STIMULATED EMISSION AND SPECTROSCOPIC INVESTIGATIONS OF DOUBLE LANTHANUM-SODIUM MOLYBDATE SINGLE CRYSTALS WITH NEODYMIUM IMPURITIES

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A single crystal of double lanthanum-sodium molybdate containing a neodymium impurity was investigated spectroscopically. This crystal is of interest as a possible active substance for lasers. Optical and EPR data yielded an explanation as to why the Nd^{3+} ion spectrum lines were broader than the corresponding lines in crystals of the $CaWO_4$ type. The relative quantum yield of the luminescence of Nd^{3+} ions in $NaLa(MoO_4)_2$ crystals was measured as a function of the active ion concentration. Stimulated emission in the crystal was observed at room temperature with a threshold of 5.5 J.

CRYSTALS of double molybdate and tungstate type [$Na(RE)(MoO_4)_2$ and $Na(Re)(WO_4)_2$, where RE is a rare earth] are interesting as possible active materials for lasers. Introduction of trivalent rare-earth ion dopants into these crystals does not require charge compensation, and such crystals can be grown with any concentration of the active ion, right up to complete substitution.

Peterson and Bridenbaugh[1] investigated $NaGd(WO_4)_2$ crystals with Nd^{3+} ion impurities. They established that the width of the luminescence line of these crystals was 30 times greater than the corresponding width of the neodymium line in $CaWO_4$. Nevertheless, these crystals emitted stimulated radiation at room temperature. A footnote in Peterson and Bridenbaugh's paper mentioned that Johnson and his colleagues achieved stimulated emission in a $NaLa(MoO_4)_2$ crystal doped with Nd.

A study of $NaLa(MoO_4)_2$ single crystals with Nd^{3+} ion impurities is undoubtedly of interest in connection with lasers, because such crystals are transparent over a wide range of wavelengths.[2] Moreover, we may expect the width of the bands in the absorption spectrum of the active ion to be greater in such crystals than the corresponding width in $CaWO_4$-type crystals, which should help in making more efficient use of the light from the pumping lamps. On the other hand, such single-crystals have a thermal conductivity which is high compared with glass: equal to ≈22 mW-cm^{-1} deg^{-1} at room temperature.[1)] Heindl et al.[3] reported that $NaLa(MoO_4)_2$ crystals with neodymium im-

purities emitted stimulated radiation.

The present paper reports an investigation of the optical spectra of single crystals of $NaLa(MoO_4)_2$ (we shall denote this by NLM) with neodymium impurities, as well as the EPR and stimulated emission spectra of such crystals. Crystals with a range of concentrations of neodymium were grown by the Czochralski method.[4]

The investigation of the luminescence and absorption spectra was carried out using diffraction monochromators: DFS-12 with an FÉU-22 photomultiplier and MDR-2 with a PbS photoresistor. The investigated crystals were in the form of unpolished cylinders, whose geometrical axes were parallel to the optical axes. In the investigation of the luminescence spectra, the optical axis was parallel to the entry slit of the monochromator.

The absorption spectrum of an NLM crystal containing neodymium impurity was similar to the spectra of $CaWO_4$[5] and $SrMoO_4$ crystals. However, the lines in the spectrum of the NLM crystal were somewhat broader, as shown in Fig. 1, which gives parts of the absorption spectra of the Nd^{3+} ion in NLM and $SrMoO_4$ crystals.

The luminescence spectra in the wavelength range $\lambda \approx 0.9$ and $1.06~\mu$ are shown in Figs. 2 and 3. These spectra are similar to the spectrum of the Nd^{3+} ion in a single crystal of $SrMoO_4$. However, the lines are considerably broader in the case of NLM crystals. The lines become somewhat narrower on cooling the crystal to liquid nitrogen temperature (Fig. 3), but they still remain considerably broader than in the case of $SrMoO_4$.

We investigated crystals with Nd concentrations of 0.05, 0.5, 1.0, 2.0, 4.0, 10, 20, and 100%.

[1)]The thermal conductivity of a $NaLa(MoO_4)_2$ crystal was measured by N. N. Stupachenko.

