

LUMINESCENCE OF Cr³⁺ IN NATURAL AND CALCINED DIASPORE

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Abstract

The luminescence of Cr³⁺ in natural and calcined diaspoire is applied to probe structural properties of the phases. Steady-state luminescence spectra of the natural diaspoire [α -AlO(OH)] are typical of ²E→⁴A₂ transitions of Cr³⁺ luminescence centers (R-lines) substituting for Al³⁺ in six-fold coordination. The dehydroxylated phase of the diaspoire is characterized by a low degree of crystallinity. This phase is not detectable by XRD and Raman spectroscopy up to 900°C. The time-resolved luminescence spectra of the diaspoire treated at 900°C showed two variations: the first is an R-line of Cr³⁺ luminescence in octahedral sites with a strong crystal field in a very disordered environment, and the second is a broad band of Cr³⁺ luminescence in weaker crystal field sites. The crystalline phase of corundum [α -Al₂O₃] is detected by XRD and Raman spectroscopy after treating the diaspoire at 1000°C and above (up to 1300°C). The lines in the spectrum of the diaspoire treated at this temperature are typical of Cr³⁺ luminescence centers (R-lines) in Cr–corundum (ruby) structure.

Keywords: corundum, Cr³⁺, diaspoire, FT-IR, luminescence, Micro-Raman

Introduction

The thermal transformation from aluminum hydroxides to alumina is well documented in ceramic research [1]. The hydroxide precursors (gibbsite, bayerite, and boehmite) derivable directly from the Bayer process decompose to nanocrystalline transition aluminas upon dehydration between 300 and 600°C [2]. A number of intermediate crystalline alumina structures (χ -, η -, γ -, κ -, θ - and δ -alumina) are formed in the various precursors between the temperature of dehydroxylation and the crystallization of α -alumina [3, 4]. The α -alumina is the end-structure formed above 1000°C. One well-known alumina precursor with exceptional dehydration behavior is diaspoire. This aluminum hydroxide decomposes to nanocrystalline α -alumina at temperatures as low as 500°C [2, 3].

In this paper, the thermal transformation of natural diaspoire collected from residual soils (bauxite and laterite) was investigated. In such diaspoire, Cr³⁺ appears as a

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trace constituent substituting for Al^{3+} [5]. The luminescence of Cr^{3+} in natural and calcined diaspoire is applied here to probe the structural properties. Cr^{3+} exists in a d^3 configuration, and the electronic repulsion, which results from placing three electrons in the same set of d-orbitals, yields several states identified as “free ion” energy levels [6]. The placement of this ion in a crystal lattice produces further splitting of the free ion levels. The exact energy spacing between the energy levels is therefore determined by the strength of the crystal field experienced by the Cr^{3+} ion. Since different crystal field strengths are anticipated for each mineral host into which Cr^{3+} can be placed, the luminescence may be a reliable indicator of the mineral structure properties. Laser-based spectroscopy of Cr^{3+} ions makes it possible to follow the thermal crystallization process in a cordierite glass, by following the variation of Cr^{3+} environment during heat treatment [7].

In the preliminary study using steady-state spectroscopy [8], we found lines at 691 and 694 nm in the luminescence spectra of natural diaspoire and attributed them to R lines of Cr^{3+} substituting for Al^{3+} . The lines at 692 and 694 nm in the spectra of diaspoire treated at 1000°C were attributed to R lines of Cr^{3+} in the high temperature phase of corundum. As a next step, we used laser-induced time-resolved luminescence spectroscopy which enables detection of luminescence centers with similar spectra but different decay times. Such a method enables much more sensitive luminescent probing, which has been seen for rare-earth elements [9].

Materials and methods

Samples

Diaspoire concentrated in pisolites within bauxite and laterite was selected and analyzed. Bauxite from Missouri (samples MB) was purchased from Ward's Natural Science Establishment, Inc., Rochester, NY. Laterite (samples RL) was collected in the Makhtesh Ramon flint-clay quarry, Israel [10]. Thermal treatment was performed in an electric furnace by heating at different temperatures up to 1300°C. The heating time was 2 h at each temperature. Measurements were obtained at room temperature.

Methods

X-ray diffractometry (XRD)

Acquired on powder samples with a Philips PW-1820 diffractometer using CuK_α radiation, 35 kV – 40 mA, and a curved graphite monochromator.

Chemical analysis

Obtained using a JEOL (JSM-840) Scanning Electron Microscope (SEM) with an attached LINK 1000 EDS (Oxford ISIS). Calculations were performed using the ZAF4/FLS program.

