Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 6349–6352

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and thermal expansion properties of $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2)

Hongfei Liu[a,*], Xiaocen Wang[a], Zhiping Zhang[b], Xiaobing Chen[a]

[a]School of Physics Science and Technology, Yang zhou University, Yang zhou 225002, PR China
[b]Department of Electrical and Mechanical Engineering, Jianghai College, Yang zhou 225009, PR China

Received 1 April 2012; received in revised form 3 May 2012; accepted 3 May 2012
Available online 11 May 2012

Abstract

$Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics were successfully synthesized by the solid state reaction method. The microstructure, composition and thermal expansion property of the resulting samples were investigated by X-ray diffraction (XRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and dilatometry. Results indicate that the $Y_{1.5}La_{0.5}Mo_3O_{12}$ crystallizes in monoclinic $Tb_2Mo_3O_{12}$-type structure and it is non-hygroscopic. The $Y_{1.5}La_{0.5}Mo_3O_{12}$ ceramic is denser than the $Y_2Mo_3O_{12}$ and $La_2Mo_3O_{12}$ ceramics, and its relative density can reach 94.12% of the theoretical value. Most importantly, it shows almost zero thermal expansion and its thermal coefficient is $0.87\times10^{-6}\,K^{-1}$ from 178 °C to 600 °C. $Y_2Mo_3O_{12}$ ceramic shows negative thermal expansion whereas $La_2Mo_3O_{12}$ ceramic shows positive thermal expansion, their thermal expansion coefficients being $-12.06\times10^{-6}\,K^{-1}$ and $8.88\times10^{-6}\times10^{-6}\,K^{-1}$, respectively.

Keywords: Molybdates; Ceramics; Crystal structure; Thermal expansion

1. Introduction

Thermal expansion is one of the properties which must be considered in the application of highly functional materials because the mismatch of thermal expansion between component materials can cause problems, such as mechanical destruction and positional deviation, in electrical, optical and high-temperature devices. One of the possible methods that can solve these problems is preparing materials with controllable or near-zero expansion coefficient. The preparation of materials with low or zero thermal expansion would increase the mechanical reliability and long-term duration. A simple idea to prepare them is combining negative thermal expansion materials with positive thermal expansion materials [1–8].

Recently, materials with the general formula $A_2Mo_3O_{12}$ have been extensively studied owing to their interesting physical and chemical properties. One remarkable feature of $A_2Mo_3O_{12}$ is that A cation can dramatically influence the thermal expansion properties of $A_2Mo_3O_{12}$. It has been found that there are two structures in the family $A_2Mo_3O_{12}$ compounds, some $A_2Mo_3O_{12}$ compounds with monoclinic structures show positive thermal expansion, such as $Gd_2Mo_3O_{12}$ [9], $Cr_2Mo_3O_{12}$ [10], and $La_2Mo_3O_{12}$ [11]. Some $A_2Mo_3O_{12}$ compounds with orthorhombic structures show negative thermal expansion, such as $Y_2Mo_3O_{12}$, $Yb_2Mo_3O_{12}$, $Lu_2Mo_3O_{12}$and $Er_2Mo_3O_{12}$ [11–14].

It is reported that low or near-zero thermal expansion coefficient in $A_2Mo_3O_{12}$ may be obtained by partial chemical substitution of the A cation by another trivalent cation [13,14]. $Y_2Mo_3O_{12}$ crystallizes in an orthorhombic symmetry (*Pnca*) and exhibits negative thermal expansion; $La_2Mo_3O_{12}$ crystallizes in a monoclinic symmetry (*C2/c*) and exhibits positive thermal expansion [11]. It is therefore possible to obtain the $Y_{2-x}La_xMo_3O_{12}$ ceramics with near-zero thermal expansion coefficients by partial substitution of Y^{3+} with La^{3+}. Here in this report, a new non-hygroscopic solid solution $Y_{1.5}La_{0.5}Mo_3O_{12}$ with near-zero thermal expansion coefficient was successfully prepared by solid state reaction method, and the effects of

*Corresponding author. Tel.: +86 514 87975466; fax: +86 514 87975467.
E-mail address: liuhf@yzu.edu.cn (H. Liu).

0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.05.006

substituted lanthanum on the microstructure, density, hygroscopicity and thermal expansion property of the $Y_{1.5}La_{0.5}Mo_3O_{12}$ were also studied.