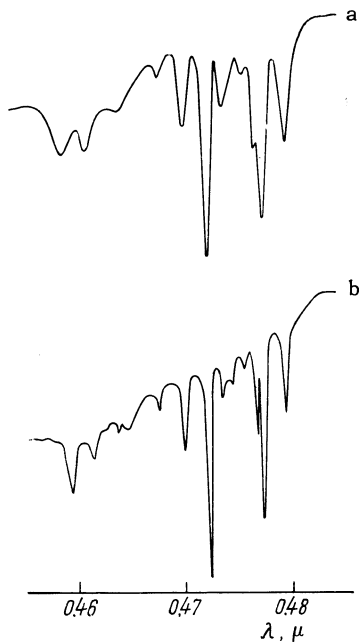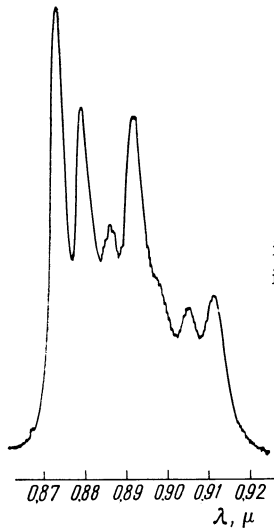FIG. 1. Absorption spectra of the Nd^{3+} ion in single crystals of: a) $NaLa(MoO_4)_2$; b) $SrMoO_4$. T = 77°K.

FIG. 2. Luminescence spectrum, in the region of 0.9 μ, of the Nd^{3+} ion in an $NaLa(MoO_4)_2$ crystal; T = 300°K.

FIG. 3. Luminescence spectrum, in the region of 1.06 μ, of the Nd^{3+} ion in an $NaLa(MoO_4)_2$ crystal.

The spectral line widths were practically the same for all concentrations. Thus, the observed line width cannot be due to the interaction with the crystal lattice or to the interaction of ions with one another. The observed line width is probably associated with changes in the crystal field parameters at the sites of neodymium ions due to incomplete order in the distribution of La^{3+} and Na^+ ions in the lattice.

To check this hypothesis, we determined the EPR spectrum of the Nd^{3+} ion in an NLM single crystal at a frequency of 15 Gc at helium temperature. The EPR line was found to be two orders of magnitude broader than the line in ordinary
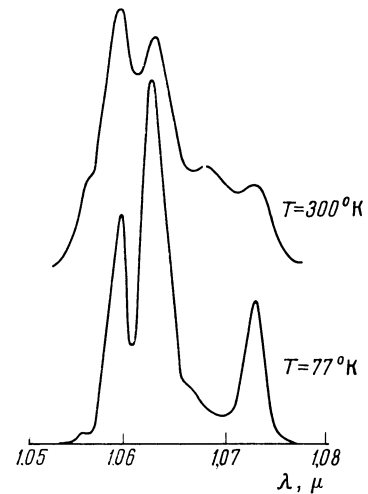
scheelites: for the H ‖ C orientation (where C is a fourfold axis) the width at half-amplitude was 2500 Oe. The value of the g-factor for this orientation ($g_{\|}$) was 1.74: the values of the g-factor corresponding to the points at half-amplitude points were ≈ 1.45 and 2.20.

Examination of the parameters of unit cells in the molybdate series shows that NLM lies between $CaMoO_4$ and $SrMoO_4$ crystals (cf. table).

The values of $g_{\|}$ for $CaMoO_4$ and $SrMoO_4$ are nearly the same as the values of $g_{\|}$ at half-amplitude for NLM. Thus, we may assume that, due to the disordered distribution of La^{3+} and Na^+ ions in the double molybdate lattice, the parameters of the crystal field at the sites of the activator ion range from the value corresponding to the $CaMoO_4$ lattice to a value close to that for the $SrMoO_4$ lattice.[2] Further confirmation of this hypothesis is provided by a comparison of the luminescence spectrum of Nd in NLM with a combined spectrum obtained by adding the spectra of neodymium in the $CaMoO_4$ and $SrMoO_4$ lattices (the spectra of all three crystals were recorded using the same instrument with the same resolution). It can be seen from Figs. 4 and 2 that these spectra are practically identical. The widths of the lines in the NLM spectrum are equal to the widths of the lines in the combined spectrum of $CaMoO_4$ and $SrMoO_4$. It is interesting to note that the narrower lines of the Nd^{3+} ion in the NLM

