

Y₂Mo₃O₁₂: Negative thermal expansion and heat capacity at low temperatures

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Abstract –Y₂Mo₃O₁₂ was analyzed through high-resolution X-ray powder diffraction (10K to 450K), heat capacity (2K to 390K) and differential scanning calorimetry (103K to 673K). This orthorhombic (Pbcn) phase consists of corner-sharing YO₆ octahedra and MoO₄ tetrahedra, Fig.1a. The overall thermal expansion is negative, α_1 is $-9.02 \times 10^{-6} \text{K}^{-1}$, and no phase transition was observed. An analysis of polyhedral distortion shows a new relationship between it with the thermal expansion. Negative thermal expansion is attributed to the reduction of the mean Y-Mo non-bonded distances and Y-O-Mo bond angles with increasing temperature, the joint action of high-energy optical and low-energy translational and librational modes [1].

Y₂Mo₃O₁₂ was produced by solid state reaction. To verify the phase composition of the synthesized samples was used a microscope (SEM) equipped with EDS. To determine the thermal expansion, a high resolution X-ray powder diffraction data were collected at 20, 150, 300 and 450K, using a commercial closed-cycle He cryostat at Brazilian Synchrotron Light Laboratory (LNLS, D10B-XPD beamline). Data were obtained from 10 to 70° (2 theta), steps of 0.004° with remaining time of 2s and $\lambda = 1,23989\text{\AA}$. The linear thermal expansion coefficient was $-9.02 \times 10^{-6} \text{K}^{-1}$ determined by Rietveld refinement performed using Topas academic [2], Fig. 2. No change in the structure (orthorhombic, Pbcn) neither first phase transition was observed on the whole range studied by heat capacity measurements and DSC. Heat capacity was determined over the temperature range of 2K to 390K, using a commercial relaxation calorimeter (Physical Property Measurement System 6000 from Quantum Design) and DSC was analyzed at TA Instruments Q200 series DSC equipped with an LNCS cooling head and a helium atmosphere was used to investigate the presence of any thermal anomalies in anhydrous Y₂Mo₃O₁₂ from 103K to 673K following preheating at 403K. An analysis of polyhedral distortion was executed by IVTON program [3] on some compounds of the A₂M₃O₁₂ family and it was observed a new relationship between it with the linear thermal expansion, Fig. 1b. The polyhedral distortion increases with temperature increasing. **Acknowledgements:** Authors thanks LNLS for D10B-XPD 7756 project and Ari M. thanks FAPERJ for postdoctoral fellowship.

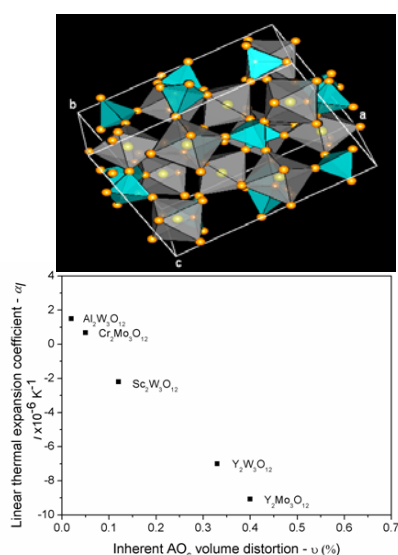


Figure 1: (a) Y₂Mo₃O₁₂ (b) linear coefficient thermal expansion (α_1) as a function of AO₆ volume distortion

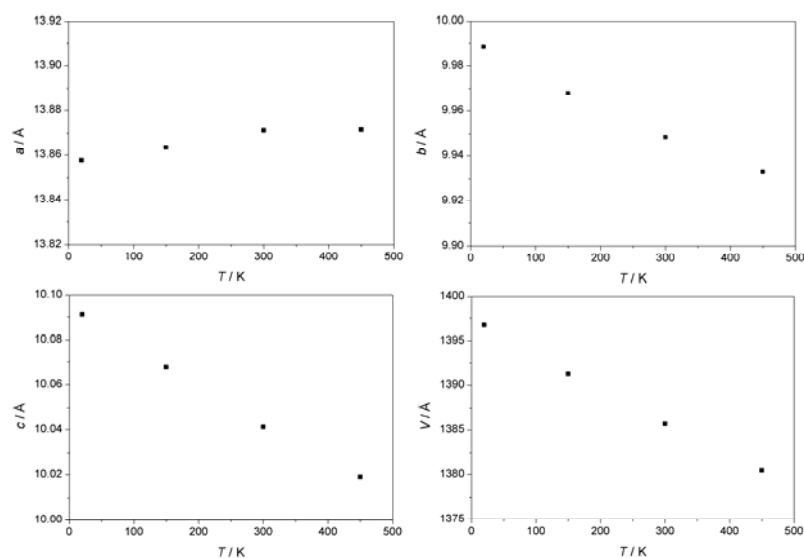


Figure 2: Lattice parameters of Y₂Mo₃O₁₂ as a function of temperature.

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