2. Experimental

2.1. Preparation of the $Y_{2-x}La_xMo_3O_{12}$ ($0 \le x \le 2$) samples

The samples of $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics were prepared by the conventional solid state reaction method. Starting materials were Y_2O_3 (purity $\geq$ 99.9%), La_2O_3 (purity $\geq$ 99.5%) and MoO_3 (purity $\geq$ 99.5%). All the starting materials were preheated at 300 °C for 24 h before weighting to protect from H_2O. Stoichiometric ratios of the reactants were milled for 10 h to form a uniform mixture and then the mixture was pre-calcined at 500 °C for 10 h, after pre-sintering, the mixture was pressed into pellets (5 mm diameter, 2.5 mm height) and finally calcined at 750 °C in air for 10 h.

2.2. Experimental techniques

The resulting samples were characterized by powder X-ray diffraction (XRD) using Cu*Ka* radiation ($\lambda=$ 0.15418 nm) with 40 kV/200 mA (D/max2500, Rigaku). The XRD data were collected with a scanning speed of 5° (2θ)/ min in the 2θ range from 10° to 70° by continuum scanning method. The thermogravimetric curves of the samples were collected in the open air from room temperature to 300 °C using thermogravimetric analysis (TGA, Pyris1). The heating rate is 10 °C/min. The microstructure and composition of the samples were observed by a field emission scanning electron microscopy (FESEM, Hitachi S-4800) and energy dispersive spectroscopy (EDS, NORAN System Six). Densities of the samples were measured using Archimedes' method. The thermal expansion coefficients of the samples were measured by a dilatometry (NETZSCH DIL 402C). The measurements were carried out at the rate of 10 °C/min in the open air from room temperature to 700 °C.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics. As one can see in Fig. 1(a), the strong and sharp diffraction peaks appearing in the XRD diagram have obvious relevance with the well-crystallized sample. All the peak positions of the obtained sample are well indexed to monoclinic $La_2Mo_3O_{12}$ (JCPDS 26–0821). In Fig. 1(c), All the peak positions of the obtained sample are well indexed to $Y_2Mo_3O_{12}$ (JCPDS 28–1451). The XRD pattern of the obtained $Y_2Mo_3O_{12}$ is similar to that reported by Sumithra et al. [11], and $Y_2Mo_3O_{12}$ is hygroscopic at room temperature. The board humps in the XRD patterns indicate that some amorphous phase might form owing to the absorption of water

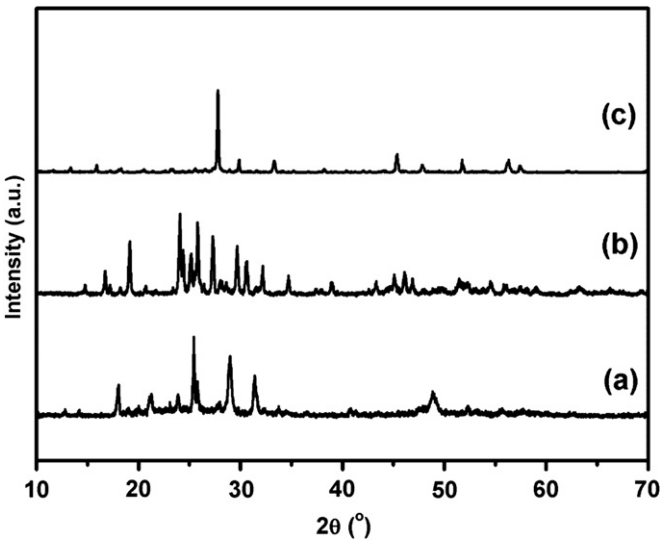

Fig. 1. XRD patterns of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics (a) $Y_2Mo_3O_{12}$; (b) $Y_{1.5}La_{0.5}Mo_3O_{12}$; (c) $La_2Mo_3O_{12}$.

