

Raman spectroscopic study on structure and phase transition of zirconium tungstate synthesized with a CO₂ laser

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Abstract. Negative thermal expansion material of ZrW₂O₈ has been successfully synthesized by rapid solidification with a CO₂ laser. The materials solidified in densely packed blocks with both smooth surface and dark green color. Raman spectroscopic and XRD analysis reveal that the samples solidified in an orthorhombic structure. It is analyzed that the compressive stress can be effectively reduced by lowering the laser scan speed. ZrW₂O₈ samples with cubic structure were produced when the laser scan speed was less than 2mm/s. The samples cooled by water are mainly dominated by α phase which demonstrates that a phase transition from γ to α has occurred after annealing.

1. Introduction

Materials with negative thermal expansion (NTE) have attracted significant attention in recent years due to scientific curiosity and technological interest [1-7]. Among these materials, ZrW₂O₈ is of considerable interest due to their large isotropic NTE over a wide range of temperature. It exhibits a framework structure that consists of the corner-sharing WO₄ tetrahedra and ZrO₆ octahedra. The polyhedra in ZrW₂O₈ are connected at almost all vertices, the exception being one terminal oxygen atom in each WO₄ tetrahedron. The NTE in ZrW₂O₈ was explained in terms of the rigid unit mode (RUM) model [5].

Several methods have been developed for the production of ZrW₂O₈ such as solid state reactions [8], sol-gel method [9] and combustion route. The methods are not only tedious, but also highly time and energy wasting. Another difficulty associated with this procedure is the volatility of WO₃ at elevated temperatures. In this paper, ZrW₂O₈ blocks have been successfully synthesized by rapid solidification with a CO₂ laser and Raman spectroscopic study the structure and phase transition of zirconium tungstate. With this technique a sample can be produced within a few seconds. Laser synthetic route is a rapid and green manufacturing technology with which a sample can be produced within a few seconds. It is easy to realize industrial mass production by continuous feeding of raw materials.

2. Experimental procedure

The commercial chemicals of ZrO₂ and WO₃ (99.9% purity) were mixed according to the stoichiometric ratios of destination materials of ZrO₂ and WO₃. The mixtures were ground in a mortar for 2 hours and then pressed into cylindrical pellets by uni-axial cold press with a steel mould at a pressure of 10 MPa. The mixtures were ground in a mortar for 2 hours and then pressed into cylindrical pellets by uni-axial cold press with a steel mould at a pressure of 10 MPa. The synthesis was performed by using a 5 KW continuous-wave CO₂ laser. The laser beam was striking onto the pellets



which were placed in a distance where the defocus length was set to 120 mm. In this case, the beam spot on the samples was approximately 10.4 mm in diameter. During the synthesis, either the pellets or the laser beam run straight at a scan speed of 1-5 mm/s. The laser power was varied from 400W to 800 W.

All the samples were analyzed by Raman spectroscopy with a Renishaw MR-2000 Raman spectrometer. Laser excitation wavelengths of 633nm and 532nm were used (the laser power was 3mW). X-ray diffraction (XRD) measurements were carried with an X'Pert PRO X-Ray Diffractometer.

