

GROWTH OF ALEXANDRITE CRYSTALS AND INVESTIGATION OF THEIR PROPERTIES

G.V. BUKIN and V.N. MATROSOV

Institute of Geology and Geophysics, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk 630090, USSR

V.P. OREKHOVA, Yu.L. REMIGAILO and B.K. SEVASTYANOV

Institute of Crystallography, Academy of Sciences of the USSR, Moscow 117333, USSR

and

E.G. SYOMIN, V.P. SOLNTSEV and E.G. TSVETKOV

Institute of Geology and Geophysics, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk 630090, USSR

Optically homogeneous alexandrite crystals ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) up to 120 mm long and to 20 mm in diameter have been grown by the Czochralski method in an inert gas atmosphere using induction heating in iridium crucibles. There is a distinct growth rate anisotropy: maximum along [001], intermediate along [010], and minimum along [100] directions. The absorption, luminescence and excitation spectra have been investigated at 77 K, and comparison with the results obtained earlier at 300 K has been made. Pulsed lasing characteristics of alexandrite cylindrical specimens cut along the *c*-axis were studied at room temperature.

1. Introduction

Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) is a crystal which belongs to the chrysoberyl group of minerals (BeAl_2O_4 : iron group ions). Its structure is isomorphous with olivine, the space group is D_{2h}^{16} , orthorhombic, with four molecules per unit cell. The lattice parameters are: $a = 9.404 \text{ \AA}$, $b = 5.476 \text{ \AA}$, $c = 4.427 \text{ \AA}$ [1].

Cr^{3+} ions substitute isomorphically for two types of Al^{3+} ion in the chrysoberyl structure: Al^{3+} (I) in octahedral sites with a plane of symmetry and Al^{3+} (II) in octahedral sites with a center of symmetry. These chromium ions are designated Cr^{3+} (I) and Cr^{3+} (II).

Since natural alexandrite is a very attractive and expensive gemstone, but extremely rare, there have been many attempts to synthesize this crystal. The first experiments on the growth of chrysoberyl crystals consisted mainly in melting of a $\text{BeO} + \text{Al}_2\text{O}_3$ mixture in the presence of various mineralizers [2]. Later on, the molten solution technique [3], hydrothermal synthesis [4] and Verneuil method [5] were used. The

crystals obtained in these experiments were small and frequently contained inclusions of the crucible and flux materials.

The data on spectroscopic characteristics of alexandrite available in the literature until 1978 were usually obtained on natural minerals. Therefore, they were distorted by the presence of various impurities in these samples.

The first detailed measurements of the absorption spectra of artificially grown alexandrite crystals were described in ref. [6]. Optical generation at the R_1 -line with temperature adjustment of the lasing wavelength from 697.86 to 680.33 nm was obtained on an alexandrite crystal sample cut along the *a*-axis. The sample temperature was varied from 77 to 300 K [6]. Lasing at the R_1 -line at room temperature (680.33 nm) in alexandrite crystals cut along the *c*-axis has been reported in ref. [7]. In 1979 papers were published concerning *Q*-switch lasing at the R_1 -line [8] and on laser frequency adjustment from 701 to 794 nm [9].

Though the results of the above papers suggest that alexandrite is likely to become a promising

laser material, there are scanty data in the literature on its growth and physical properties. In this paper we present data on the synthesis and growth of alexandrite crystals, their absorption, luminescence, excitation spectra, and pulsed lasing at room temperature. Colour characteristics of the crystals doped with different combinations of iron group ions are discussed.

2. Chrysoberyl formation kinetics

Before growing chrysoberyl single crystals we attempted synthesis by solid phase reactions. Oxides, nitrates, and fluorides of beryllium and aluminium were used as the initial reagents. Chrysoberyl formation kinetics were studied in the temperature range from 600 to 1200°C. The synthesis was carried out according to a technique described previously [10]. The reaction products were determined by X-ray phase analysis, and kinetic curves (fig. 1) were plotted on the basis of the data obtained.