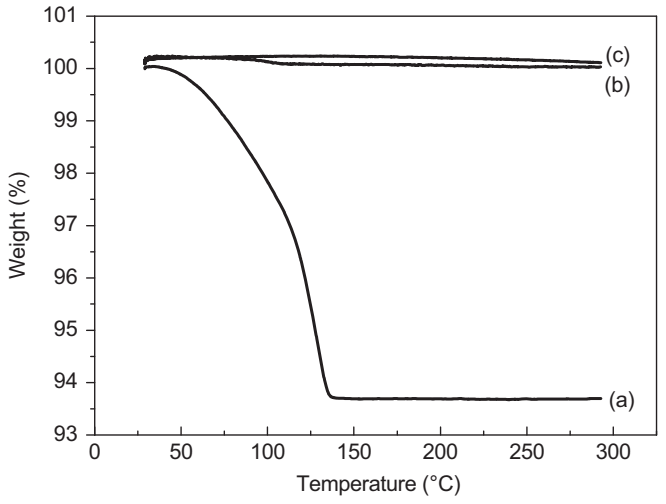

Fig. 2. Thermogravimetric curves of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics (a) $Y_2Mo_3O_{12}$; (b) $Y_{1.5}La_{0.5}Mo_3O_{12}$; (c) $La_2Mo_3O_{12}$.

molecules in the frame-structure. More interestingly, as shown in Fig. 1(b), all the peak positions of the obtained $Y_{1.5}La_{0.5}W_3O_{12}$ sample are well indexed to monoclinic $Tb_2Mo_3O_{12}$ (JCPDS 25-0934), and no obvious diffraction peaks arising from the possible phases such as $La_2Mo_3O_{12}$, $Y_2Mo_3O_{12}$, etc. are visible. Therefore, the $Y_{1.5}La_{0.5}W_3O_{12}$ crystallizes in monoclinic $Tb_2Mo_3O_{12}$-type structure. It is also indicated that the Y^{3+}cation can be submitted by La^{3+} and form solid solution when $x=0.5$. The ionic radii of La^{3+} is 106.1 pm, Tb^{3+} is 92.3 pm and that of Y^{3+} is 90 pm. This is in agreement with the Vegard's law, and on the other hand it proves that the $Y_{1.5}La_{0.5}W_3O_{12}$ compound has been successfully synthesized (Fig. 2).

Fig. 3 shows the thermogravimetric (TG) curves of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) samples. As shown in Fig. 3(a), it can be found that there is a mass

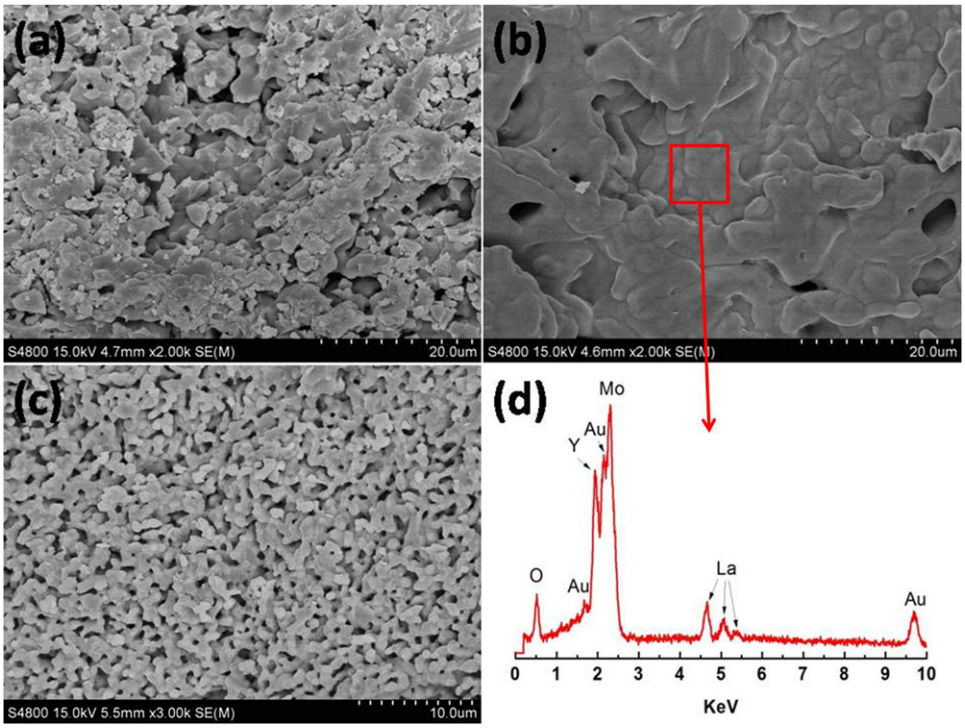

Fig. 3. SEM images of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics (a) $Y_2Mo_3O_{12}$; (b) $Y_{1.5}La_{0.5}Mo_3O_{12}$; (c) $La_2Mo_3O_{12}$ and (d) EDS analysis of $Y_{1.5}La_{0.5}Mo_3O_{12}$.

