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^{151}Eu-Mössbauer Spectroscopic Study on Ceramics beloging to $ZrO_2 – Eu_2O_3 –Y_2O_3$ System

E. VOLCEANOV*, C. PLĂPCIANU[a], V. KUNCSER[a], A. VOLCEANOV[b], B. MATOVIC[c], S. MOTOC
Metallurgical Research Institute, Bucharest, Romania
[a]*National Institute for Materials Physics, Măgurele-Bucharest, Romania*
[b]*University Politehnica of Bucharest, Romania*
[c]*Institute of Nuclear Science "Vinca", Belgrade, Serbia*

In the last years the ternary stabilized zirconia ceramics have attracted a considerable attention as a source of materials for structural ceramics. In present paper, the simultaneous influence of Eu^{3+} and Y^{3+} cations on zirconia powders (obtained by co-precipitation of aqueous salts solutions) on stabilization process in conjunction with the structural characteristics was investigated.A conventional sintering method (in electric furnace) at 1350 °C temperature range was applied. SEM+EDAX and XPS (X-ray Photoelectron Spectroscopic) analysis were performed. The Eu^{3+}Mössbauer parameters: isomer shift and quadrupole splitting have been obtained for 21.6 keV radiation of ^{151}Eu are in good agreement with the XPS and XRD-obtained crystallographic data of the studied compositions.

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1. Introduction

Nuclei in atoms undergo a variety of energy level transitions, often associated with the emission or absorption of a gamma ray. These energy levels are influenced by their surrounding environment, both electronic and magnetic, which can change or split these energy levels. These changes in the energy levels can provide information about the atom's local environment within a system and ought to be observed using resonance-fluorescence. There are, however, two major obstacles in obtaining this information: the 'hyperfine' interactions between the nucleus and its environment are extremely small, and the recoil of the nucleus as the gamma-ray is emitted or absorbed prevents resonance [1-3]. Key to the success of the Mössbauer spectroscopy technique is the discovery of recoilless gamma ray emission and absorption, now referred to as the 'Mössbauer Effect''. The energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the Isomer Shift, Quadrupole Splitting and Magnetic Splitting [4-5].

The isomer shift arises due to the non-zero volume of the nucleus and the electron charge density due to s-electrons within it. This leads to a monopole (Coulomb) interaction, altering the nuclear energy levels. Any difference in the s-electron environment between the source and absorber thus produces a shift in the resonance energy of the transition. This shifts the whole spectrum positively or negatively depending upon the s-electron density, and sets the centroid of the spectrum. As the shift cannot be measured directly it is quoted relative to a known absorber. The isomer shift is useful for determining valency states, ligand bonding states, electron shielding and the electron-drawing power of electronegative groups.

Quadrupole Splitting. Nuclei in states with an angular momentum quantum number I>1/2 have a non-spherical charge distribution. This produces a nuclear quadrupole moment. In the presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or ligand arrangement) this splits the nuclear energy levels. The charge distribution is characterised by a single quantity called the Electric Field Gradient (EFG). *Magnetic Splitting.* In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field ie Zeeman splitting. There are many sources of magnetic fields that can be experienced by the nucleus. This magnetic field splits nuclear levels with a spin of I into (2I+1) substrates.

In this paper, the Mössbauer parameters: isomer shift and quadrupole splitting have been investigated for 21.6 keV radiation of ^{151}Eu for stabilized zirconia powder obtained through wet co-precipitation route.

The transformation of zirconia from tetragonal to monoclinic is rapid and is accompanied by a 3 to 5 percent volume increase that causes extensive cracking in the material. This behaviour destroys the mechanical properties of fabricated components during cooling and makes pure zirconia useless for any structural or mechanical application. Several oxides which dissolve in the zirconia crystal structure can slow down or eliminate these crystal structure changes. Commonly used effective additives are MgO, CaO, Y_2O_3 [6] with sufficient amounts added, the high temperature cubic structure can be maintained to room temperature. Cubic stabilized zirconia is a useful refractory and technical ceramic material because it does not go through destructive phase transitions during heating and cooling. The controlled, stress induced volume expansion of the tetragonal to monoclinic inversion is used to produce very high strength, hard, tough varieties of zirconia for mechanical and structural applications [7]. This paper aims the study of $ZrO_2 – Eu_2O_3 – Y_2O_3$ ternary zirconia powder synthesis by chemical route and stabilization mechanism by using the Mössbauer spectroscopy to determine the valency states of oxide stabilizers.

