

MS31.P34*Acta Cryst.* (2011) **A67**, C437**Synthesis of ytterbium-doped yttrium aluminum garnet nano-powders by carbonate altogether precipitation methods**Zhang Xuejian Zou Guangtian,^a Li Chun Liu Jinghe^a *Jilin University*^b, *Changchun University of Science and Technology Changchun (China)*. E-mail: zxj_0620@163.com

Yb³⁺-co-doped YAG transparent ceramic nano-powders were prepared by carbonate altogether precipitation methods, and their structure, morphology and properties were also analyzed by X-ray diffraction, absorption and fluorescence spectra. The results show Yb³⁺:YAG nano-powders are obtained with higher sintering performance and purity, and the particle shapes are regular with average diameter in the range of 100 nm. The crystalline size grew with the increase of the heat treatment temperature. The size of powder calcined at 1100°C was about 70–150 nm, which is favorable for good sinterability of Yb³⁺:YAG ceramics.

Keywords: Yb:YAG laser materials, transparent ceramics, nano-powder**MS31.P35***Acta Cryst.* (2011) **A67**, C437**Synthesis of Yb:GGG laser ceramic nanopowder**Zhang Xuejian, Liu Jinghe, *Jilin Architectural and civil Engineering institute Changchun (China)*. E-mail: zxj_0620@163.com

The sol-gel combustion method was used to synthesize Yb:GGG laser ceramic nanopowder. The phase structure, thermal stability, particle size and morphology of Yb:GGG powder were studied by means of XRD, TG-DTA, IR and SEM methods. It was found that the as-synthesized powder belongs to GGG phase. The crystalline size grew with the increase of the heat treatment temperature. The size of powder calcined at 900°C was about 40–50 nm, which is favorable for good sinterability of Yb:GGG ceramics.

Keywords: Yb:GGG, nanopowder, structure and morphology**MS31.P36***Acta Cryst.* (2011) **A67**, C437**Structure and properties of Mo(II) complexes with dinitrogen bidentate ligands**

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Reaction of $[M(\eta^3-C_3H_5)(CO)_2X(NCMe)_2]$ ($M = Mo, W$; $X =$ halide) complexes with bidentate nitrogen ligands leads to substitution of the two nitriles, and two different isomers may be formed. The two carbonyls and the centroid of the allyl group always adopt a facial arrangement in the pseudo octahedral environment around Mo(II), with the halide occupying a position trans (equatorial isomer) or cis (axial isomer) to the allyl. When $C_5H_4NCH=N(CH_2)_2CH_3$ (pyca) is used, the two main isomers have very close energies (DFT calculations) and they coexist in the crystal. With the other ligands, only one isomer is

observed in the solid, though often several are detected in solution, especially when ligands are small, owing to the fluxional behavior of the complexes in solution (NMR).

Some of the complexes display catalytic activity, both in homogeneous and heterogeneous conditions, in olefin oxidation in the presence of t-butylhydroperoxide.[1] and others can act as anti tumor agents.[2] The antitumor properties have been tested in vitro against human cancer cell lines such as cervical carcinoma (HeLa) and breast carcinoma (MCF-7), using the MTT metabolic activity test (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide). 1,10-phenanthroline (phen) seems to be the most effective ligand, with a IC_{50} of 23.7 μM (Mo, Br). The substitution of Br by triflate usually enhances the cytotoxic activity. In $[M(\eta^3-C_3H_5)(CO)_2(CF_3SO_3)(phen)_2]$, for instance, it drops to 2.9 μM . The binding constant of this complex with ct DNA, determined by absorption titration, is $2.08 (\pm 0.98) \times 10^5 M^{-1}$, a value comparable to the one determined for ethidium bromide. This result suggests that the complexes may interact with DNA changing its conformation. The molecular structures may give information about the possibility of complex intercalation in DNA. Crystal structures exhibit different features (inter and intra molecular hydrogen bond, π - π stacking) depending on the functional groups available.

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Keywords: molybdenum, nitrogen ligand, antitumor**MS31.P37***Acta Cryst.* (2011) **A67**, C437**Crystal structure of bacterial citrate lyase**

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Citrate lyase activity exists in eukaryotes, bacteria, and archaea. This underscores its central importance in energy metabolism and biosynthesis. There are two types of citrate lyases, ATP-dependent and non ATP-dependent. The latter bacterial citrate lyase converts citrate to acetate and oxaloacetate by a two-step reaction for which a complex of α - β - γ -lyase is required. We present the crystal structure of the bacterial citrate lyase complex comprising six copies of α -, β -, and γ -lyase at 4 Å resolution. The structure reveals how the 18-subunit complex is assembled and provides insights into citrate catalysis.

