

Stability of PbWO_4 crystal lattice

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An attempt has been done to precise the conditions of the PbWO_4 crystal structure stability under account for the existence possibility of two structure types. Diffraction patterns obtained at different temperatures up to 1000°C show neither changes in the crystal structure nor phase transitions. The PbWO_4 crystals grown in atmosphere enriched in Ar have been shown to have a high transmittance and no significant absorption in the region of the additional absorption band at 350 nm and no band at 420 nm. Changes in the crystal optical properties due to high-temperature annealing at 1000°C in air, dynamic and static vacuum, water vapor and lead vapor are considered.

Сделана попытка уточнить условия стабильности кристаллической структуры PbWO_4 , учитывая возможность существования двух структурных типов. Дифрактограммы, снятые при температурах до 1000°C , не обнаружили изменений кристаллической структуры и присутствия фазового перехода. Показано, что кристаллы PbWO_4 , выращенные в среде, обогащенной аргоном, отличаются высокой прозрачностью и незначительным поглощением в области полосы дополнительного поглощения 350 нм и отсутствием полосы 420 нм. Анализируются изменения оптических свойств кристалла в результате высокотемпературного отжига при 1000°C в воздухе, динамическом и статическом вакууме, парах воды и свинца.

Molybdenum and tungsten oxycations form a series of compounds having a simple stoichiometric composition of general formula ABO_4 with bivalent cations of II and VIII Groups as well as with Cu, Mn, and Pb ions. Tungstates and molybdates belonging to the class of so-called self-activated crystal luminophors emit in the visible spectral region under excitation with short-wave UV light, gamma, X-rays and cathode rays. In the tungstate series, the wolframite structure type transits to the scheelite one at the Cd–Ca bound while in the molybdate series, at the Mn–Cd one. Lead tungstate is believed to may crystallize itself in two structure types, namely, as sheelite $\beta\text{-PbWO}_4$ (stolzite) due to a large ionic radius of Pb^{2+} and as wolframite $\alpha\text{-PbWO}_4$ (raspite) basing on polarization effect [1, 2]. In laboratories, only PbWO_4 crystals of the scheelite struc-

ture are obtained from the melt while those of the raspite structure are found only in some deposits (Broken Hill, Australia; Schwarzwald, Germany; etc.). The crystals grown in laboratory conditions are in a stressed state, but no failures ascribable to the crystal structure change are observed.

To date, the absorption and emission of tungstates and molybdates are believed to occur in one and the same atomic configuration [1]. In particular, this may be a W (or Mo) configuration with neighboring oxygen atoms that is common for both compounds. A specific feature of lead tungstate is to be noted here. The luminescence under X-ray excitation can be observed in 420–450 nm range (blue emission) or in 510–550 nm one (green emission). There are numerous models [3, 4] that elucidate the nature of those emission bands, but the question is not fully understood. Similarly, the additional