2. Experimental

Powders synthesis

The co-precipitation method of a mixture of aqueous salt solutions (2M) of: $ZrOCl_2.8H_2O$ (Merck), $YCl_3.6H_2O$ (Merck), $EuCl_3.6H_2O$ (China) and a solution of ammonia hydroxide NH_4OH (c=25%, Chimopar) was applied. The precipitates were washed out with water and isopropyl alcohol. The obtained powder composition was calculated for a weight ratio of 86:8:6 of the ZrO_2: Eu_2O_3: Y_2O_3. The synthesized zirconia powder presented a 20.4 m^2/g adsorption cumulative area measured by BET method.

Powder sintering

In order stabilize the zirconia powder, two kind of heat consolidation techniques were applied on nanosized ternary zirconia powder: 1) conventional pressure less sintering in an electric furnace at 1350 ^{o}C during 2 hours. The batches submitted to conventional sintering were pressed as cylinders (φ =h =18 mm) at 15 MPa.

Characterisation methods

The density was calculated from measured mass and specimen size using a 0.1 mg Mettler Toledo balance (AB204-S type) and a 0.001 mm digital Mitutoyo micrometer. X-ray diffraction (XRD) patterns on sintered samples were obtained with a DRON 3 diffractometer using CuKα radiation.

The surface area was determined by BET nitrogen adsorptive method. The sintering bulk density was measured by the hydrostatic method.

A Hitachi S 2600 N scanning electron microscope (SEM) incorporating a microanalysis detector for energy dispersive X-rays (EDS) was used to observe the surface microstructure of samples. XPS (X-ray Photoelectron Spectroscopic) analysis were performed.

The Eu^{3+}Mössbauer parameters: isomer shift and quadrupole splitting have been obtained for 21.6 keV radiation of ^{151}Eu.

3. Results

The XRD pattern for zirconia powder is given in Fig.1, corresponding to a partial stabilized powder with cubic, tetragonal and monoclinc polymorphs.

SEM micrograph detail is given in Fig.2 and EDS signal on zirconia sample after 1350°C is presented in Fig. 3.

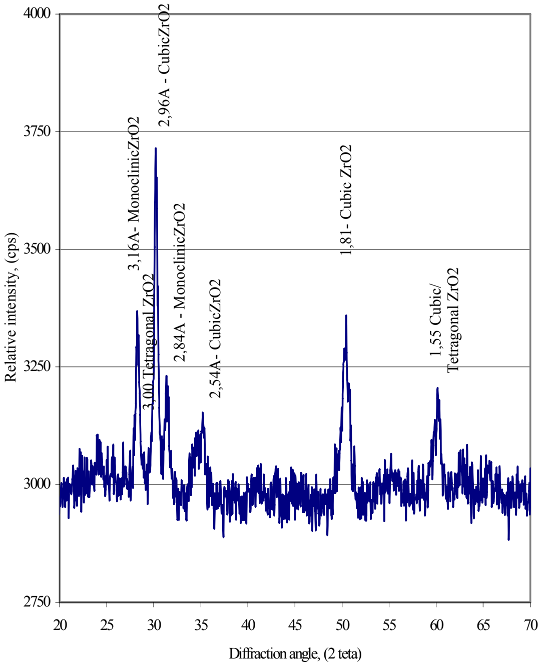

Fig. 1. XRD pattern of ternary zirconia powders.