The well known formal kinetic equation for a diffusion process,

$$K\tau = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}, \quad (1)$$

was used to analyse the kinetic data obtained. Here α is the transformation degree, τ is the reaction duration (min) and K is a coefficient

proportional to the reaction rate constant. The activation energy was determined from the Arrhenius equation

$$K = C \exp(-E/RT), \quad (2)$$

where E is the activation energy (kcal/mole), R is the gas constant and T the temperature (K). To establish the mechanism of oxide interaction, we used the inert label method (with platinum as label) and layer-by-layer chemical analysis of the reaction products with respect to beryllium and aluminium. The position of layers of reacting substances, platinum label and the reaction product $\text{Al}_2\text{O}_3\text{-Al}_2\text{BeO}_4\text{-(Pt-label)-Al}_2\text{BeO}_4\text{-BeO}$ showed that the substance is transferred across the product layer via the counter-displacement of equivalent amounts of Be^{2+} and Al^{3+} ions. The mass transfer depended both on the technique of preparing the initial reagents and on their structural features. When using single-crystalline BeO, the substance was transferred across the reaction product layer mainly due to diffusion of Al^{3+} ions and when single-crystalline Al_2O_3 was used, the reaction proceeded mainly by diffusion of Be^{2+} ions. This indicates that defects in the reacting materials are of major importance in the process of solid-phase synthesis.

The mean activation energy of chrysoberyl formation is 17.3 kcal/mol when oxides are used. Heterophase additions of 4f element oxides into

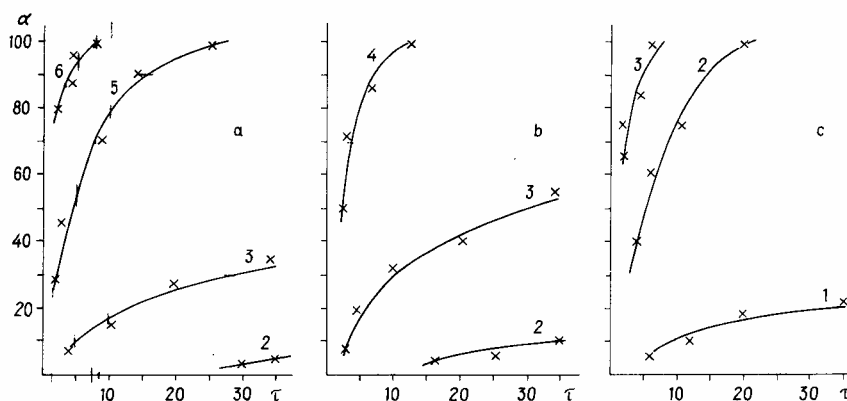


Fig. 1. Kinetic curves of chrysoberyl formation in the solid phase: (a) from oxides; (b) from nitrates; (c) from fluorides; α is the transformation degree (%); τ is the duration of the experiment (h). Temperature (°C) is: (1) 850; (2) 900; (3) 1000; (4) 1050; (5) 1100, (6) 1200.

the mixture $\text{BeO} + \text{Al}_2\text{O}_3$ led as a rule to decrease in the activation energy. This is likely to be related to the fact that quasi-amorphous phases with a high degree of disorder are formed as intermediate compounds. The formation of compounds with β -alumina structure, contributing to rapid mass transfer in the system, cannot be ruled out [11]. With the use of oxides (fig. 1a) the reaction is completed at 1100°C within 25 h and at 1200°C within 8 h. The use of nitrates reduces the temperature and duration of the reaction down to 12 h at 1050°C (fig. 1b) and of fluorides to 7 h at 1000°C (fig. 1c).

3. Crystal growth and morphology

Since BeAl_2O_4 melts congruently we used the Czochralski method with induction heating, iridium crucibles, and inert atmosphere to grow the crystals. The melting temperature of alexandrite is 2073 K. A special system of shielding thermocouples against high-frequency radiation permitted their use for investigating temperature fields in the melt. The temperature distribution along the crucible walls in the melt was almost uniform from 10 mm below the melt surface down to the bottom. However, in the central part of the crucible the temperature rose sharply 15 mm below the melt surface. This resulted in irregular convection and considerable temperature fluctuations. Their maximum value near the crystallization interface was 5.4°C , while near the crucible walls the fluctuations did not exceed 1.7°C .

In our experiments we have grown optical quality alexandrite crystals up to 120 mm long and up to 20 mm in diameter. It was found by ESR that increasing the chromium concentration in the crystals led to increase in the $\text{Cr}^{3+}(\text{II})/\text{Cr}^{3+}(\text{I})$ ratio [12]. Ions of the iron group, such as Fe^{3+} , V^{3+} , Ti^{3+} , Mn^{3+} , Co^{3+} and Ni^{3+} in small concentrations usually substitute for $\text{Al}^{3+}(\text{I})$ ions.

The crystallization was performed on seeds oriented along [100], [010] and [001] directions (crystal class mmm). Alexandrite crystals exhibit a distinct anisotropy of the growth rate: it is a maximum along [001] and a minimum along

[100] directions. The crystal rotation rate was chosen so as to make the crystallization interface as flat as possible. Its value depended on the crystal and crucible diameter and also on the thermal conditions in the melt.

