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Conventional Synthesis and Characterization of Zirconium Molybdate, $Nd_2Zr_3(MoO_4)_9$

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***Abstract*—**Rare earths containing complex metal oxides have drawn much attention due to physical, chemical and optical properties which make them feasible in so many areas such as non-linear optical materials and ion exchanger. We have researched a systematic study to obtain rare earth containing zirconium molybdate compound, characterization, investigation of crystal system and calculation of unit cell parameters. After a successful synthesis of $Nd_2Zr_3(MoO_4)_9$ which is a member of rare earth metal containing complex oxides family, X-ray diffraction (XRD), High Score Plus/Rietveld refinement analysis, and Fourier Transform Infrared Spectroscopy (FTIR) were completed to determine the crystal structure. Morphological properties and elemental composition were determined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Thermal properties were observed via Thermogravimetric-differential thermal analysis (TG/DTA).

***Keywords*—**$Nd_2Zr_3(MoO_4)_9$, solid state synthesis, powder x-ray diffraction, zirconium molybdates.

I. Introduction

COMPLEX metal oxides are useful materials due to their physicochemical, electro-physical and optical properties. The researches in molybdenum area investigate convenient materials with wide range of properties [1]. On the other hand, zirconia containing complex metal oxides primarily as a catalyst has drawn much more attention because of silica-like structure which is mesoporous [2]. The increased concern to zirconia–molybdenum complex metal oxides is related to applicability in many areas such as catalysis [2], metathesis [3], [4], ionic exchange [5], [6], solid conductivity [7]-[9], oxidation [10], non-linear optic [11], and eliminate radioactive waste [12]. Besides, cubic $ZrMo_2O_8$ has greatly attracted the exhibition of isotropic negative thermal expansion (NTE) in a wide range of temperature (0.3–1050 and 11–573 K) [13]-[15]. For the purpose of absorption of radioactive waste, a lanthanide ion in the structure works as a redirect to fractionate of high-level of effluents [12].

The epoch-making side of this study is conventional synthesis of $Nd_2Zr_3(MoO_4)_9$ in a triple oxide system Nd_2O_3–MoO_3–ZrO_2 which is usable as inorganic ion exchanger, radiation absorber, catalyst and solid electrolytes.

II. Experimental Details

All the reagents were supplied by Merck and Riedel Companies as analytical grade. The dineodymium trizirkonium nonakis(molybdates), Nd_2O_3, MoO_3 and ZrO_2 were measured with 1/3:3:1, 2/3:3:1, and 4/3:3:1 molar ratios to complete the synthesis. After grounding the starting materials in an agate mortar, they are put into a porcelain crucible. The three mixtures were heated at 400 °C for 1 h for calcination, and heated 1000 °C for 8 h after many grindings.

The samples were characterized by XRD pattern using Panalytical X'Pert Pro Diffractometer and Cu K_α radiation (λ=1.54056 Á, 40 mA, 50 kV). The calculated and observed XRD data were compared for successive synthesis by Rietveld Refinement Method which transfers powder diffraction to unit cell parameters. FTIR were recorded between 4000 and 600 cm^{-1} using Perkin Elmer Spectrum 100 FTIR Spectrometer. Protherm conventional high temperature furnace was used to heat treatment in conventional solid state technique. TG/DTA was carried out by Perkin Elmer Diamond TG/DTA. Morphological properties and semi-quantitative analyze of the sample were realized by ZEISS Supra 40 VP.

III. Results and Discussion

In Fig. 1, The XRD patterns of the three triple metal oxides systems were given to determine the phases and formations. Table I exhibits mass percentages and phases of the three systems. While $Nd_2Zr_3(MoO_4)_9$ (Inorganic Crystal Structure Database (ICSD)=009-2600) is marked as "+" symbol; $Zr(MoO_4)_2$ (ICSD=016-4733) is pointed "*". In the first Nd_2O_3–MoO_3–ZrO_2 system, $Nd_2Zr_3(MoO_4)_9$ (ICSD=009-2600) and $Zr(MoO_4)_2$ (ICSD=016-4733) compounds are identified as double phase with mass percentages 40.2% and 59.8%, respectively. The second system also contains same phases with an increased ratio of the target compound: 66.4% and 33.6%. The last Nd_2O_3–MoO_3–ZrO_2 system with molar ratio 4/3:3:1 is the most appropriate one where second phase $Zr(MoO_4)_2$ (ICSD=016-4733) is not formed.