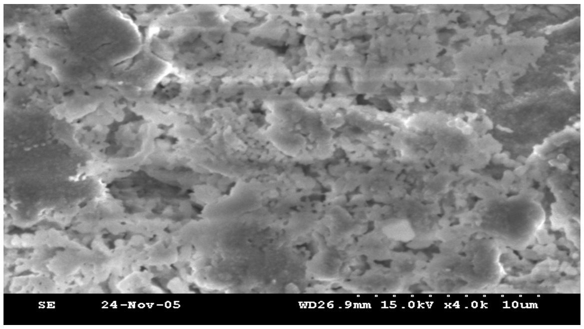

Fig. 2 SEM image on the surface of 86Z-6Y-8E zirconia sample fired at 1350 ^{o}C.

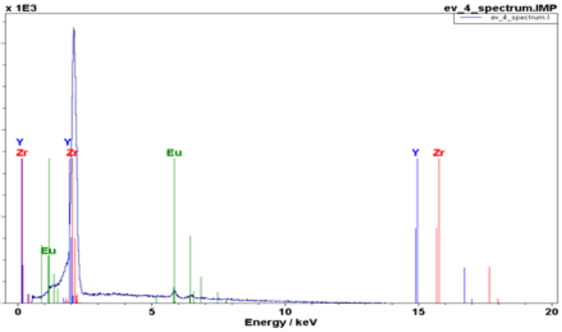

Fig. 3. EDS signals on 86Z-6Y-8E zirconia sample surface fired at 1350 ^{o}C.

XPS spectra recorded on the surface of powders with europium oxide content and thermally treated al 1350 °C have been considered through O^{1s}, Zr^{3d} and Eu^{4d} signals- as seen in Figs. 4-6.

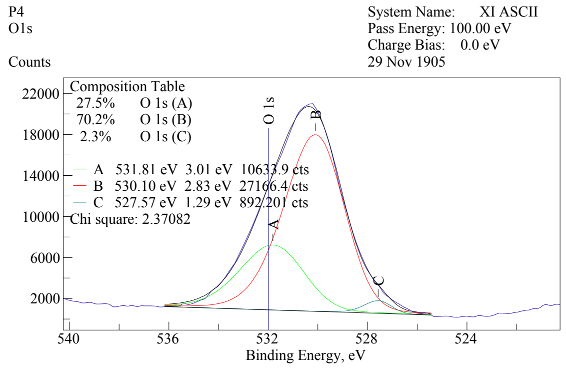

Fig. 4. XPS signals for O^{1s} line on 86Z-6Y-8E zirconia sample surface fired at 1350 °C.

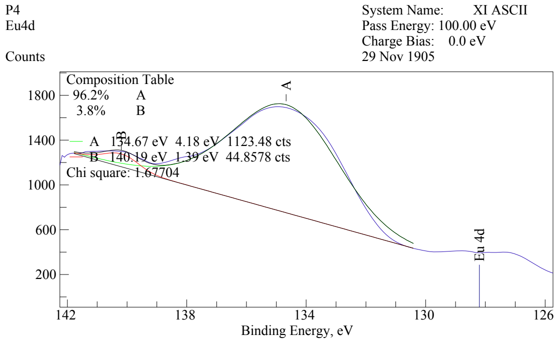

Fig. 5. XPS signals for Eu^{4d} line on 86Z-6Y-8E zirconia sample surface fired at 1350 °C.

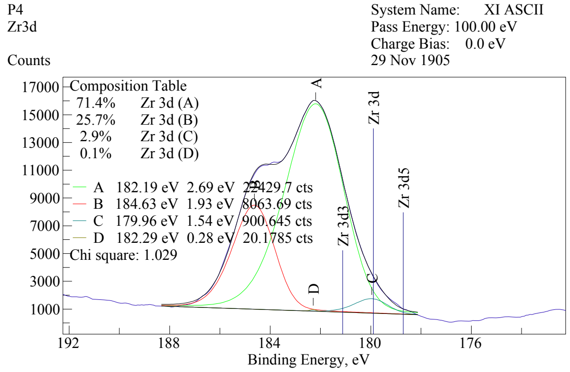

Fig. 6. XPS signals for Zr^{3d} line on 86Z-6Y-8E zirconia sample surface fired at 1350 °C.

