Post-annealing green luminescence of sulfate crystals

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Alkali sulfate crystals M_2SO_4 (M = K, Rb, or Cs) have been shown to exhibit an intense luminescence after annealing in vacuum at temperatures near structure phase transition points. The luminescence is similar to that of donor-acceptor pairs in $A^{II}B^{VI}$ semiconductors in its behavior depending on temperature, the exciting radiation power, etc. Consideration of data obtained has shown that the luminescence mentioned is similar in characteristics to that of donor-acceptor pairs in CdS crystal. It is supposed that due to heat treatment, microcrystalline inclusions of metal sulfides, M_2S, are formed in the sulfate crystals. The gap width have been estimated for those crystallites as well as the energy characteristics of donor-acceptor pairs formed therein.

Показано, что кристаллы сульфатов щелочных металлов M_2SO_4 (M = K, Rb и Cs) после их отжига в вакууме при температурах, близких к температурам структурных фазовых переходов, обнаруживают интенсивную люминесценцию, которая по своему поведению в зависимости от температуры, мощности возбуждающего излучения и т.п. подобна люминесценции донорно-акцепторных пар в полупроводниковых материалах группы $A^{II}B^{VI}$. Анализ полученных результатов показал, что эта люминесценция близка к характеристикам люминесценции донорно-акцепторных пар в кристалле сульфида кадмия CdS. По совокупности данных сделано предположение, что вследствие термообработки в кристаллах сульфатов образуются включения микрокристаллов сульфидов щелочных металлов M_2S. Выполнены оценки как ширины запрещенной зоны для этих кристаллитов, так и энергетических характеристик донорно-акцепторных пар, которые в них образуются.

Alkali metals sulfate M_2SO_4 (M = K, Rb and Cs) crystals are similar to each other in crystal structure and in peculiarities of temperature phase transformations [1, 2]. The unit cell of the crystals includes four formula units; besides, the crystals are characterized by the same space symmetry group $P_{mna} \equiv D_{2h}^{16}$ in the low-temperature β-phase (existing at $T < 860$ K for K_2SO_4 crystals and at $T < 930$ K for Rb_2SO_4 one).

Tetrahedral molecular anions (MA) are the main crystal elements: these MA determine its main properties. The reorientation of SO_4^{2-} molecular anions for K_2SO_4 crystals starts at $T \cong 673$ K when the temperature increases from room temperature ($T = RT$) and then a turn of SO_4^{2-} anion about (001) axis becomes possible at the point of first-order phase transition ($T \sim 860$ K). So, these crystals are characterized with intermediate incommensurate phase in the temperature range 860 to 864 K. The space symmetry group is $P63/mmc \equiv D_{6h}^4$ at the high-temperature hexagonal α-phase (for K_2SO_4 crystals, at $T > 860$ K and at $T > 930$ K for Rb_2SO_4 ones). The transformations noted above are rather slow, so that several phases may exist simultaneously after crossing of the phase transition temperature point.

Besides, some chemical transformations occur in the crystal composition due to heating [3, 4]. Then, the crystals grown from water solution are destroyed under