Near-IR luminescence in bismuth-doped AgCl crystals

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Experimental and computer-modeling studies of spectral properties of crystalline AgCl doped with metal bismuth or bismuth chloride are performed. Broad near-IR luminescence band in the 0.8–1.2 µm range with time dependence described by two exponential components corresponding to the lifetimes of 1.5 and 10.3 µs is excited mainly by 0.39–0.44 µm radiation. Computer modeling of probable Bi-related centers in AgCl lattice is performed. On the basis of experimental and calculation data a conclusion is drawn that the IR luminescence can be caused by Bi+ ion centers substituted for Ag+ ions.

During the last decade bismuth-doped bulk glasses and optical fibers are extensively investigated due to their characteristic broadband IR luminescence in the 1.0–1.7 µm range, enabling one to develop optical lasers and amplifiers for fiber-optic communication systems (e.g., see review [1]). However the origin of bismuth-related IR luminescence centers is not established yet, thus impeding the development of this field. Recently (see, for example, discussion in Ref. [2]) an opinion is strengthened that the IR luminescence is caused by bismuth in subvalent states, and first of all in monovalent state (Bi+). To study the optical characteristics of bismuth-related centers of such a nature it is convenient to use crystalline halides of monovalent elements as a modeling host with a simple structure (primitive, Pm3m, or face-centered, Fm3m, cubic lattices), in which the impurity bismuth should form substantial centers just in monovalent state.

The IR luminescence in bismuth-doped crystalline halides of monovalent metals was found and investigated for the first time in CsI:Bi (primitive Pm3m lattice), and possible structure of the centers responsible for the luminescence were suggested [3, 4]. Later the IR luminescence was observed in TiCl3:Bi crystals (Pm3m lattice) [5]. Probable IR luminescence centers in CsI and TiCl3 were studied then by computer simulation technique [6, 7].

The present paper is devoted to the study of IR luminescence in AgCl:Bi crystals with face-centered Fm3m lattice.

The crystal was grown from silver chloride salts deposited from aqueous AgNO3 solution after drying and purification by the method of directional (oriented) melt crystallization. Before growth 30 g of AgCl ligature with metal bismuth (Bi) or bismuth chloride (BiCl3) dopant (0.076 mass.% of Bi) were prepared. Ligature was sealed in vacuum inside 16 mm-diameter ampule and melted at 400–450 °C. The melt was mixed no less than 5–6 times by the method of ampule reverse (flip-chip) and cured for 3 days. After cooling to room temperature the ligature was overloaded into the growth ampule 18 mm in diameter, supplied with pure silver chloride to total 100 g, melted in vacuum, mixed 3–5 times again and grown up by Bridgman-Stockbarger method at a rate of 1 mm/h. Growth was proceeded for about 7 days. After growth the crystal was quenched to room temperature at a rate of 50–60 °C/h. BiCl3-doped samples have appeared to be dim or opaque. In samples doped with metal bismuth the inclusions in the form of metal flakes (presumably silver) were observed. For spectroscopic measurements two samples of 18 mm diameter and 5 mm thickness were cut from the grown crystals, one from initial part of the crystal (where crystallization starts during crystal growth), and the other from the final one (where crystallization ends). X-ray diffraction (XRD) analysis of powders of all the samples was performed on DRON 3M diffractometer using filtered Cu Kα radiation. JCPDS database was used to identify crystalline phases. The XRD measurements revealed diffraction patterns typical for rock-salt-type AgCl crystal (Fig. 1). Lattice constant was found to be 0.5596(1) nm in metal-doped AgCl and 0.5574(1) nm in BiCl3-doped AgCl (to be compared with 0.5597(1) nm in reference non-doped AgCl crystal).

The transmission spectra were measured on Perkin-Elmer Lambda 900 spectrometer, and the luminescence spectra on Edinburgh Instruments FLSP920 spectrometer. The transmission spectra of two samples are shown in Fig. 2. The short-wave transmission edge of AgCl sample doped with metal bismuth is near 0.41 µm that fits well with the known experimental data for pure AgCl (transmission edge is near 0.42 µm [2], indirect energy gap is about 3.2 eV [8]). In AgCl samples doped with bismuth chloride a considerable decrease in transmission is observed in the near IR range. In the spectra of both samples there are no distinctly expressed absorption bands.