3. Results and discussion

Figure 1a shows the Raman spectrum of zirconium tungstate synthesized by a CO₂ laser with 800 W laser power and 5 mm/s scan speed. For comparison, the Raman spectrum of ZrW₂O₈ prepared by solid state reaction is shown in figure 1c. It is obvious that the Raman spectrum of ZrW₂O₈ synthesized by a CO₂ laser is very different from that by solid state reaction [8]. The Raman modes at 1031, 1015, 974 and 932 cm⁻¹ can be assigned to symmetric stretching (ν_s) while those at 903, 889, 870, 868, 802, 777, 745, 722, 707, 683 and 654 cm⁻¹ to asymmetric stretching vibrations (ν_{as}) of the WO₄ tetrahedra. The peaks at 432, 413, 392, 375, 351 and 329 cm⁻¹ are ascribed to the asymmetric bending (δ_{as}) where as those at 313, 301 and 268 cm⁻¹ is from the symmetric bending (δ_s) modes. The other modes observed at 242, 235, 202, 183, 141, 137, 92, 84, 75 and 64 cm⁻¹ originate from lattice modes arising from Zr atom motion and translational and librational (hindered rotation) modes of WO₄. As compared to the Raman spectrum of ZrW₂O₈ by solid state reaction, the most distinctive features of the Raman spectrum of ZrW₂O₈ synthesized by a CO₂ laser are (i) appearance of more Raman peak, which have strong peak at 840, 745, 707, 683, 654, 432, 413, 392, 351, 242, 202, 137 and 75 cm⁻¹; (ii) disappearance of modes at 931, 902 and 888 cm⁻¹; (iii) the characteristic Raman spectra of ZrW₂O₈ become weak and wide. These features suggest that the ZrW₂O₈ synthesized by CO₂ laser solidified in orthorhombic structure (γ phase) instead of cubic (α phase).

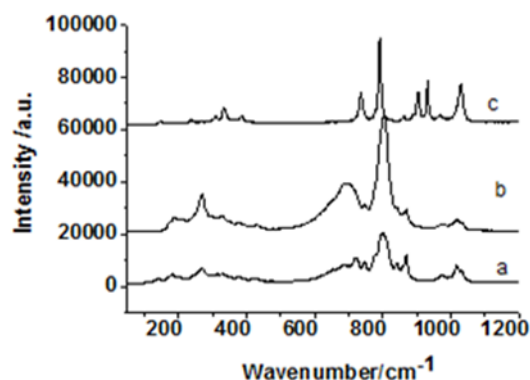


Figure 1. Raman spectra of ZrW₂O₈: (a) synthesized by CO₂ laser; (b) synthesized by laser and annealed; (c) synthesized by solid state reaction.

Figure 1b shows the Raman spectrum of zirconium tungstate synthesized by a CO₂ laser after annealing. When the sample after annealing, the Raman modes at 903 and 932 cm⁻¹ vanished and the ν_{as} modes split into a number of peaks (see spectrum in figure 1b). Besides, the mode at 1015 cm⁻¹ regained its intensity. The restoration for the δ_{as} and δ_s modes occurred as well. This suggests that a reverse phase transition from cubic to orthorhombic took place when the sample was cooled. Since phase transition from α to γ and the disappearance of the bands at 899 and 936 cm⁻¹ were only observed under pressures above 0.21 and 0.5 GPa previously, it can be inferred that the ZrW₂O₈ block synthesized by a CO₂ laser still encounters a compressive stress after the temperature circle. It is the compressive stress that accounts for the recovery of the γ phase after annealing.

Through literature survey found that ZrW_2O_8 crystallizes are cubic phase with the space group $P2_13$ by all the previously reported synthetic methods [8]. But there is some γ phase ZrW_2O_8 crystallizes in the laser synthesis which suggests that the sample under the certain pressure during the solidification process, which is because the γ phase belongs to high pressure phase only under the effect of pressure α phase shift to γ phase. Sudden drop of temperature from the molten pool to the ambience during the solidification should account for the compressive stress generation. High pressure neutron diffraction studies showed that ZrW_2O_8 undergo an irreversible structural transition from α (cubic) to the γ (orthorhombic) phase at 0.2 GPa and finishes at about 0.5 GPa [10]. Ravindran, et al have carried out high pressure Raman spectroscopic study of ZrW_2O_8 [11]. They observed a dramatic splitting of the degenerate ν_3 modes of the WO_4 into a large number of components at pressures above 0.21 GPa and the disappearance of the Raman modes at 904 and 932 cm^{-1} when the pressure was increased to above 0.4 ~ 0.5 GPa.