Chrysoberyl single crystals grown by the Czochralski method are characterized by faceted and rounded growth shapes (figs. 2c–2e). The crystal morphology shows that there is a distinct trend for the crystal to become faceted with simple shapes typical for crystals grown under conditions close to equilibrium (figs. 2a and 2b). The formation of these shapes is almost independent of the growth conditions – pulling and rotation rate – and also of the thermal conditions in the melt. However, the growth regime may considerably affect the chrysoberyl growth rate anisotropy and as a consequence, the configuration of the crystal cross-section, and also the area of development of faceted shapes.

The cross-section of crystals grown along the [100] directions tends to be close to circular (fig. 2c). The {010} faces develop intensively as the melt supercooling decreases. If the seed is oriented along the [010] direction, the crystals have a flattened, plate-like shape and are characterized by the intensive development of stable {100} faces (fig. 2d). Crystals grown in the [001] direction are characterized by the development of stable {100} and {010} faces (fig. 2e).

4. Spectroscopic and lasing characteristics of alexandrite

In this part of the paper we present absorption, luminescence and excitation spectra of

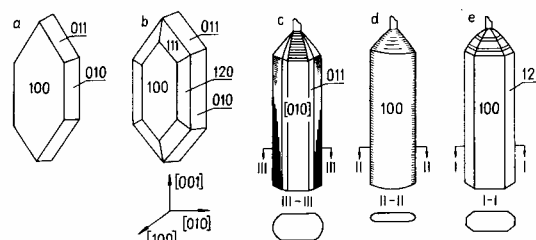


Fig. 2. Morphology of alexandrite crystals grown under various conditions: (a) CVD system; (b) natural sample; (c), (d), (e) Czochralski method.

alexandrite at 77 K and lasing properties at room temperature.

Fig. 3 shows the absorption spectra of alexandrite at 77 K. Comparing it with fig. 1 in ref. [6] we may conclude that the intensity of R-lines for polarization $E \parallel b$ increases sharply, exceeding the U-band intensity; the R-lines shift to the short-wavelength region by 8 Å. At 567, 468 and 471.2 nm B-lines ($4A_2 \rightarrow 2T_1$) are also clearly seen for polarization $E \parallel b$ and $E \parallel c$.

A distinct vibronic structure appears at the long-wavelength edge of the absorption band. For polarization $E \parallel c$ the vibronic structure also appears but much less than for polarization $E \parallel b$. It is interesting to note that for polarization $E \parallel a$ the vibronic structure does not arise, the B-lines are absent and the R-lines are very weak. The short wavelength part of the luminescence spectrum at 77 K is completely frozen-in while the long-wavelength part contains several doublet maxima (fig. 4). It can be seen that for polarizations $E \parallel c$ and $E \parallel a$ the luminescence intensity is much lower than for polarization $E \parallel b$.

Fig. 5 shows the excitation spectrum of the R_1 -line at 77 K. The pronounced similarity be-

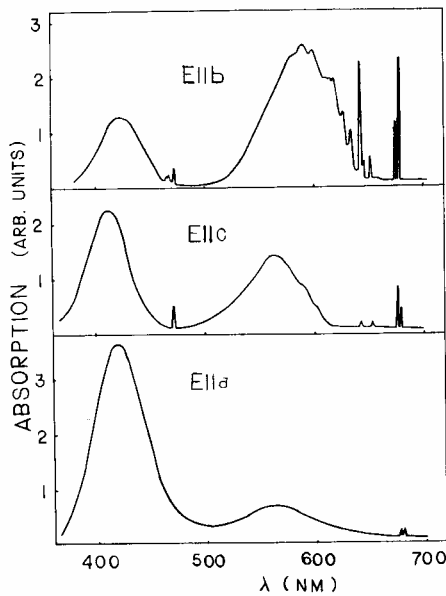


Fig. 3. Absorption spectrum of alexandrite ($T = 77$ K).

