

Optical properties of Cr (III)-doped glasses*

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Here are reported the absorption and fluorescence spectra of Cr (III) in different inorganic glasses. Their properties are discussed in views of applicability for luminescence solar concentrators.

1. Introduction

The spectroscopic properties of Cr (III) in glass have been the subject of numerous studies in last years. Recently, this interest has been focused on Cr (III)-doped glasses as active materials for luminescent solar concentrators [1]–[5]. In such devices the luminescence in the region of 0.9–1.0 μm is utilized. A possibility of such luminescence is offered by the low-ligand field Cr (III) materials. As it is known, the luminescence properties of Cr (III) ion are strongly dependent on ligand field strength. The simplified energy level diagram of Cr (III) in an octahedral environment is shown in Fig. 1. This diagram relates the normalized energy of excited states to the normalized strength of crystal field. The Racah parameter B is the normalization constant. The energy distance between the ground ${}^4A_{2g}$ state and the maximum ${}^4T_{2g}$ state in absorption spectrum is equal to $10 Dq$.

The luminescence of Cr (III) originates from the lowest excited states. In the low ligand field environment characterized by condition $Dq/B < 2.3$ it is the broad band fluorescence ${}^4T_{2g} \rightarrow {}^4A_{2g}$. In the high ligand field environment $Dq/B > 2.3$ the narrow-band phosphorescence ${}^2E_g \rightarrow {}^4A_{2g}$ is the dominant process. In the intermediate case $Dq/B \simeq 2.3$ both processes appear in the spectra. Most of Cr (III)-doped glasses are characterized by low ligand field condition. However, their practical application for luminescent solar concentrators is limited by low yield of luminescence. It was found that luminescence yield is dependent on the composition of base glass [1].

The purpose of this work was to perform the comparative studies of spectroscopic properties of Cr (III) in different glasses. In particular, on a basis of absorption and luminescence measurement we shall discuss the quantities relevant to luminescent solar concentrators.

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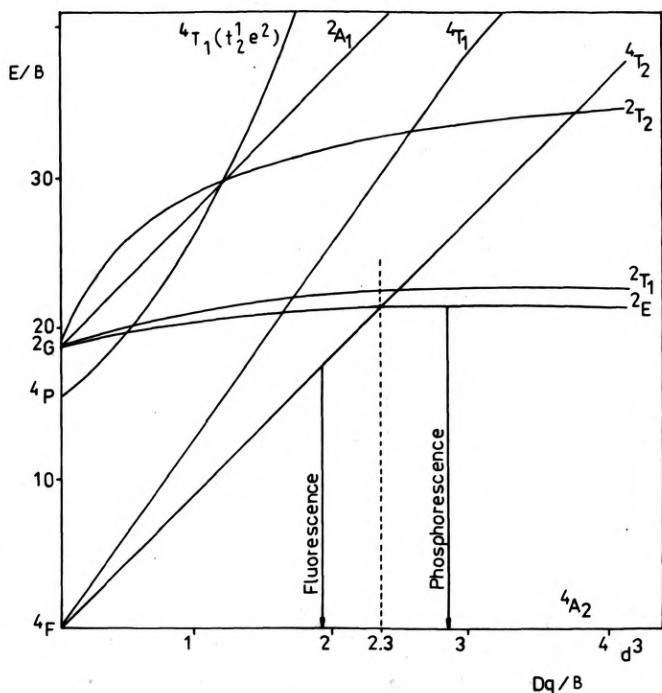


Fig. 1. Energy level diagram of Cr (III) ion O_h symmetry

2. Experimental

2.1. Preparation of glasses

The glass samples were kindly supplied by Jelenia Góra Optical Works (Poland). The samples were prepared first as the basis glasses with the composition given in Table 1. The glasses were powdered and after adding 0.2 wt% Cr_2O_3 , melted in appropriate temperatures for several hours, being stirred occasionally. Then, the melt was poured into a form and annealed. The samples were cut and polished to cubes and plates of 10 and 1 mm thick. To avoid the $Cr^{3+} \rightarrow Cr^{6+}$ oxidation, 1 wt% of Sb_2O_3 was added to the basis glass.

Table 1. Compositions of 0.2 wt% Cr_2O_3 doped glasses and melt temperatures

No.	Type	Compositions				Melt temperature [°C]
51	K-Ba-silicate	SiO ₂ -60.7	K ₂ O-14.4	BaO 24.0	Sb ₂ O ₃ -0.9	1450
61	Na-Cd-silicate	SiO ₂ -60.0	Na ₂ O-12.4	CdO 26.6	Sb ₂ O ₃ -1.0	1480
66	Phosphate	P ₂ O ₅ -81.0	Na ₂ O-10.0	Li ₂ O-2.0	Al ₂ O ₃ -7.0	1200
81	Borosilicate	B ₂ O ₃ -53.2	SiO ₂ -23.1	Na ₂ O-23.1	Sb ₂ O ₃ -1.0	1150
76	Tellurite	TeO ₂ -84.4	Na ₂ O-4.3	BaO-9.1	MgO-1.1, ZnO-1.1	750

2.2. Optical measurements

Absorption spectra were recorded with Varian 2300 spectrophotometer. Luminescence spectra were measured with a fluorescence spectrophotometer constructed in our laboratory using GDM 1000 (C. Zeiss, Jena) monochromator. As an excitation source a 488 nm line argon ion laser was used. The spectra were detected by photomultiplier (S1) connected with preamplifier and BCI 280 (ZWG, Berlin, DDR) boxcar-integrator. The spectra, as presented, have been corrected for photomultiplier response. The measurements were carried out at room temperature.