TABLE I
Molecular Compositions of Nd_2O_3–MoO_3–ZrO_2 Systems

Nd_2O_3–MoO_3–ZrO_2 systems	Phases percentages	
	$Nd_2Zr_3(MoO_4)_9$ (ICSD=009-2600)	$Zr(MoO_4)_2$ (ICSD=016-4733)
(a) 1/3 Nd_2O_3–3 MoO_3–1 ZrO_2	40.2 %	59.8 %
(b) 2/3 Nd_2O_3–3 MoO_3–1 ZrO_2	66.4 %	33.6 %
(c) 4/3 Nd_2O_3–3 MoO_3–1 ZrO_2	100.0 %	0.0 %

The powder XRD pattern of pure $Nd_2Zr_3(MoO_4)_9$ (ICSD=009-2600) contains (Fig. 2) only diffractions of the pure phase without any impurity.

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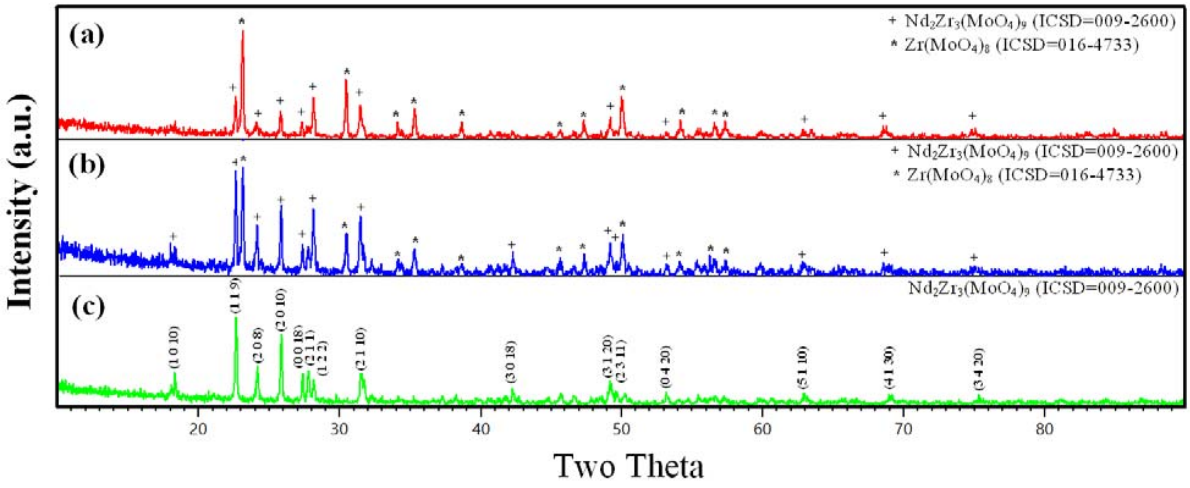

