. The nonstoichiometric spinel has other ratio of oxides. It is found that the single crystals of the stoichiometric spinel contain only 20%, but in the nonstoichiometric spinel approximate 40% from the introduced amounts of manganese. The increase of the Al_2O_3 contents in the spinel composition leads to the reducing of the lattice parameter in the crystals. Using the X-ray diffraction measurements for the determination of the lattice parameter and the obtained values of magnesium - aluminium relations the quick evaluation of the quality of the crystals is possible.

5. CONCLUSION

The techniques of the simultaneous determinations of the main components Fe, Zn, Ni, Co in ferrite are elaborated. They allow defining the above-mentioned components within the following limits: 40 -50% iron, 1 -15% zinc, 1.5 - 40% nickel and 0.05 -0.5% cobalt. The method is developed for the determination of the macrocomponent of magnesium and aluminium in the magnesium-aluminium spinel, as well as the strategy of finding the impurities of Cr, Sc, Mn, Fe, Co, Ni, Eu, Hf.

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