

**s8.m27.p24 Relationship between Composition, Structure, Preparation and Properties of Langasite Family Phases.** Tyunina E., Kuz'micheva G., Domoroschina E., Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia. E-mail: galkuz@orc.ru

**Keywords: Growth; Structure; Properties**

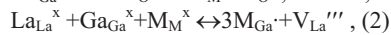
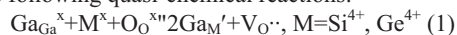
Single crystals of compounds with the  $\text{La}_3\text{Ga}_5\text{SiO}_{14}$  structure (langasite) have been reported to be promising piezoelectric materials for fabrication of filters with large pass bandwidths and oscillators with high-frequency stability.

In this work, we demonstrate an analysis of results of X-ray diffraction study in common with various properties.

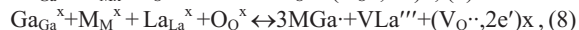
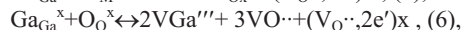
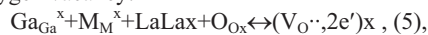
These crystals belong to the sp.gr. P321 and have four kinds of cation sites in this structure. La and Ga(1) are located on a decahedral site (twist Thomson cube) coordinated by eight oxygens and an octahedral site coordinated by six oxygens, respectively. Ga(2) and (GaSi)(3) occupy tetrahedral and trigonal-pyramidal sites, respectively. They are coordinated by four oxygens.

X-ray diffraction (XRD) of  $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$  indicates the presence of two isostructural solid solutions with  $a = 8.16 \div 8.19 \text{ \AA}$ ,  $c = 5.09 \div 5.11 \text{ \AA}$  (I) and  $a = 8.11 \div 8.16 \text{ \AA}$ ,  $c = 5.06 \div 5.09 \text{ \AA}$  (II). Based on the crystal structure of  $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ , it is reasonable to assume that the difference in composition may arise from variations in the occupancies of Ga and Si on the (GaSi)(3) site. The cell parameters of the stoichiometric composition (Ga=Si) is  $a \sim 8.163$ ,  $c \sim 5.092 \text{ \AA}$ .

The XRD examination of  $\text{La}_3\text{Ga}_4[\text{Ga}(\text{Si},\text{Ge})]\text{O}_{14}$  and  $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$  with the different ratio of the Ga:Si (Ga>Si and Si>Ga), in conjunction with a crystallochemical analysis, shown a point defects formation into the crystals according to the following quasi-chemical reactions:



Moreover, it is possible the formation of their associates, mainly the  $(\text{V}_{\text{O}}^{\cdot\cdot}, 2\text{e}')^{\text{x}}$  associates- two electrons localized at an oxygen vacancy:



An analysis of obtained data does not exclude an orange color of crystals with Si>Ga and Ga>Si which is caused by presence of the  $(\text{V}_{\text{O}}^{\cdot\cdot}, 2\text{e}\phi)^{\text{x}}$  associates into crystals. These associates are formed by the reactions 8 and 7, respectively. In the last case an appearance of the crystal color is due to the ratio of the  $\text{V}_{\text{O}}^{\cdot\cdot} : (\text{V}_{\text{O}}^{\cdot\cdot}, 2\text{e}')^{\text{x}}$ : by the  $\text{V}_{\text{O}}^{\cdot\cdot} < (\text{V}_{\text{O}}^{\cdot\cdot}, 2\text{e}')^{\text{x}}$  the crystals are colored, by the  $\text{V}_{\text{O}}^{\cdot\cdot} > (\text{V}_{\text{O}}^{\cdot\cdot}, 2\text{e}')^{\text{x}}$  - crystals are colorless.

We observed the polarity reversal of structure of langasite crystals having various compositions. Assuming that the Ga and M atoms can occupy of the (GaM)(3) sites both orderly and part-orderly, it is possible the reduction of symmetry of langasite from P321 to P3.