4. Discussions

On XPS spectra, one effect is clearly visible: the splitting of Zr ^{3d} line due to different polymorphic states of Zr atoms whilst in the case of the other recorded types of lines this effect cannot be detected. It is interesting to mention that Eu seems to remain only in valence 3+.

The splitting of *3d* line within a doublet is characteristic for all states with orbital angular momentum $l>0$ as an effect of spin-orbit interaction. Parallel or antiparallel orientation of *s* spin with orbital momentum *l* partially removes the degeneration of orbital *l* with the splitting of the corresponding level in two levels $j=l\pm 1/2$, with different energies.

Beside the mentioned energy parameters, Mossbauer spectra provide additional data through other two dynamic parameters: ***i)*** *line width* of Mossbauer spectrum that might be influenced by diffusional phenomena, anisotropy of lattice or lattice-nucleus-atom relaxation; ***ii)*** *surface area of subspectra*, dynamic parameter providing the relative and sometimes absolute weight of the components, and that describes the distributions of ions and certain crystallographic positions.

The experimental data were obtained and processed using NORMOS package.

Mossbauer spectroscopy (^{151}Eu) was used to analyze the sample with the highest Eu concentration (8% wt) within the system ZrO_2-Eu_2O_3-Y_2O_3. Mossbauer spectra of Eu_2O_3 as reference sample(upper curve) and that of sample with 8 % Eu from ZrO_2 -Y_2O_3 system (lower curve) are given in Fig.7.

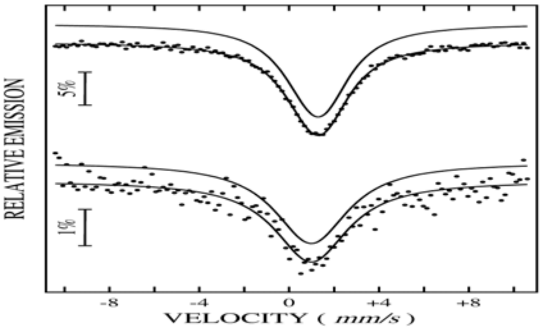

Fig.7 *^{151}Eu Mössbauer spectra of trivalent Europium compounds. As with the fluoride, the isomer shifts are all close to zero.*

Such complex spectra where additionally the quadrupole perturbation is of the same order of magnitude with the width of the spectral signal, must be fitted by taking into account the complete perturbation Hamiltonian. The spectrum will contain very overlapped signals that generate an unique, large and asymmetric absorption (as seen in the Fig.8 a, b).

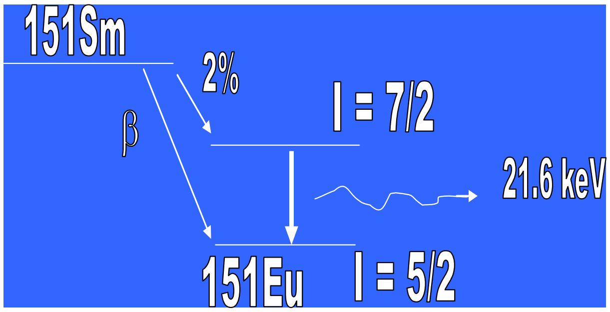

Fig.8 a. *^{151}Eu Mössbauer uses the 21.6 keV level which is populated by the decay of 87 year ^{151}Sm.*