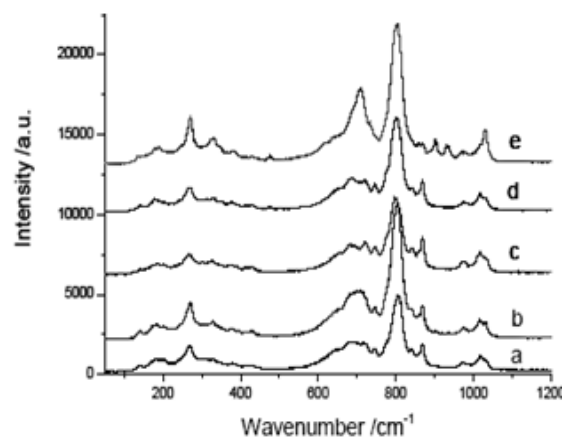


Figure 2. Raman spectra of ZrW_2O_8 synthesized with different scan speeds at 500W laser power: (a) 5mm/s; (b) 4 mm/s; (c) 3 mm/s; (d) 2 mm/s and (e) 1 mm/s.

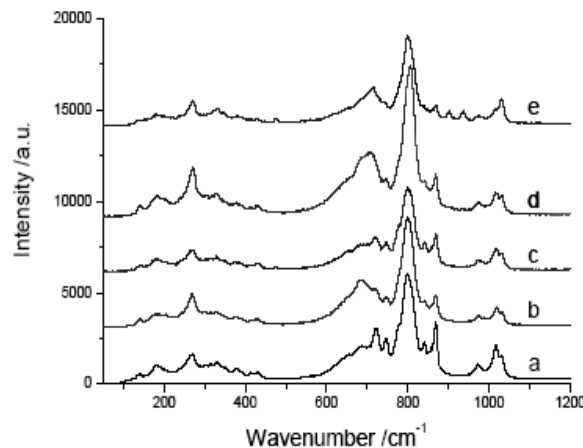


Figure 3. Raman spectra of ZrW_2O_8 synthesized with 800W laser power at different speed: (a) 5mm/s (b) 4 mm/s (c) 3 mm/s (d) 2 mm/s (e) 1 mm/s.

Figures 2a ~ 2e and figures 3a ~ 3e show the Raman spectra of ZrW_2O_8 synthesized with 500 W and 800 W at different scan speeds. The prerequisite condition for α phase production is the compressive stress under 0.2 GPa. The strength of the compressive stress is proportional to the cooling rate which is proportional to the temperature difference between the molten pool and the ambient, and inversely proportional to the time for the sample to cool. It is analyzed and confirmed that the compressive stress can be effectively reduced by lowering the laser scan speed. It is obvious that the γ phase

dominates when the scan speed is more than 2 mm/s. However, with lower scan speed, α phase is produced as indicated by the degeneration of the ν_{as} modes, and the disappearance of the Raman modes at 899, 936 and 1015 cm^{-1} . These results show that the compressive stress can be tuned by laser synthetic parameters and it can be used to the production of different phases of ZrW_2O_8 .

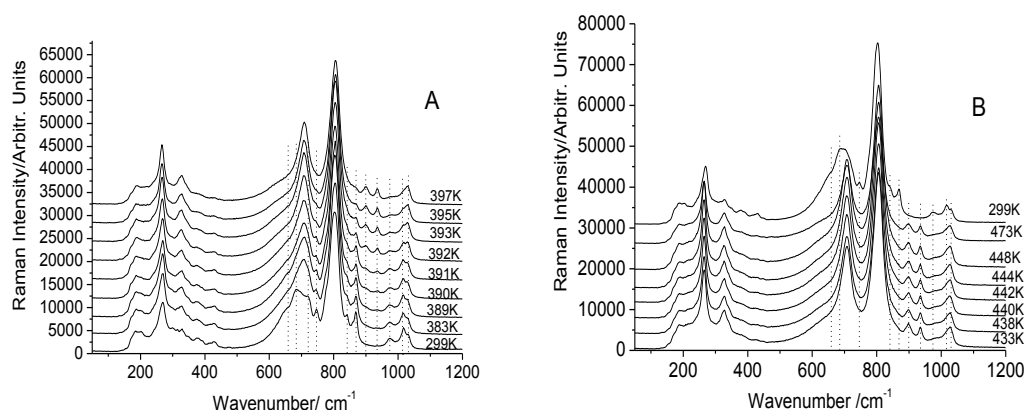


Figure 4. Raman spectra of HfW_2O_8 synthesized with 700W laser power and 1mm/s scan speed at different temperature.