Micro-Raman and steady state luminescence spectroscopy

Recorded with a Dilor XY confocal micro-Raman spectrometer with a focal length of 500 mm. This instrument is equipped with an Olympus optical microscope, a triple monochromator and a Charge Coupled Device (CCD) EG&G multichannel detector. Spectra were obtained with a 50× objective at a resolution of 3 cm⁻¹. Accumulation times of 360 s were used. The 514.5 nm line of a Spectra Physics 2016 Argon ion laser was used for excitation.

FT-IR spectroscopy

Obtained using a Nicolet FT-IR spectrometer and 'Omnic' software. KBr disks were employed.

Time-resolve luminescence spectroscopy

Laser-induced time-resolve luminescence spectra were analyzed using an InstaSpec IV CCD detection system. Computer-controlled acquisition enables detection of time-resolved spectra with delay times and strobe pulse durations from 20 ns to 9 ms. Second, third and fourth harmonics of YAG (532, 355 and 266 nm) were used for luminescence excitations.

Results

X-ray diffractometry

The natural samples consist of diaspore with accessory anatase and kaolinite. The dehydroxylated phase of the diaspore is not detectable by XRD up to 900°C, indicating a low degree of crystallinity or X-ray amorphous phase. After treating the diaspore at 1000°C, broad peaks indicative of corundum appear. The intensities of these peaks increase after heating at 1300°C.

Chemical analysis

Table 1 shows the major elements that compose the natural diaspore samples. The TiO₂ and SiO₂ content are due to the accessory anatase and kaolinite, respectively. The FeO content is related to Fe-bearing diaspore and to accessory hematite in laterite [10]. The presence of Cr³⁺ in the diaspore is indicated by the Cr₂O₃ content.

Micro-Raman spectroscopy

Raman spectra of the natural and calcined diaspore are shown in Fig. 1. In the spectra of the natural samples, Raman bands indicative of diaspore [10] are observed at 497, 447 and 327 cm⁻¹. Broad and weak bands are detected after treating the diaspore at 900°C, indicating low degree of ordering within the dehydroxylated. After treating at 1000°C, weak Raman bands indicative of corundum [11, 12] are observed at 580,

563, 449, 430, 417, 379 and 252 cm^{-1} . The intensities of these bands increase after heating at 1300°C.

Table 1 The major elements composition of the natural diaspore samples. Diaspore concentrated in pisolites within bauxite and laterite was selected and analyzed

Residual soil	Sample	Al ₂ O ₃ /	SiO ₂ /	TiO ₂ /	FeO/	Cr ₂ O ₃ /
		%				
Bauxite	Word's, MB-1	96.76	–	1.65	0.72	0.04
Bauxite	Word's, MB-2	96.70	–	1.65	0.70	0.04
Bauxite	Word's, MB-3	95.41	–	2.75	0.87	0.02
Laterite	Ramon, RL-1	80.49	12.93	4.05	0.63	0.03
Laterite	Ramon, RL-2	78.01	8.18	7.47	4.49	0.08

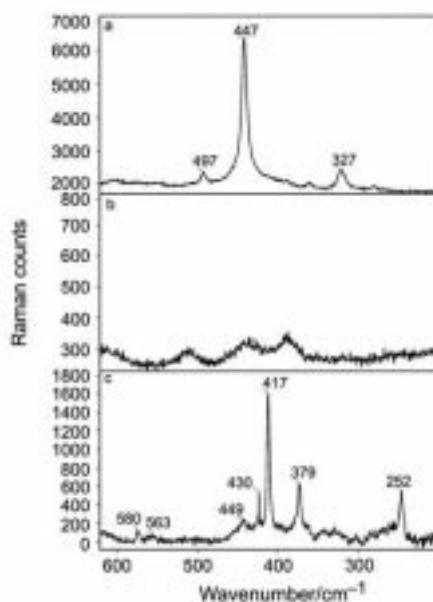


Fig. 1 Raman spectra of a – natural diaspore, b – diaspore treated at 900°C and c – 1000°C

FT-IR spectroscopy

FT-IR spectra of the natural and calcined diaspore are shown in Fig. 2. In the spectra of the natural samples, IR bands indicative of diaspore [10] are observed at about 1054, 959, 744, 563 and 480 cm^{-1} . After treating at 900°C, broad IR bands appear, in agreement with a low degree of ordering within the dehydroxylated phase. After treating the diaspore at 1000°C, IR bands indicative of corundum [11, 12] are observed at about 1085, 1035, 728, 640, 598 and 455 cm^{-1} .