In the luminescence spectra a wide IR luminescence

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band is discovered with a maximum near 0.90 µm and width about 0.30 µm (Fig. 3). The luminescence in this band is excited mainly in the absorption band with a maximum near 0.42 µm (Fig. 4). The efficiency of luminescence excitation at other wavelengths is much lower. No luminescence is found in AgCl samples containing no bismuth.

The intensity of IR luminescence in AgCl samples doped with metal bismuth is considerably (about two times) higher in comparison with the samples doped with bismuth chloride. On the other hand, in metal-doped AgCl samples the luminescence intensity noticeably changes along the grown crystal length: the sample cut from the final part exhibits much more intensive luminescence. This fact could be explained by bismuth displacement together with the moving crystallization zone resulting in the content of active bismuth centers increasing from initial part to the final part of the produced crystal.

The suppression of IR luminescence from measurement to measurement is found out: with each new irradiation of the sample near the main excitation band, i.e. within 0.39–0.44 µm range, the luminescence intensity decreases. At the same time, the shape of the luminescence spectrum actually does not change. At excitation in a longer-wave range, e.g. near 0.53 µm (Fig. 4), the effect of degradation is practically absent; however the efficiency of luminescence excitation is extremely low.

Time dependence of IR luminescence is described by two exponential components \( a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \), where \( a_1 \approx 0.2, a_2 \approx 0.8 \) (in arbitrary units), \( \tau_1 \approx 10.4 \mu s, \tau_2 \approx 1.5 \mu s \). Within the fitting accuracy (about 10%) these parameters do not differ in metal-doped and chloride-doped samples. The luminescence lifetimes are considerably shorter than those in CsI:Bi (130 and 210 µs [3, 4]) and in TlCl:Bi (200–350 µs [5]) crystals, presumably due to high degree of disorder typical for cation sublattice in AgCl crystals.

Transmission decrease in the near IR range in BiCl₃-doped AgCl samples can be explained by the fact that for such a doping technique bismuth is incorporated in the crystal lattice mainly in trivalent state (Bi³⁺), substituting for silver ion. This substitution should be accompanied by a formation of two cation vacancies compensating an excess charge of substitutional center. Thus, instead of three sites with monovalent cations there are: a site with trivalent cation, two cation vacancies and two monovalent interstitial Ag⁺ ions (in other words, two Frenkel pairs). Similar lattice disordering can be followed by an increase both in scattering and absorption near the shortwave edge as a result of occurrence of localized states in the forbidden zone. In the case of metal doping, bismuth is most likely introduced in the crystal lattice mainly as monovalent substitutional impurity (Bi⁺), without causing an appreciable lattice disordering, and accordingly, a significant absorption or scattering. Rather low intensity of IR luminescence of BiCl₃-doped AgCl samples in comparison with metal-doped AgCl samples can be presumably explained just by considerable optical losses in the first-type samples.

To understand the origin of bismuth-related centers responsible for the revealed IR luminescence, we performed computer simulation of the structure and absorp-
FIG. 3. Luminescence spectra excited at 0.42 µm wavelength: (a) AgCl doped with bismuth chloride; (b) AgCl doped with metal bismuth.

FIG. 4. Excitation spectrum of 0.90 µm luminescence in AgCl sample doped with metal bismuth.

FIG. 5. Energy levels and transitions between them calculated for monovalent substitutional bismuth center Bi⁺.

For all bismuth-related centers studied there are bases to consider the Stokes shift small and to estimate the luminescence wavelength without taking the shift into account. Detailed description of the calculation technique is given in Refs. [5, 6].