A: (a)299 K(b)383 K(c)389 K(d)390 K(e)391 K(f)392 K(g)393 K(h)395 K(i)397 K

B: (a)433 K(b)438 K(c)440K(d)442 K(e)444 K(f)448 K(g)473 K and(h)cooled back to 299 K

Figures 4A and 4B show the Raman spectra of the sample synthesized by a CO_2 laser with 500 W laser power and 4 mm/s scan speed at different temperatures from 299 K to 473 K and then cooled back to 299 K, respectively. With temperature increase, distinct changes in the Raman spectra are observed: (i) The Raman modes at 903 and 931 cm^{-1} appear at about 390 K and increase in intensity till to 397 K; (ii) The Raman band at 745,840,861,974 and 1015 cm^{-1} vanishes progressively above 390 K; (iii) Only two of the ν_{as} modes at about 707 and 798 cm^{-1} survive and others disappear. As the temperature continues to increase, the number of the Raman bands remains unchanged. Most of the Raman bands shift to red.

It is obvious that several Raman mode frequencies change discontinuously around 390 K. These changes indicate that a phase transition from orthorhombic to cubic occur at about 390 K. In α phase, the structure of ZrW_2O_8 is a framework of corner-sharing ZrO_6 octahedra and WO_4 tetrahedra. The octahedra share all their six corners with six different WO_4 tetrahedra while WO_4 tetrahedra share only three of their four oxygens with the neighboring ZrO_6 octahedra. The remaining oxygen in each WO_4 tetrahedron is formally singly coordinated. An isostructural order-disorder transition to another cubic Pa_3 structure is expected at about 430 K due to the disordering of the WO_4 tetrahedra. The disordered phase has higher oxygen mobility. However, no obvious changes in the Raman spectra can be seen in this temperature region. These give the evidence that the ZrW_2O_8 synthesized by CO_2 laser is γ - ZrW_2O_8 .

As can be seen from figures 4 some of the high-frequency stretching modes, particularly the asymmetric stretching modes, give rise also to negative slopes vs temperature and hence contribute also to the negative thermal expansion. This confirms that the correlated motions of translation and libration with the asymmetric stretching vibrations of the polyhedra are responsible for the negative thermal expansion in the low-temperature phase. Above 440 K, some of the correlated motions may be destroyed as evidenced by the disappearance of the coupled librational motion around 40 cm^{-1} with the marked weakening of the out-of-phase asymmetric stretching vibration across the order-disorder phase transition and cause a smaller negative thermal expansion of the β phase. From figure 2B we can see that when the sample cooled to room temperature, the Raman modes at 899 and 936 cm^{-1} vanished and the ν_{as} modes split into a number of peaks. Besides, the ν_s mode at 1015 cm^{-1} restored its original

intensity. The restoration for the δ_{as} and δ_s modes occurred as well. This suggests that a reverse phase transition from cubic to orthorhombic took place when the sample was cooled. Since phase transition from α to γ and the disappearance of the bands at 899 and 936 cm^{-1} were only observed under pressures above 0.21 and 0.5 GPa previously, it can be inferred that the ZrW_2O_8 block synthesized by a CO_2 laser still encounters a compressive stress after the temperature circle. It is the compressive stress that accounts for the recovery of the phase after annealing.

