

## 05.2-17 THE INFLUENCE OF SITE SYMMETRY ON THE SPECTROSCOPIC PROPERTIES OF LASER IONS.

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Three different classes of materials suitable for solid state lasers are pointed out i. e. tungstates, sapphire and garnets which are grown from the melt by the Czochralski method.

As optical active ions  $\text{Cr}^{3+}$ ,  $\text{Ti}^{3+}$  and manganese with various valencies are doped during the crystal growth.

It is shown that the site symmetry and the strength of the crystal field are sensitive parameters for the spectroscopic properties of the laser ions. This is demonstrated for  $\text{Cr}^{3+}$  doped in  $\text{ZnWO}_4$  (rather weak crystal field) compared with ruby (strong crystal field). In the case of  $\text{Ti}^{3+}$  doped in sapphire the reduction of symmetry by Jahn-Teller distortion can be observed spectroscopically.

Furthermore manganese doped in garnets is investigated. Because of the necessity of charge compensation  $\text{Mn}^{2+}$  is realized by codoping with silicon, for  $\text{Mn}^{3+}$  no codoping is necessary and  $\text{Mn}^{4+}$  is incorporated together with  $\text{Mg}^{2+}$ . Depending on the ion size and coordination number these ions occupy the three different cation sites offered in the garnet structure.

## 05.2-18 ON THE CORRELATION BETWEEN STRUCTURE AND OPTICAL ACTIVITY OF CRYSTALS. By A.M. Glazer, J.R.L. Moxon, K.M. Stadnicka\* and P.A. Thomas, Clarendon Laboratory, Parks Rd., Oxford OX1 3PU, UK.

Although anomalous x-ray scattering techniques have been available for many years, thus permitting correlation between chirality and optical activity of crystals to be determined, a careful study of the literature has shown many errors and ambiguities. The result is that the causes of optical activity are still largely unknown. Even a proper understanding of the structures of chiral crystals has been evident in the past, leading to considerable confusion, as in the well known case of quartz (Donnay and Le Page, Acta Cryst. (1978) A38, 584). Apart from a detailed theoretical understanding of optical activity, what is required first is the answer to the question: does light rotate with or against any particular spiral arrangement of atoms in the crystal structure? It appears that, as far as uniaxial enantiomorphic crystals are concerned, where definite symmetry spirals exist, there are only a very few examples where the correlation made can be trusted: quartz,  $\text{AlPO}_4$ , dicalcium strontium/lead phosphates (DSP & DLP). In all the cases it can be shown that light rotates with an atomic spiral, chosen in the crystal structure in some way. This choice has to be made with care, because within a single structure one can usually find spirals of opposite handedness. For example it has been said that in  $\text{HgS}$  crystals the sense of optical rotation is opposite to the spiral of atoms (Auvray, Bull. Soc. Fr. Mineral. Cristallogr. (1976) 99, 373); however an appropriately chosen spiral can be found which does have the same sense as the light. We shall demonstrate the rules with which the correct spiral arrangement should be selected.

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## 05.2-19

## CRYSTALLOGRAPHIC ENGINEERING &amp; DESIGN OF CERAMICS

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Engineering with oxide ceramics is commonplace, engineering of ceramics is not. Engineering of ceramics requires the construction of microscopic and macroscopic structures that are durable and perform useful functions in a given environment. On a microscopic scale, there are at least two levels of design: first, lattice or ionic design and next, grain boundary organization. The crystallographic principles for each will be illustrated using corrosion properties of alkaline-earth systems. Problems are diverse as hydration (of significance in cement chemistry) and potential barriers (in electronic ceramics) will be addressed with the same crystallographic engineering tools.

Lattice engineering of  $\text{MgO-MgR}_2\text{O}_4$  spinels ( $R = \text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ...) uses solid solubility, defect chemistry,  $\text{Po}_2$  cycles as the tools. Phase assemblages are crafted where, by promoting or suppressing point defects, phase boundaries can be shifted. E.g., it will be shown that basic corrosion can be reduced if only intracrystalline precipitation occurs. For hydration reduction, defect compensation is necessary. With different building blocks (viz., perovskites) useful semiconductors can be fashioned with the same tools.

Grain boundary engineering is recent and more radical. Two approaches will be presented. In the first method, intercrystalline precipitation is induced creating a secondary spinel-MgO diphasic assembly that is resistant to acidic corrosion. Alternately, the grain boundary can be modified by ion-exchange (e.g., readily hydrated cations can be removed or added to alter hydration propensity) or a second phase can be diffused-in (e.g., by liquid or vapor transport). Again, with semiconducting ferroelectrics, the latter method can be used to fabricate PTC devices.

05.2-20 STUDIES OF  $(\text{TMTSF})_2\text{AsF}_6$  AT HIGH PRESSURE AND AT LOW TEMPERATURE. By L. W. Finger, Carnegie Institution of Washington, Washington DC 20008; M. A. Beno and J. M. Williams, Argonne National Laboratory, Argonne IL 60439; and R. M. Hazen, Carnegie Institution of Washington.

The organic radical cation tetramethyltetraselenafulvalene (TMTSF) forms the basis for several organic conductors. One of these,  $(\text{TMTSF})_2\text{AsF}_6$ , which becomes a superconductor at high pressure and low temperature, has been studied at pressures to 2.65 GPa in the single-crystal diamond-anvil cell and the results compared with previously reported low temperature (125 K) data. The material has large, nonlinear, and anisotropic compressibility. The bulk modulus is 6.6(9) GPa and its pressure derivative is 12(3) for a Murnaghan equation of state. This unusually large curvature implies significant changes in intermolecular bonding characteristics with pressure. The principle component of strain perpendicular to the plane of the TMTSF molecules is nearly three times that within the plane. The orientations of these principle components of compression are within  $10^\circ$  of those of thermal expansion. As a result, the effects of raising pressure are very nearly the same as those of lowering temperature.

Various constraint models to demonstrate molecular configuration and to reduce the number of variable parameters have been tested using the 125 K data set. For a rigid-body thermal model, the number of adjustable quantities is reduced from 195 to 131, yet the weighted residual changes only from 0.0353 to 0.0360. Molecular thermal motion is also anisotropic. The eigenvalues for the T-tensor range from 0.007 to  $0.014 \text{ \AA}^2$ , whereas those for L vary from 0.000 to  $0.007 \text{ rad}^2$ . No refinement with molecular shape constraints has converged to  $wR$  less than 0.041; thus, the presence of extra symmetry in the TMTSF molecule cannot be demonstrated.