Calculation results on bismuth-related centers are convenient for interpreting within the limits of the models used earlier for bismuth-related centers in TlCl:Bi, CsI:Bi, [5], SiO₂, and GeO₂ [6]. As is known, the ground and the first two excited states of Bi⁺ ion arise from 3P triplet (an electronic configuration 6s²p²) split by strong spin-orbit interaction into components: 3P₀ (ground state), 3P₁ and 3P₂ (excited states with the energies for a free ion near 13300 and 17000 cm⁻¹, accordingly). These states can be split and mixed under the influence of the environment of the Bi⁺ ion in the crystal lattice.

In the case of monovalent substitutional Bi⁺ center such a transformation of states is due to a redistribution of electronic density between the bismuth ion and the neighboring chlorine ions, but is not due to the crystal field (owing to a cubic symmetry of the substitutional center). According to the calculations, in AgCl:Bi such a redistribution appears to be rather weak. Energy levels and transitions between them calculated for monovalent substitutional bismuth center Bi⁺ are shown in Fig. 5.

It is worth noticing that splitting the first excited state 3P₁ is insignificant. Considering in accordance with the above-said the Stokes shift to be small, one could expect for monovalent substitutional bismuth center, Bi⁺, the...
FIG. 5. Calculated levels and transitions of impurity substitutional Bi$^+$ center (energy levels in $10^3$ cm$^{-1}$, transition wavelengths in µm).

occurrence of IR luminescence in the 0.9–1.0 µm region excited in two absorption bands near 0.4 and 0.5 µm.

Calculation results have shown that the influence of AgCl lattice on other bismuth-related centers under study is substantially reduced to the crystal field effect and in a qualitative sense is described by the model similar to that suggested in Ref. [11] and used in Refs. [5, 6]. However, we should emphasize that although this model allows visual interpreting of the origin of states in bismuth-related centers, it describes the occurring electronic structure only in the rough. The quantitative conclusions are based on the performed calculation results.

In the case of interstitial Bi$^+$ ion the crystal field appears to be too weak and causes only insignificant splitting and shift of ion states. Therefore the interstitial Bi$^+$ ion in AgCl, like Bi$^+$ ions in chloride solutions [12], can cause a weak absorption in the bands near 0.7, 0.6 and 0.5 µm, accompanied by a luminescence near 0.7 µm. The experimental data available do not allow to make certain conclusions about the presence or absence of interstitial Bi$^+$ ions in AgCl:Bi.

On the contrary, in the complex formed by substitutional bismuth center and chlorine vacancy in the nearest lattice site, the crystal field appears to be strong. Thus there is a redistribution of electronic density between bismuth atom and chlorine vacancy, so that in rough approximation such a complex represents a pair of charged centers: Bi$^+$ ion in cation site and negatively charged chlorine vacancy. In axial crystal field influenced by the vacancy, the ground state of Bi$^+$ ion ($^3P_0$) is not split at all, the excited $^3P_1$ state is split into two levels with the energies about 4400 and 10500 cm$^{-1}$, and the excited $^3P_2$ state is split into three levels with the energies about 12000, 17000 and 22000 cm$^{-1}$. Considering the Stokes shift to be small, it is possible to expect for the complex “substitutional bismuth center — chlorine vacancy” the IR luminescence in the > 2.0 µm region, and probably in the 1 µm region, excited in absorption bands near 0.8, 0.6 and 0.4 µm. As follows from a comparison of these results with the experimental data, similar complexes can make only an insignificant contribution to the IR luminescence observed in AgCl:Bi.

As to the complex “substitutional bismuth center — silver vacancy”, it was found to be highly unstable in our calculations: owing to lattice transformation in the vicinity of the complex, silver ion from the next coordination shell fills the vacancy and so the complex actually disappears.

Thus, the performed modeling gives the grounds to believe that the main contribution to the IR luminescence in AgCl:Bi is made by monovalent substitutional bismuth centers, Bi$^+$. In this case an observable decrease in intensity of the luminescence excited in absorption band near 0.42 µm can be explained. Radiation with wavelength close to the edge of interband absorption of AgCl excites the electron-hole pairs. Capturing electrons from the conductivity band, monovalent substitutional bismuth centers Bi$^+$ are restored to neutral Bi$^0$ centers, making no contribution to the IR luminescence.

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