[2]In addition to a variation in the crystal field parameters, the disorientation of elementary oxygen octahedra can also make a contribution to the EPR line width. However, in this case we would expect an asymmetric EPR line profile, whereas in our case the EPR line was symmetrical.
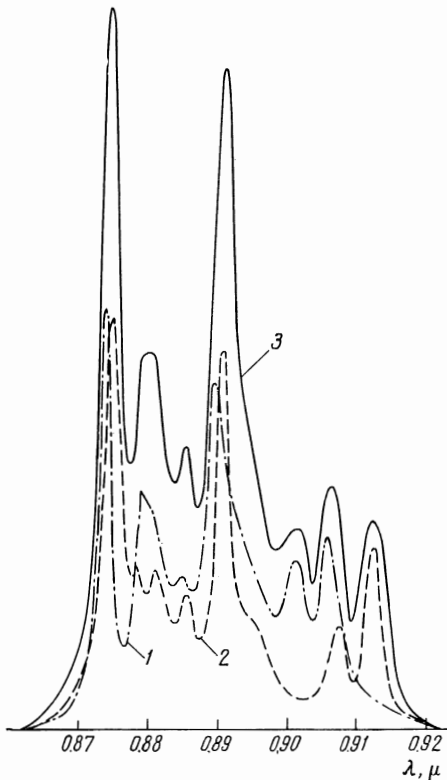
FIG. 4. Luminescence spectra of the Nd^{3+} ion in $SrMoO_4$ and $CaMoO_4$ (2) crystals at T = 300°K and the spectra for both crystals combined (3).

Crystal type	Cell parameters, Å		$g_{\parallel}$ of Nd^{3+} ion in crystals
	a	c	
$CaMoO_4$	5.23	11.44	2.024
$NaLa(MoO_4)_2$	5.33	11.70	1.74
$SrMoO_4$	5.38	11.97	1.44

spectrum correspond to those lines in the $CaMoO_4$ and $SrMoO_4$ spectra which show practically no shift on transition from one lattice to the other and, conversely, the broad lines of NLM correspond to those lines which shift on transition from $CaMoO_4$ to $SrMoO_4$.

The similarly-combined spectrum of the luminescence of Nd^{3+} ions in $SrMoO_4$ and $CaMoO_4$ crystals, obtained for the region $\lambda \approx 1.06\,\mu$, also coincides with the spectrum of NLM.

It seemed very interesting to measure the quantum yield of the luminescence of NLM crystals containing various amounts of neodymium. The relative value of the quantum yield was determined. Samples oriented in the same way were placed in an integrating sphere and excited with monochromatic light in the $0.58\,\mu$ band. A diffraction-grating monochromator was used for excitation; the width of the exciting spectrum was 70 Å. The luminescence in the region of $\lambda \approx 0.9\,\mu$

was selected with an IKS-3 optical filter; for the $\lambda \approx 1.06\,\mu$ region we used an interference filter. The light absorbed by a sample was estimated from the difference between the total intensity of the incident light and the intensity of the transmitted light.

Figure 5 shows the dependence of the quantum yield on the concentration of Nd^{3+} ion in the crystal. When the concentration was increased from 1 to 4% the quantum yield decreased by a factor of two. In our earlier investigations of $SrMoO_4$ crystals containing Nd^{3+} ions in concentrations falling within the same range, we found that the quantum yield decreased twice as much. The weaker concentration quenching of the luminescence in NLM indicated a weak resonance interaction of Nd^{3+} ions in the crystal lattice, which could have been associated with the large line width.
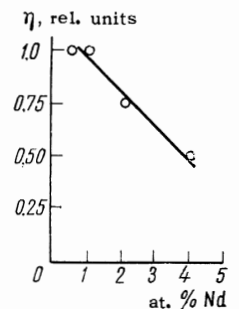

FIG. 5. Dependence of the luminescence quantum yield η on the concentration of Nd^{3+} ions in a single crystal of $NaLa(MoO_4)_2$; T = 300°K.

The lifetime of the $^4F_{3/2}$ level of the Nd^{3+} ion when present in a concentration of 1% in an NLM crystal was 190 μsec at room temperature. NLM crystals with 1% Nd (the samples were 35 mm long and of 4 mm diameter), when placed in an elliptical reflector, emitted stimulated radiation at room temperature, and the threshold for this emission was 5.5 J. An IFP-800 pulse discharge lamp was used for pumping. In a sample whose geometrical axis was parallel to the optical axis, the stimulated emission took place at a wavelength of 10 595 Å. The width of the line generated at room temperature was 5 cm^{-1} for a pumping level ten times the threshold value.

Thus, single crystals of double lanthanum-sodium molybdate with neodymium impurities were found to be active laser materials with a low generation threshold. The use of optimum (higher) concentrations of neodymium may further reduce the laser action threshold.

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