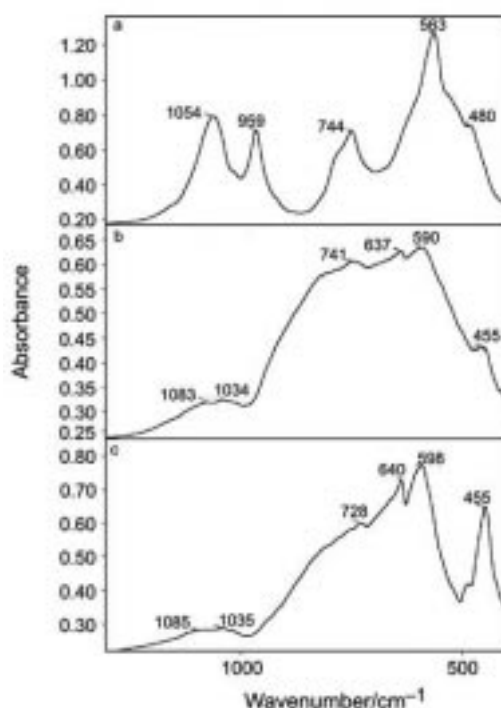


Fig. 2 FT-IR spectra of a – natural diaspore, b – diaspore treated at 900°C and c – 1000°C

Luminescence spectroscopy

Steady-state luminescence spectra of the natural and calcined diaspore are shown in Fig. 3. Time-resolved luminescence spectra of these samples are demonstrated in Fig. 4. In the steady-state luminescence spectra of the natural diaspore, lines are observed at 691.0 and 693.7 nm (Fig. 3a). Two narrow lines at 692 and 694 nm, accompanied by a line at 659 nm and phonon repetitions at 707 and 714 nm characterize the time-resolved luminescence spectra (Fig. 4a). After a long delay of several ms, the relative intensity of the line at 692 nm becomes stronger (Fig. 4b), evidently because this line has a longer decay time compared to the line at 694 nm. After heating at 900°C, the spectra were pronouncedly changed and broad bands appear (Fig. 3b). The time-resolved luminescence spectra contain a relatively broad line at 692 nm and a broad band peaking at 780 nm, which dominates the spectra with narrow gate (Fig. 4c, 4d). Such behavior indicates that the broad band at 780 nm has very short decay time compared with the broad line at 692 nm. After heating at 1000 and 1300°C, the spectra again contain two narrow lines at 692.5 and 693.9 nm in the steady-state luminescence spectra (Fig. 3c) and at 692 and 694 nm in the time-resolved luminescence spectra (Fig. 4e, 4f). However, in contrast to the natural diaspore, their relative intensities in time-resolved spectra are not changed, indicating that they have similar decay times. It should be noted that luminescence of Cr^{3+} is not known in natural anatase and rutile, which appear as accessory minerals.

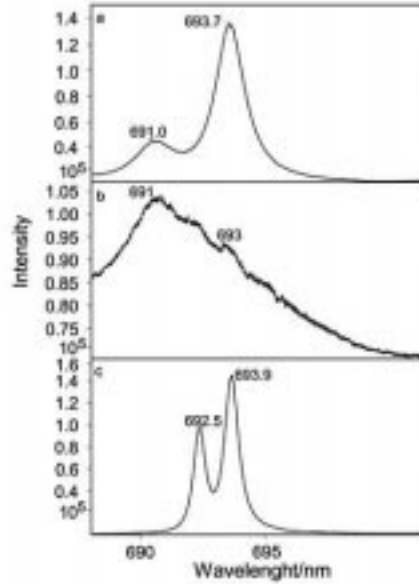


Fig. 3 Steady-state luminescence spectra of a – natural diasporite, b – diasporite treated at 900°C and c – 1000°C

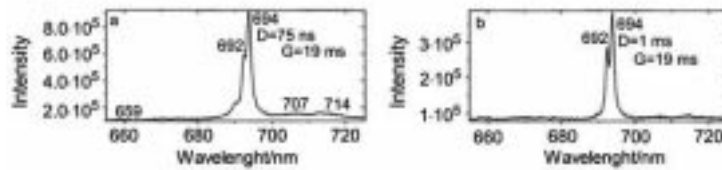


Fig. 4a, b Time-resolved luminescence spectra of natural diasporite. D=delay time and G=gate width