loss region from 50 °C to 140 °C in the TG curve of the $Y_2Mo_3O_{12}$ sample, indicating the $Y_2Mo_3O_{12}$ is highly hygroscopic at room temperature, and the mass loss is about 6.297%. The corresponding number of water molecules per formula unit is calculated to be 2.45. This hygroscopic phenomenon also has been found in some other orthorhombic $A_2Mo_3O_{12}$ (A=Er, Lu and Y) [11]. However, in the same testing temperature range, there is no obvious inclination can be observed in the TG curves of the $Y_{1.5}La_{0.5}Mo_3O_{12}$ and $La_2W_3O_{12}$ (see Fig. 3(b) and Fig. 3(c)), indicating no water of adsorbed moisture in the samples. Similar phenomenon was also observed in some other monoclinic $A_2M_3O_{12}$ (A=La, Ce, Dy, Nd; M=W, Mo) compounds [2,11–17].

The SEM fractographs of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics are shown in Fig. 3. In Fig. 3(a) and (c), it can be seen that the microstructures of the $Y_2Mo_3O_{12}$ and $La_2Mo_3O_{12}$ both consist of small grains and with some pores inside. The average particle size of $Y_2Mo_3O_{12}$ is larger than the one of $La_2Mo_3O_{12}$. Comparing with the $La_2Mo_3O_{12}$ and $Y_2Mo_3O_{12}$ ceramics, as shown in Fig. 3(b), the $Y_{1.5}La_{0.5}Mo_3O_{12}$ ceramic became denser, and the pores obviously reduced. To further investigate the densities of the resulting $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics, all the densities of the samples were measured using Archimedes' method and the theoretical densities are calculated from theoretical values for $La_2Mo_3O_{12}$ (3.66 g/cm^3) and $Y_2Mo_3O_{12}$ (3.30 g/cm^3). The relative densities of the $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics can reach 83.79%, 94.12%, 85.71% of the theoretical values, respectively, which is in good agreement

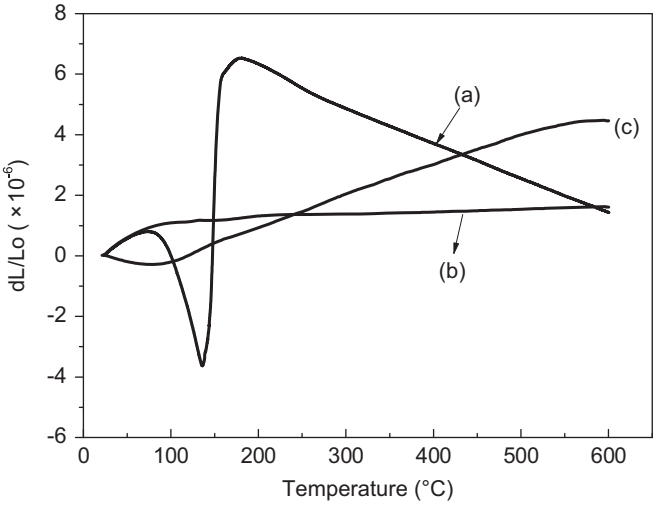

Fig. 4. Thermal expansion curves of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics (a) $Y_2Mo_3O_{12}$; (b) $Y_{1.5}La_{0.5}Mo_3O_{12}$; (c) $La_2Mo_3O_{12}$.

with the above SEM analysis. Fig. 3(d) shows the EDS spectra of $Y_{1.5}La_{0.5}Mo_3O_{12}$ sample, According to the EDS analysis of the sample, the mole ratio of elements *n* (Y): *n* (La): *n* (Mo): *n* (O) is 3:0.97:5.95:24.33, which is close to the stoichiometry of $Y_{1.5}La_{0.5}Mo_3O_{12}$.