Through the mechanism of laser synthesis route we can understand the reasons for the formation of γ phase [11, 12]. In the laser synthesis, laser energy is absorbed by ZrO_2 and WO_3 efficiently, and translated into heat on its own where the chemical reaction took place. When the laser beam to move forward the reaction products can fast curing, which is very similar to the process of laser cladding. For most of the laser cladding alloy coating, very big tensile stress in the process of rapid solidification so often leads to the cladding layer crack. The pressure is unavoidable in the process of rapid solidification of ZrW_2O_8 samples. Since ZrW_2O_8 is negative expansion material, making a compressive stress and not tensile stress. It is the compressive stress led to ZrW_2O_8 exists in orthogonal structure. In fact, the laser power and speed are key technological parameter whether the sample can directly sinter into the shape. The laser power and speed can denote with the laser energy of unit time. When the laser power is higher and scan speed is slower, more heat transfer into the sample. It is favorable to solidification level sand sinter levels to connect well. But if the unit time laser energy excessively high cause the commixture powder be prone to gasify which leads to pit, cave and even sink and the sinter level have the warp distortion and so on. And if the unit time laser energy excessively smaller which influence the conjunction between solidification level and sinter level even unable to take shape.

In order to confirm the above analysis, the sample was characterized by XRD which is shown in figure 5. It shows the sample is in accordance with that of an orthorhombic structure ZrW_2O_8 with space group $\text{P}2_12_12_1$, indicating that the sample which is natural cooled by air is indeed dominated by the γ phase. Figure 4b shows the XRD of a sample for comparison. The sample is cooled by water with space group $\text{P}2_13$, which is almost α - ZrW_2O_8 . It demonstrates that a phase transition from γ to α has occurred after annealing. The water cooling to reduce the γ - ZrW_2O_8 , show that the compressive stress decreases in the samples. It is noticed that the XRD and Raman peaks of the sample synthesized by laser are relatively broad. This may indicate that the sample is composed of nano-crystallines and amorphous phases. The samples which are just sintered by laser and were quickly put into the water. Due to the water has a large heat capacity and the high thermal conductivity, the heat will be quickly absorbed by the water in the laser sintering samples. So the temperature field have been rapidly eroded and this will decrease the compressive stress in the sample, thereby reducing the γ - ZrW_2O_8 generated.

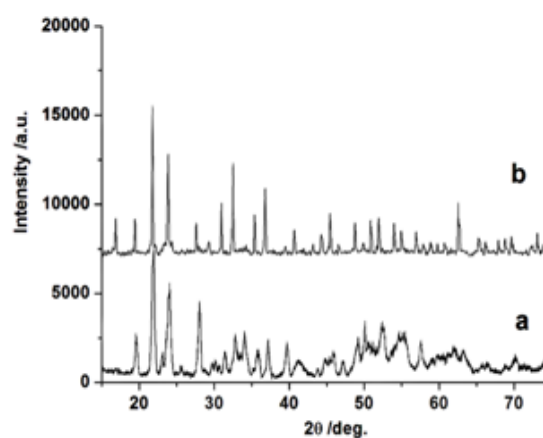


Figure 5. XRD patterns of ZrW_2O_8 synthesized with 500 W laser power and 2 mm/s scan speed; (a) naturally cooled by air (b) cooled by water.

4. Conclusion

ZrW₂O₈ has successfully been synthesized with a high power CO₂ laser. It is a rapid process in which a sample can be produced in few seconds. The sample of laser synthesis compare with the samples which are synthesized by solid state reaction or other chemistry methods, there is γ phase in the sample. The γ phase formation gives a definite indication that a compressive stress was induced during the solidification process. Analyzing by the mechanisms of the laser synthetic route, the strength of the compressive stress is proportional to the cooling rate which is proportional to the temperature difference between the molten pool and the ambient, and inversely proportional to the time for the sample to cool. A recovery of the γ phase has been observed when the samples were cooled to room temperature. This suggests that cubic structure is only metastable at temperatures above 390 K and at room temperature the γ phase is preferred. It is analyzed and confirmed that the compressive stress can be effectively reduced by lowering the laser scan speed. ZrW₂O₈ samples with cubic structure were produced when the laser scan speed was less than 2mm/s. The samples cooled by water are mainly dominated by α -ZrW₂O₈. We also attempt to avoid the appearance of γ phase by another method which improves the resist compression of material.

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