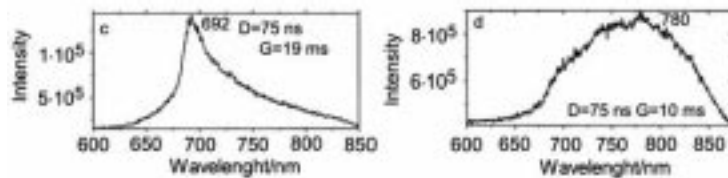


Fig. 4c, d Time-resolved luminescence spectra of diasporite treated at 900°C. D=delay time and G=gate width

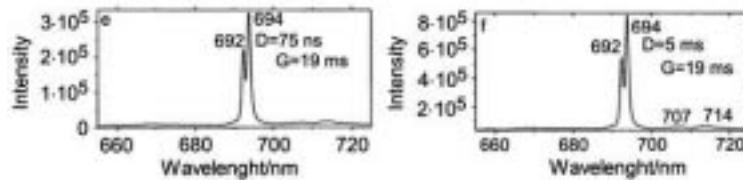


Fig. 4e, f Time-resolved luminescence spectra of 1000°C. D=delay time and G=gate width

Discussion

Natural diaspoire

In diaspoire the oxygens are in a hexagonal close packed layer [13]. Steady-state luminescence spectra of the natural diaspoire are typical of ${}^2E \rightarrow {}^4A_2$ transitions of Cr^{3+} luminescence centers (R-lines) substituting for Al^{3+} in six-fold coordination [14]. This is in accordance with the spectra observed by cathodoluminescence [15]. The most important free ion states in Cr^{3+} are 4F ground level and excited 2H level. In an octahedral field, the 4F level splits into the 4A_2 ground state and the excited 4T_2 and 4T_1 states [16, 17]. The spin allowed transitions that could therefore be used to populate the excited states directly correspond to ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$. Cr^{3+} mainly appears in minerals as a trace constituent substituting for Al^{3+} in six-fold coordination. As such, the larger Cr^{3+} ion is placed in a site with small metal–ligand distances and the crystal field is large, typically $1650\text{--}1750\text{ cm}^{-1}$. If the crystal field is sufficiently strong to make the doublet state the lowest energy excited state, there will be red luminescence with narrow lines. Because the doublet state belongs to the same orbital configuration as the ground state, the Stokes shift and Condon offset will be small. As a result, the line width of emission is narrow and a considerable amount of phonon fine structure is observed even at room temperature. Such transition is forbidden by symmetry and spin selection rules and decay time is usually very long.

Although the Cr^{3+} narrow line emission is essentially independent of crystal field and thus of site size and symmetry, the energy of the double levels does depend on Racah parameters B and C, which are dependent on the covalence of the metal–ligand bond. Thus there is some variability in the line emission from mineral to mineral [6]. Time-resolved spectra of the natural diaspoire demonstrate that R-lines have different decay times. The different radiative lifetimes of the two R-components have been connected with large splitting that causes a substantial difference in the population of the two components [18]. Nevertheless, in diaspoire, the splitting of the R-lines is very low and a different explanation is needed.

The calcined diaspoire

The dehydroxylated phase of the diaspoire is characterized by a low degree of crystallinity. This phase is not detectable by XRD and Raman spectroscopy up to 900°C . The broad IR bands are in agreement with a low degree of ordering. The direct transformation of diaspoire to α -alumina has been attributed to the structural similarities between diaspoire and corundum [2, 19]. Both structures are based on hexagonal close-packed anion (O, OH) sub-lattices and, therefore, the transformation is thought to require only small rearrangements of the oxygen and aluminum positions [3, 20].

The lines in the luminescence spectra of diaspoire treated at 900°C are related to Cr^{3+} luminescence in the dehydroxylated phase. The broad asymmetric line peaking at 692 nm with a long decay time (Fig. 4c) is evidently connected with inhomogeneously broadened R-lines of Cr^{3+} luminescence in octahedral sites with a strong crystal field and a very disordered environment. The broad band peaking at 780 nm with a much shorter

decay time (Fig. 4d) is attributed to Cr^{3+} luminescence in the weaker crystal fields where a strong broadband quartet–quartet ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition appears, which is only symmetry forbidden. These spectral types are similar to those of Al_2O_3 powders heated to temperatures from 400 to 1000°C [21].

Crystalline phase of corundum is detected after treating the diaspoire at 1000°C and above (up to 1300°C). The lines in the spectrum of the diaspoire treated at this temperature are typical of ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transitions of Cr^{3+} luminescence centers (R-lines) of Cr–corundum (ruby), which are characteristic of Cr^{3+} luminescence substituting for Al^{3+} in strong field sites. Both lines are long-lived and have the same decay times.

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