The thermal expansion curves of the obtained $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics are shown in the Fig. 4. In Fig. 4(a), it can be seen that the thermal expansion curve of the $Y_2Mo_3O_{12}$ ceramic shows an initial expansion due to the removal of the water molecules, which is supported by the above thermogravimetric

analysis. The general feature of $Y_2Mo_3O_{12}$ ceramic in the thermal expansion behavior is similar to the ones of the bulk $Yb_2Mo_3O_{12}$ and $Er_2Mo_3O_{12}$ reported [11]. The $Y_2Mo_3O_{12}$ sample is easy to absorb moisture in air. It is reported that water molecules would occupy the crystallographic voids in hydrated $A_2Mo_3O_{12}$ structure, and the A–O–Mo linkages bend away from 180° due to the water molecules enter the compound. The incorporation of water in the framework structure will hinder the transverse vibrations of A–O–Mo linkages and prevent negative thermal expansion [10]. After the complete removal of water molecules, negative thermal expansion is observed in $Y_2Mo_3O_{12}$. The average linear thermal expansion coefficient of the $Y_2Mo_3O_{12}$ ceramic is measured to be $-12.06\times10^{-6}\,K^{-1}$ in the corresponding temperature range from 178 °C to 600 °C. Compared with the $Y_2Mo_3O_{12}$ ceramic, there is almost no thermal expansion hysteresis observed in the thermal expansion curve shown in Fig. 4(c). The average linear thermal expansion coefficient of the $La_2Mo_3O_{12}$ sample is measured to be $8.88\times10^{-6}\,K^{-1}$ in the corresponding temperature range from 178 °C to 600 °C.

In the former research work, when $x\leq0.5$, the solid solutions $A_{2-x}B_xM_3O_{12}$ (A=Y, Yb, Er; B=Sm, Ce, Dy, Nd; M=W, Mo) all crystallize in orthorhombic $A_2M_3O_{12}$-type structures, and they are highly hygroscopic at room temperature [2,13–17]. The hygroscopic water molecules will hinder negative thermal expansion, and which will also influence their applications. Based on the above XRD and thermogravimetric analysis of $Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics, it is found that the $Y_{1.5}La_{0.5}Mo_3O_{12}$ sample is abnormal and it crystallizes in monoclinic structure, and there is no water of adsorbed moisture. Most importantly, compared with the $Y_2Mo_3O_{12}$ ceramic, there is almost no thermal expansion hysteresis observed in the thermal expansion curve shown in Fig. 4(b), and the $Y_{1.5}La_{0.5}Mo_3O_{12}$ ceramic shows almost zero thermal expansion, its average linear thermal expansion coefficient is measured to be $0.87\times10^{-6}\,K^{-1}$ in the corresponding temperature range from 178 °C to 600 °C. This non-hygroscopic and low thermal expansion material $Y_{1.5}La_{0.5}Mo_3O_{12}$ was prepared for the first time and it will have a variety of applications.

4. Conclusions

$Y_{2-x}La_xMo_3O_{12}$ ($x=0$, 0.5, 2) ceramics were successfully synthesized by solid state reaction method. The solid solution $Y_{1.5}La_{0.5}W_3O_{12}$ crystallizes in monoclinic $Tb_2Mo_3O_{12}$-type structure. TG analysis shows that $Y_2Mo_3O_{12}$ was highly hygroscopic at room temperature. However, $Y_{2-x}La_xMo_3O_{12}$ ($x=0.5$, 2) are in contrast. The $Y_2Mo_3O_{12}$ and $La_2Mo_3O_{12}$ both consisted of small grains and with some pores inside, the solid solution $Y_{1.5}La_{0.5}W_3O_{12}$ become denser, and its relative density can reach 94.12% of the theoretical value. The obtained $Y_{1.5}La_{0.5}W_3O_{12}$ ceramic almost exhibits zero thermal expansion and its average linear thermal expansion coefficient is $0.87\times10^{-6}\,K^{-1}$ from 178 °C to 600 °C.

Acknowledgments

The authors thank the Nation Natural Science Foundation of China (No. 51102207) and Yangzhou University Science and Technique Innovation Foundation (No. 2010CXJ081).