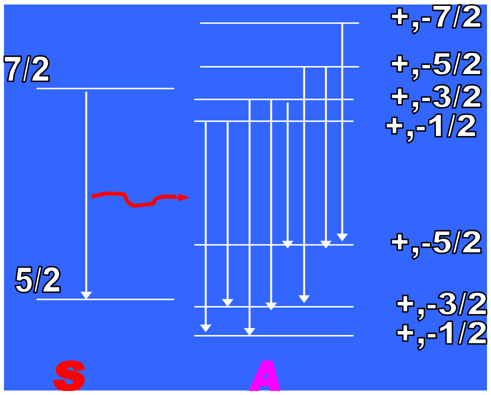

Fig.8 b *Mossbauer spectroscopy with ^{151}Eu uses the 21.6 keV radiation obtained from de-excitation of the first excited level of Eu (I=7/2) to the ground state (I=5/2). Therefore, even the spectrum of a paramagnetic compound is extremely complicated and showing 8 spectral signals (e.g. see possible transitions in the absence of the magnetic moment.*

The hyperfine parameters obtained through such a fit are given in Table 1 for Eu_2O_3 at calibration and in Table 2 respectively for the sample 86Z-6Y-8E fired at 1350 °C .

Table 1. Values of the fit-variables for Eu_2O_3 calibration.

Index Name	Initial	Final	Error (1*STD)
1 BKG(1)	109073.	109645.	± 56.6099
15 WID	1.30000	3.00701	± 0.108038
16 ARE	0.100000	0.709179	± 121764E-01
17 ISO	0.500000	1.14713	± 0.242063E-01
18 QUA	0.300000	1.88827	± 0.433998

Table 2. Values of the fit-variables for sample 86Z-6Y-8E. fired at 1350 °C

Index Name	Initial	Final	Error (1*STD)
1 BKG(1)	174068.	73622.	± 99.0191
15 WID	1.30000	3.97760	± 0.834401
16 ARE	0.100000	0.139374	± 0.161025E-01
17 ISO	0.900000	0.885563	± 0.692487E-01
18 QUA	0.600000	-0.393929E-04	± 6830.94

It can be noticed the following two major differences between the standard Eu_2O_3 spectrum and the Eu_2O_3 containing sample spectrum: 1) the isomer shifting in the prepared sample is near 0.90 mm/s and on standard spectrum is (Eu_2O_3 powder) is around 1.14 mm/s; and 2) the spectrum *line width* is approx. 4 mm/s in the prepared sample, and on standard spectrum is 3 mm/s. The relative large width of the absorption of the zirconia sample can be observed also. Finally, quadrupole splitting is very weak, but in the standard Eu_2O_3.powder is 1.9mm/s.

Consequently from the isomer shifts analysis on can be assumed that the oxidation state of Europium compounds remain trivalent after zirconia stabilization.

It should be noticed that +3 valency of Europium leads to some isomer shifts which are close to zero, while the +2 valency presents an important negative shift, aprox. -15 mm/s). In this case an isomer shifting in 86Z-6Y-8E zirconia sample of 0.25 mm/s comparatively with the standard Eu_2O_3.powder seem to be not significant, whatever indicating a lower oxidation level in zirconia sample and very close to those of Eu_2O_3 powder .

The broadening of spectrum line for 86Z-6Y-8E sample can be assigned to a higher structural disorder of Eu_2O_3 dispersed in zirconia matrix, comparatively with the standard powder. On the other hand the quadrupole splitting is obviously inferior in the zirconia sample suggests a high degree of interaction of Eu with the matrix (probably with a higher symmetry.

In conclusion, on can make the assumption that zirconia matrix contains the europium in trivalent valency distributed in very small grains, being very sensitive to the grain size influence. This can explain also the slight variation quadrupole splitting and the broadening of absorption line due to the enhanced structural disorder, typically for the very small size grains (of nanometre level) .

4. Conclusions

Mössbauer spectroscopy is a versatile technique that can be used to provide information about the chemical, structural disorder of zirconia ceramics belonging to the $ZrO_2 – Eu_2O_3 –Y_2O_3$ system.

The isomer shift is useful for determining valency states of stabilizer oxides for zirconia matrix.

Quadrupole splitting of zirconia powder stabilized with Eu_2O_3 and Y_2O_3 is very weak, but in the standard Eu_2O_3 powders is 1.9mm/s.

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[*] Corresponding author: evolceanov@gmail.com