Fig. 1 The XRD patterns of Nd_2O_3–MoO_3–ZrO_2 systems

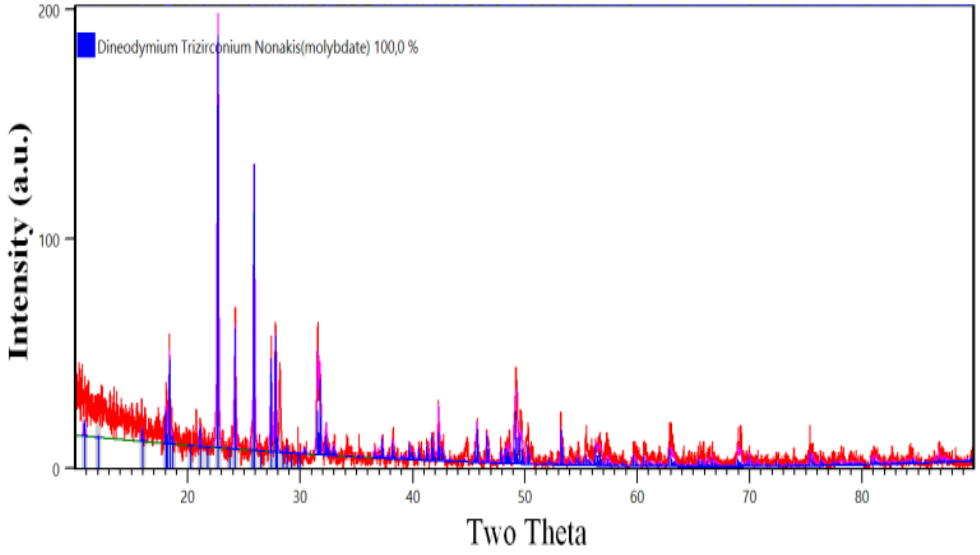

Fig. 2 The XRD pattern of $Nd_2Zr_3(MoO_4)_9$

TABLE II
OBSERVED AND CALCULATED XRD DATA OF $ND_2ZR_3(MOO_4)_9$

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	h k l
4.8297	4.8285	1 0 10
3.9221	3.9212	1 1 9
3.6776	3.6780	2 0 8
3.4428	3.4414	2 0 10
3.2565	3.2545	0 0 18
3.2087	3.2094	2 1 1
3.1656	3.1950	1 2 2
2.8152	2.8173	2 1 10
2.1377	2.1362	3 0 18
1.8360	1.8356	3 1 20
1.8159	1.8304	2 3 11
1.7212	1.7191	0 4 20
1.5465	1.5253	5 1 10
1.3585	1.3437	4 1 30
1.2613	1.2602	3 4 20

TABLE III
UNIT CELL PARAMETERS OF DINEODYMIUM TRIZIRCONIUM NONAKIS(MOLYBDATE)

Crystal system	Unit cell parameters	
	a=b (Å)	c(Å)
Hexagonal	9.8029	58.4801

The calculated and observed XRD data of $Nd_2Zr_3(MoO_4)_9$ compared in Table II with "hkl" values. The unit cell parameters are calculated with Rietveld Refinement Method using calculated XRD data, and crosschecked to ICSD card 016-4733 which belongs to $Nd_2Zr_3(MoO_4)_9$ (Table III). As a result of calculation, $Nd_2Zr_3(MoO_4)_9$ is crystallized in hexagonal system with unit cell parameters a=b=9.8029 (Å) and c=58.4801 (Å). Also, Fig. 3 represents atomic positions of all atoms in the $Nd_2Zr_3(MoO_4)_9$ unit cell.

In Fig. 4, the FTIR spectrum of $Nd_2Zr_3(MoO_4)_9$ was given. The wave numbers at 923, 836 and 685 cm^{-1} correspond to the

vibrations of Mo–O, M–O, and O–Mo–O bond vibrations [16]-[20].

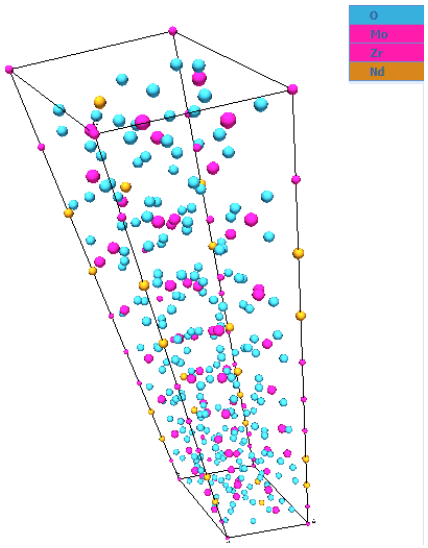

Fig. 3 Unit cell structure of $Nd_2Zr_3(MoO_4)_9$

Fig. 5 is SEM micrograph of $Nd_2Zr_3(MoO_4)_9$. The investigation of the micrograph shows a homogeneous distribution of the sample with particle size smaller than micrometer scale.

The result of EDX analyze about percentages of composition of the sample is given in Table IV. As seen in the table, results are in a good compatibility with the molar ratio 2:3:9:36 of Nd:Zr:Mo:O elements in dineodymium trizirkonium nonakis(molybdates).

Thermal analyze results of $Nd_2Zr_3(MoO_4)_9$ is given in Fig. 6. There is a significant mass loss about 25% nearly 350 ºC which is related to crystal water settled in the structure subsequently. This mass loss which is related to only crystal water displays that the compound is quite stable in the range of 400-1200 ºC.

TABLE IV
EDX RESULTS OF DINEODYMIUM TRIZIRCONIUM NONAKIS(MOLYBDATE)