References

[1] I. Toshihiro, K. Yusuke, M. Mamoru, O. Toshitaka, D. Keiji, Pressureless sintering of negative thermal expansion ZrW_2O_8/$Zr_2WP_2O_{12}$ composites, Materials Letters 62 (2008) 3913–3915.
[2] H.F. Liu, W. Zhang, Z.P. Zhang, X.B. Chen, Synthesis and negative thermal expansion properties of solid solutions $Yb_{2-x}La_xW_3O_{12}$ ($0\leq x\leq2$), Ceramics International 38 (2012) 2951–2956.
[3] P. Lommens, C.D. Meyer, E. Bruneel, K.D. Buysser, I.V. Driessche, S. Hoste, Synthesis and thermal expansion of ZrO_2/ZrW_2O_8 composites, Journal of the European Ceramic Society 25 (2005) 3605–3610.
[4] X.B. Yang, X.N. Cheng, X.H. Yan, J. Yang, T.B. Fu, J. Qiu, Synthesis of ZrO_2/ZrW_2O_8 composites with low thermal expansion,, Composites Science and Technology 67 (2007) 1167–1171.
[5] L.M. Sullivan, C.M. Lukehart, Zirconium tungstate (ZrW_2O_8)/polyimide nanocomposites exhibiting reduced coefficient of thermal expansion, Chemistry of Materials. 17 (2005) 2136–2141.
[6] Q.Q. Liu, J. Yang, X.N. Cheng, G.S. Liang, X.J. Sun, Preparation and characterization of negative thermal expansion $Sc_2W_3O_{12}$/Cu core–shell composite, Ceramics International 38 (2012) 541–545.
[7] J. Yang, Y.S. Yang, Q.Q. Liu, G.F. Xu, X.N. Cheng, Preparation of negative thermal expansion ZrW_2O_8 powders and its application in polyimide/ZrW_2O_8 composites, Journal of Materials Science and Technology 26 (2010) 665–668.
[8] J.J. Zhu, J. yang, X.N Cheng, Synthesis and tunable thermal expansion property of $Al_{2-\delta}Sc_\delta W_3O_{12}$, Solid State Science 14 (2012) 187–190.
[9] M. Keskar, N.D. Dahale, K. Krishnan, N.K. Kulkarni, Thermal expansion studies of $Gd_2Mo_3O_{12}$ and $Gd_2W_3O_{12}$, Material Research Bulletin 44 (2009) 901–905.
[10] A.K. Tyagi, S.N. Achary, M.D. Mathews, Phase transition and negative thermal expansion in $A2(MoO_4)_3$ (A=Fe^{3+}, Cr^{3+} and Al^{3+}) system, Journal of Alloys and Compounds 339 (2002) 207–210.
[11] S. Sumithra, A.M. Umarji, Negative thermal expansion in rare earth molybdates, Solid State Science 8 (2006) 1453–1458.
[12] B.A. Marinkovic, P.M. Jardim, R.R. de Avillez, F. Rizzo, Negative thermal expansion in $Y_2Mo_3O_{12}$, Solid State Science 7 (2005) 1377–1383.
[13] M.M. Wu, Z.B. Hu, Y.T. Liu, D.F. Chen, Thermal expansion properties of $Ln_{2-x}CrMo_3O_{12}$ (Ln=Er and Y), Materials Research Bulletin 44 (2009) 1943–1947.
[14] X.L. Xiao, Y.Z. Cheng, M.M. Wu, J. Peng, Z.B. Hu, The study of thermal expansion properties in solid solutions $Ln_{2-x}Cr_xMo_3O_{12}$ (Ln=Ho and Lu) by high temperature X-ray diffraction, Journal of Physics and Chemistry of Solids 73 (2012) 275–279.
[15] M.M. Wu, X.L. Xiao, Z.B. Hu, Y.T. Liu, D.F. Chen, Controllable thermal expansion and phase transition in $Yb_{2-x}Cr_xMo_3O_{12}$, Solid State Science 11 (2009) 325–329.
[16] M.M. Wu, Y.Z. Cheng, J. Peng, X.L. Xiao, D.F. Chen, R. Kiyanagi, J.S. Fieramosca, S. Short, J. Jorgensen, Z.B. Hu, Synthesis of solid solution $Er_{2-x}Ce_xW_3O_{12}$ and studies of their thermal expansion behavior, Materials Research Bulletin 42 (2007) 2090–2098.
[17] M.M. Wu, J. Peng, Y.Z. Cheng, X.L. Xiao, Y.M. Hao, Z.B. Hu, Thermal expansion in solid solution $Er_{2-x}Sm_xW_3O_{12}$, Materials Science and Engineering B 137 (2007) 144–148.