A chromium (Cr\(^{4+}\))-doped transparent glass-ceramic developed by researchers at Kyoto University (Kyoto, Japan) could lead to a new class of ultra-broad amplifiers for wavelength division multiplexing (WDM) applications.

Although the gain bandwidth of rare-earth-doped amplifiers is usually significantly less than 100 nm in near IR, depending on the host material, 3d-transition metal ions exhibit broadband emission in this area of the spectrum. Solid-state lasers such as alexandrite (Cr\(^{3+}\)) and titanium-doped sapphire are widely tunable between 1.1 and 1.6 \(\mu\)m. This means that if Cr\(^{4+}\) can be stabilized in a host material, activated material would be an excellent candidate for a new broadband amplifier for WDM.

“Tunable laser operations have been achieved in crystals such as Cr\(^{4+}\):YAG [Cr\(^{4+}\):yttrium aluminum garnet] and Cr\(^{4+}\):forsterite, but for light amplifiers, glass hosts are most favorable because they can easily be processed into fibers,” says Setsuhisa Tanabe, spokesman for the Kyoto group. “Unfortunately, the luminescence efficiencies of Cr\(^{4+}\) in glass are much lower than in crystals. So we focused on gehlenite \([\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7]\), in which Cr\(^{4+}\) can be stabilized. Cr\(^{4+}\) in gehlenite shows a broadband luminescence between 1.1 \(\mu\)m and 1.4 \(\mu\)m, centering at 1.24 \(\mu\)m,” explains Tanabe.

The team prepared a bulk glass of 50CaO-40Al\(_2\)O\(_3\)-10SiO\(_3\)-0.05Cr\(_2\)O\(_3\) composition as the starting material. The glass was melted in a platinum crucible in air at 1873K for one hour, annealed, and then cut into 10 \(\times\) 10 \(\times\) 3-mm samples. These were heat treated in two steps. The first step caused homogenous nucleation, while the second grew crystallites. Tanabe divided the samples into three batches, and differed the heat treatment for each. He based the heat-treatment conditions on differential thermal analysis of each sample.

Of three samples, sample A was not heat treated at all; sample B went through a nucleation cycle at 1183K for 6.5 hours and a growth cycle at 1273K for one hour; and sample C also went through the nucleation cycle and then a growth cycle at 1373K for one hour.

“The heat treatment obviously changed the samples,” Tanabe says. “The original sample was green. Once heat treated, sample B turned bluish green and sample C went deep blue. We subjected them to x-ray diffraction, which showed two kinds of crystals had formed—\(\beta\)-CaAl\(_2\)O\(_4\) and gehlenite.

That may mean that the temperature dependence of nucleation and growth rates of these two crystals are quite similar.”

Tanabe and his group tested the emission spectra of the three samples and found that the heat-treated ones show a single emission band that peaked at around 1240 nm (see figure 1). The untreated sample A showed two emission...
bands that peaked at 1350 nm and 1000 nm (see figure 2). “In addition, heat treatment measurably increased emission intensity,” Tanabe says. “We knew that polycrystalline Cr:gehlenite shows an emission band at around 1240 nm and that polycrystalline Cr:β-CaAl₂O₄ has a band at 1310 nm. This told us that the 1240-nm emission of samples B and C could be ascribed to Cr⁴⁺ ions in the gehlenite phase. That, we judged, confirmed that most of the Cr⁴⁺ and Cr³⁺ ions in the as-quenched glass were incorporated in the precipitated gehlenite crystallites as Cr⁴⁺ through heat treatment.” (See figure 3.)

Bill Brocklesby of the Optoelectronics Research Centre at the University of Southampton (Southampton, UK) says, “Cr⁴⁺ glass-ceramics are a very sensible research aim: The properties of the crystalline host combined with the mechanical properties of the glass form an ideal combination. The hosts developed by Tanabe look like the best transition metal candidates so far for use as an amplifier. The spectroscopic properties have to combine with favorable material properties, though, for a successful device.

“The spectroscopic properties of the Cr⁴⁺ ions as described seem ideal,” Brocklesby continues. “The spectrum is broad and centered in a very interesting region of the communications bands. However, the presence of a significant quantity of Cr³⁺ is not ideal. The selective incorporation of the Cr⁴⁺ into the crystallites will help this problem. The material properties necessary to get to a successful fiber device are more complex, however. The melting temperature and annealing temperatures of the material do not preclude its use in fiber, but much material engineering is necessary to get from the present work to a successful device. Glass-ceramic fibers have been shown to have low enough loss for active device work, so this development of Cr⁴⁺-containing material with good spectroscopic properties is very encouraging for the field.”

— Charles Whipple