Element	Mass percentages
Nd	14.56
Zr	13.51
Mo	43.02
O	28.91

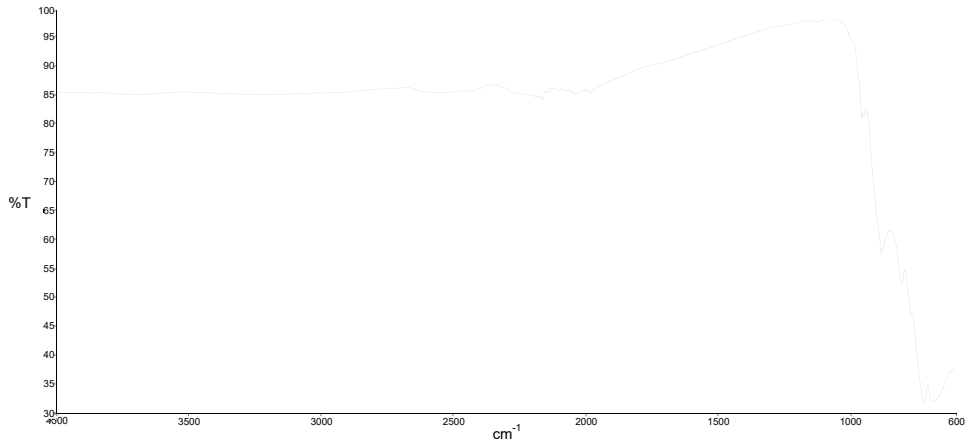

Fig. 4 The Infrared spectrum of $Nd_2Zr_3(MoO_4)_9$

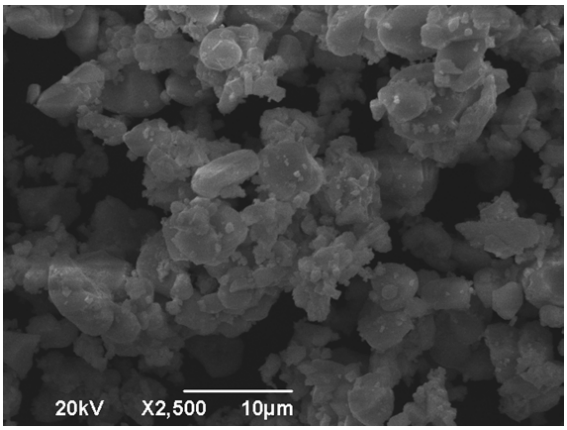

Fig. 5 SEM micrograph of $Nd_2Zr_3(MoO_4)_9$

IV. CONCLUSION

As a short brief, $Nd_2Zr_3(MoO_4)_9$ is synthesized by concentional solid state method in a high temperature furnace at 1000 °C for 8 h in Nd_2O_3–MoO_3–ZrO_2 system with molar ratio 4/3:3:1. The powder diffraction of pure phase, calculated XRD data and unit cell parameters were supplied to determine crystal structure. Morphological and thermal properties also exhibit the homogeneous distribution and thermal stability of the compound, respectively.

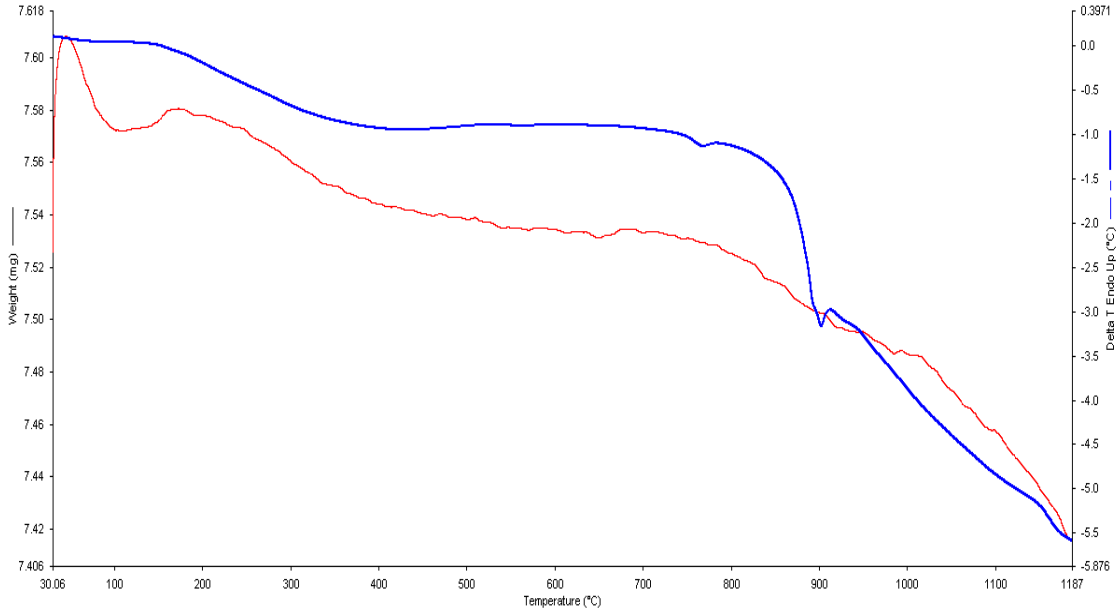

Fig. 6 TGA diagram of $Nd_2Zr_3(MoO_4)_9$

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