Keywords: structure, citrate, lyase**MS32.P01***Acta Cryst.* (2011) **A67**, C437-C438**Microstructure of synthetic Mg-Co cordierite studied by X-ray diffraction methods**

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Gels of nominal compositions $(\text{Mg}_{1-x}\text{Co}_x)_2\text{Al}_4\text{Si}_5\text{O}_{18}$ were obtained by the sol-gel method from metallic salts (nitrates) and colloidal silica. The dried gels were melted and the amorphous precursor was annealed to crystallized monophasic cordierite solid solutions. A hexagonal cordierite (indialite) [1] and orthorhombic cordierite (iolite) [2] has been studied by several authors and are very similar; both are built of six-component rings of tetrahedral Si-Al sites perpendicular to c-axis. All these cordierites have several interesting ceramic and optical properties.

X-ray powder diffraction using Cu K α radiation and scanning electron microscopy were used to follow the structural and textural evolution from gels to the final synthetic orthorhombic cordierite solid solutions. Rietveld refinement was started using Cccm space group and structure parameters derived from Terada et al. using the FullProf program [3]. The results confirm the orthorhombic crystal structure and the solid solution formation in the whole range of compositions of these Mg-Co cordierites.

The non-periodicity of nanocrystalline materials can be analyzed using the diffraction line broadening of X-ray diffraction patterns. There are several approaches to obtain microstructural information (crystallite shapes and size distribution, microstrain). We have used an integral breadth method [4], a Fourier method [5] and a statistical method for analysing polycrystalline materials [6]. In all cases the standard line profiles for instrumental line broadening were obtained from LaB₆ (SRM 660a). On average, crystallite size of these orthorhombic cordierite solid solutions is rather similar for different metal contents, but microstrain diminishes when cobalt content increases.

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Keywords: sol-gel processes, rietveld refinement, microstructure analysis

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In-situ X-ray diffraction study on the decomposition kinetics in bearing steels

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We have monitored in-situ the austenite transformation kinetics in high-carbon bearing steels undergoing creep phenomena by performing time-dependent X-ray diffraction experiments under tensile load at elevated temperatures using a 70 keV synchrotron X-ray micro-beam. Bearings are nowadays used as key precision components in a broad scope of machinery and gearboxes. The commonly used high-carbon SAE 52100 steel provides the required combination of

high strength and resistance to fatigue to produce bearings with an acceptable lifetime. The room-temperature microstructure of these steels consists of martensite, metastable austenite (10-25 vol.%) and a small amount of carbides (< 5 vol.%). Small dimensional changes in the bearing during operation influences its function and thereby that of the machine in which it operates. One key process that critically affects the bearing dimensions during operation is the decomposition of the metastable austenite phase at elevated temperatures. The austenite face-centred cubic (fcc) structure transforms into the bainite body-centred cubic structure, together with the appearance of very fine nm-sized precipitates.

The combined use of the high-energy X-rays available at the ESRF and our dedicated micro-tensile stage with heating capabilities has allowed us to monitor in-situ the austenite decomposition in the bulk microstructure as a function of time for different combinations of temperature and applied tensile stress. The measurements were performed by continuously recording the diffraction patterns on a two-dimensional detector placed behind the sample as a function of time at selected temperatures in the range of 476-504 K for an applied tensile stress of: $\sigma = 0$ and $\sigma = 295$ MPa. This combination of temperature and stress mimics the operating conditions of the bearings during its lifetime. The available optics at the ID15A beam line of the ESRF permits to reduce the beam dimensions down to $5 \times 25 \mu\text{m}^2$. This has allowed us to study both the average behaviour of the metastable austenite phase and the transformation kinetics of individual austenite grains. The observed transformation behavior has been correlated to the change in sample dimensions that are recorded simultaneously during the in-situ diffraction experiment. The Rietveld analysis of the powder diffraction data reveals that the time to completely transform the metastable austenite reduces from 6 to 3 hours when increasing the temperature from 476 to 489 K. The presence of the applied tensile stress of 295 MPa reduces the activation energy from 138 to 104 kJ/mol. We have also observed a continuous decrease in the austenite lattice parameter while keeping the sample at a constant temperature. This effect is ascribed to the depletion in carbon of the remaining austenite grains resulting from the formation of iron carbides. The results of our in-situ diffraction study constitute a key input to control the austenite stability in high-carbon steels during the industrial processing of the material, in order to keep the changes in the bearing dimensions within the required limits during its lifetime.

Keywords: steel, creep, diffraction

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A multidisciplinary study of the resolution of hydratropic acid by ephedrine

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Following the introduction of regulatory guidelines for the production of stereoisomeric drugs in 1992, the number of drugs marketed as single enantiomers has increased considerably [1]. Classical resolution is often used to obtain enantiopure compounds by the pharmaceutical industry. However, despite its importance, the choice of chiral acid/base to use as a resolving agent is still mostly made on a trial and error basis. An understanding of the relationship between the crystal structure of the diastereomeric salt pairs, their relative energies and crystallization behaviour, would lead to improvements in the separation process.

In the present study we have performed an experimental and