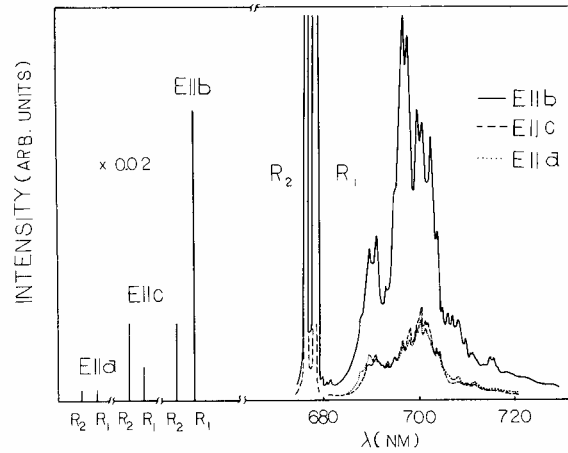


Fig. 4. Luminescence spectrum of alexandrite ($T = 77$ K).

tween this spectrum and the absorption spectrum for polarization $E \parallel b$ deserves special attention. The vibronic structure at the long-wavelength edge of the U-band is seen to be reproduced in the excitation spectrum.

Note an interesting phenomenon related to the narrow line at 643.5 nm and observed at 77 K both in absorption and excitation spectra. The fact that it is clearly seen in the excitation spectrum shows that this line can be attributed only to Cr^{3+} ions. According to its position in the absorption spectrum, this narrow line could be interpreted as an R_1 -line. But then it should be

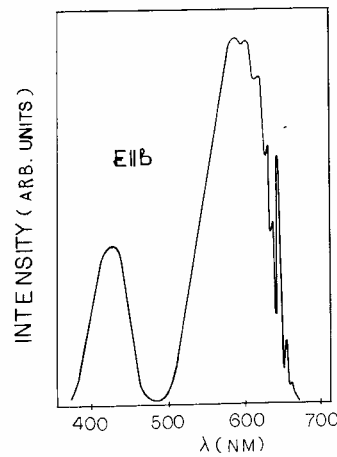


Fig. 5. Excitation spectrum of alexandrite; R_1 -line ($E_{exc} \parallel b$, $T = 77$ K).

observed in the luminescence spectrum, especially at low temperatures. However, the luminescence spectrum does not contain this line. At room temperature its intensity is so small that this line completely disappears in the absorption background. Its intensity sharply increases as the temperature is lowered. All this supports the suggestion that the narrow line in the absorption and excitation spectra at 643.5 nm is due to the phonon-free electron transition in the U-band. This result is very interesting since we are not aware of any such crystals doped with Cr^{3+} ions in which the phonon-free electron transition, causing the absorption U-band, would manifest itself so distinctly.

We have investigated the lasing characteristics of alexandrite. The specimen was a cylindrical rod 70 mm in length and 6 mm in diameter, cut along the *c*-axis. There were oscillation spikes at room temperature in the free lasing regime. The generation wavelength was found to be 680.33 nm at room temperature. The alexandrite specimen lasing threshold in our experiments coincides approximately with that of a ruby rod with the same geometrical parameters.

References

- [1] E.F. Farrell, J.H. Fang and R.E. Newnham, *Am. Mineralogist* 48 (1963) 804.
- [2] C.K. Deville and H. Caron, *Compt. Rend. (Paris)* 46 (1958) 764.
- [3] C. Palache, H. Berman and C. Frondel, *System of Mineralogy* (New York, 1944).
- [4] D. Rukl and J. Bauer, *Kristall Tech.* 3 (1969) 361.
- [5] J. Bauer, in: *Celostrati Konf. o Monikrystalech*, 1959, p. 210.
- [6] G.V. Bukin, S.Yu. Volkov, V.N. Matrosov, B.K. Sevastjanov and M.I. Timoshechkin, *Kvantovaya Elektronika* 5 (1978) 1168.
- [7] R.C. Morris and C.F. Cline, *US Patent* 3,997,853, Dec. 14, 1976.
- [8] 1979 *IEEE/OSA Conf. on Laser Engineering and Applications*, Washington, DC, 1979.
- [9] J.C. Walling, H.P. Jenssen, R.S. Morris, E.W. O'Dell and O.G. Peterson, *Opt. Letters* 4 (1979) 182.
- [10] E.G. Syomin, L.V. Zubenko, V.M. Manakov and V.P. Zubenko, *Zh. Neorg. Khim.* 21 (1975) 273.
- [11] E.G. Syomin, V.Ya. Hentov, D.V. Balashov and A.S. Migonadgiev, *Izv. Vysshykh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.* 15 (1972) 1456.
- [12] G.V. Bukin, A.V. Eliseev, V.N. Matrosov, V.P. Solntsev, E.I. Kharchenko and E.G. Tsvetkov, in: *Proc. 11th General Meeting IMA, Novosibirsk, 1978* (Nauka, Moscow, 1980) p. 317.