According to our and literature data there are relationship between the ionic radii, on the one hand, and piezoelectric constants ( $d_{ij}$ ), the electromechanical coupling factors ( $k_{ij}$ ), the relative dielectric coefficients ( $\epsilon_i$ ), the elastic stiffness coefficients ( $c_{ij}$ ), and elastic compliances ( $s_{ij}$ ), on the other hand.

**s8.m27.p25 High-Resolution XRD and Imaging Polycrystalline Microstructures by Moving Area Detector with High-Energy Synchrotron Radiation.** L. Wcislak<sup>1</sup>, H.J. Bunge<sup>2</sup>, H. Klein<sup>3</sup>, U. Garbe<sup>4</sup>, J.R. Schneider<sup>4,1</sup>, Department of Physics at the University of Denver and NIST at Boulder in Colorado, USA, <sup>2</sup> Department of Physics and Physical Technologies, Technical University of Clausthal, Germany, <sup>3</sup> Department of Crystallography, University of Gottingen, Germany, <sup>4</sup> Hamburg Synchrotron Radiation Laboratory HASYLAB at DESY, Hamburg, Germany. E-mail: wcislak@boulder.nist.gov

**Keywords: High-resolution XRD; Moving area detector; High-energy synchrotron radiation**

Crystalline solid materials are usually polycrystalline, often also polyphase. They consists of very many, small crystalline units ( *crystallites / grains* ) separated from each other by grain boundaries. The polycrystalline aggregate is characterized by the *locations and orientations* of all crystallites, the orientation stereology. The majority of physical properties of single crystals, e.g. mechanical (elasticity- plasticity), magnetic, electric, thermal, optical, acoustic properties are anisotropic. Hence, the physical properties of polycrystalline solid materials depend both on the *anisotropy* of individual crystallites and their *orientation distribution* (texture) in the material. This holds for all classes of crystalline materials including metals, their alloys, ceramics, glasses, polymers and composites but also geological and biological materials. Nano-, meso-, microstructure determination is therefore necessary in order both to understand and shape the physical properties of polycrystalline materials of any kind. This is particularly the case for materials used in advanced technologies (superconductivity, magnetism, photonics) where optimum property values of the material must be guaranteed.

The classical technique to study polycrystalline structures is by *x-ray diffraction*. Later the same technique has become available with *neutrons* and *electrons*. The main differences between these radiations are their *penetration depths*, *orientation or location resolutions* and more practical aspect; the *beam intensity* and *source brilliance*. The large *penetration power* in mm to cm range (even for medium and large Z number elements) of high-energy synchrotron x-rays photons in matter opens quite new possibilities of structural analyses in polycrystalline materials. It becomes possible to measure non-destructively the fundamental structural parameters of matter including the size, shape and arrangement of grains of several phases as well as crystallographic orientations of the crystallites in each phase. This allows the quantitative determination (real-time imaging and / or mapping) of nano-, meso-, and microstructures (layers, interfaces, coatings, textures, strains, size, stereology, anisotropy) and the prediction, controlling, shaping the macroscopic physical properties of the material such as deformability, fatigue strength, and various electrical, magnetic, optical properties.

At HASYLAB, hard x-rays up to 100 keV (photon wavelength  $\sim 0.1 \text{ \AA}$ ) are available at the storage rings DORIS and PETRA. This radiation has penetration depths up to several mm or even cm, in most materials, comparable with neutrons. It has small beam divergences in the range of some milliradians and extremely high intensities so that small beam spots in the range of  $\mu\text{m}$  can be used. The BW5 diffractometer is equipped with a 4-circle goniometer, an on-line image plate detector for the registration of diffraction images and additionally with a Bragg-angle slit system to select a sector of a chosen Debye-Scherrer cone to reach the area detector. In order to attain highest measuring resolution, conventional 'step-scan' technique was replaced by a continuous 'sweeping' technique using a moving area detector mode. The results obtained give quite new insight into the microstructure development in crystalline materials, processes kinetics, phenomena dynamics (including phase transitions, pressure and / or temperature dependent structural changes in advanced materials; polymers, shape memory alloys, ceramics, glasses, composites) and the underlying physical processes.