3. Spectra

The absorption spectra of Cr (III) doped glasses are shown in Fig. 2. The absorption data for various glasses are summarized in Table 2. Following these results we have determined the field parameters Dq and B from the position of 4T_2 and 4T_1 bands. It can be noticed that the ligand field strength determined by the Dq/B ratio increases along the following series: Ba-silicate, Gd-silicate, phosphate,

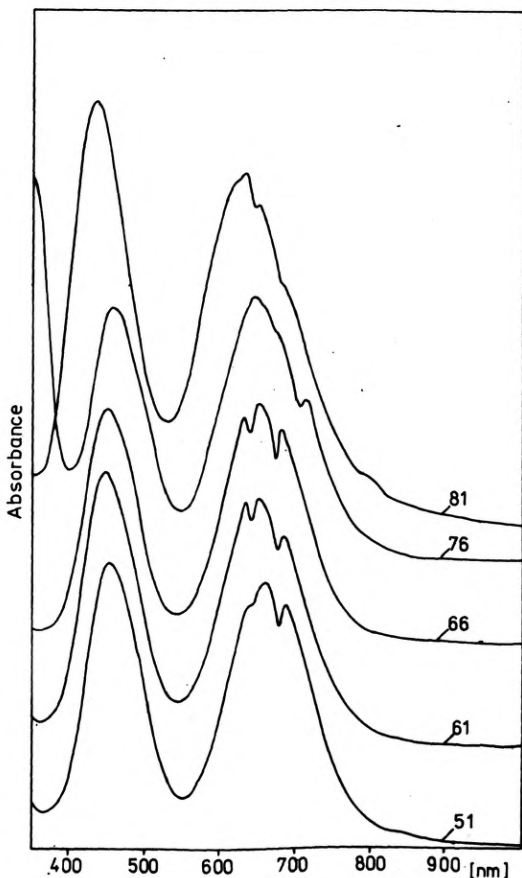


Fig. 2. Absorption spectra of 0.2 wt% Cr_2O_3 doped glasses

Table 2. Spectroscopic data for Cr(III) in glasses

No.	Type	Absorption					
		\rightarrow^2E		\rightarrow^2T_1		\rightarrow^4A_2	
		[nm]	[cm^{-1}]	[nm]	[cm^{-1}]	[nm]	[cm^{-1}]
51	K-Ba-silicate	677	14771	644	15528	667	15993
61	Na-Cd-silicate	676	14793	643	15552	654	15291
66	Phosphate	676	14793	642	15576	658	15198
81	Borosilicate	677	14771	644	15528	626	15974
76	Tellurite	705	14184	670	14925	656	15244

borate, and tellurite. The characteristic dips at envelope of 4T_2 band are combined with the location of the spin-forbidden 2T_1 and 2E bands near the maximum of spin-allowed 4T_2 band. It leads to appearance of the characteristic dips resulting from the Fano antiresonances [6]. It permits us to determine the positions

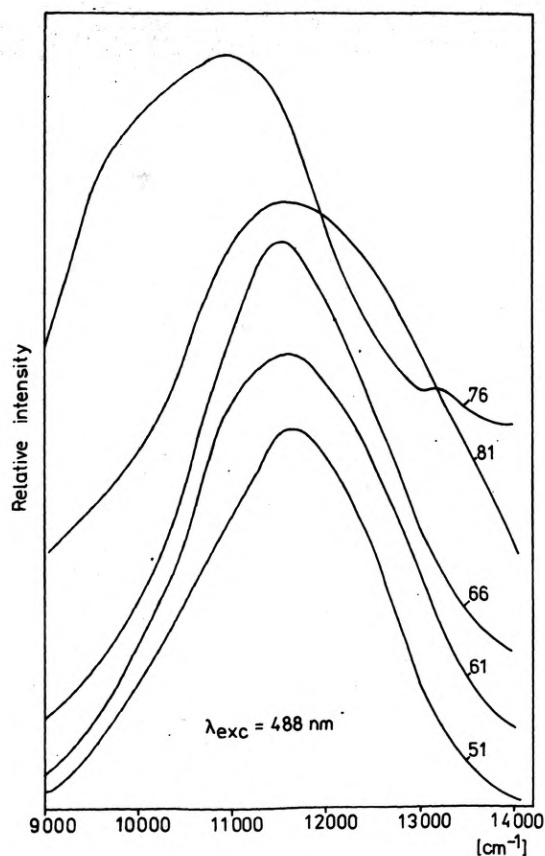


Fig. 3. Fluorescence spectra of 0.2 wt% Cr_2O_3 doped glasses

Absorption			Emission			
\rightarrow^4T_2		B	Dq/B	4T_2	\rightarrow^4A_2	$\sigma_{1/2}$
[nm]	[cm^{-1}]	[cm^{-1}]		[nm]	[cm^{-1}]	[cm^{-1}]
454	22026	754	1.99	862	11600	2400
448	22321	744	2.05	862	11600	2400
452	22124	730	2.08	862	11600	2200
435	22989	727	2.20	862	11600	2600
460	21739	665	2.29	926	10800	2700

of 2T_2 and 2E levels. We have to remember, however, that the positions of these levels were determined with some error due to the Lamb shift.

The fluorescence spectra of Cr (III) in different glasses/measured at room temperature are shown in Fig. 3. The appropriate data of the maximum peak positions and halfwidth are summarized in Table 2. The most interesting feature of these spectra is a fact that the fluorescence peak positions are less sensitive to the glass composition than the absorption band. Only some irregular variations of the band widths were observed. Also, there was noticed the dependence of pumping line of argon laser on the band width. On the basis of a high value of Dq/B of Cr (III) in tellurite glass it is possible to predict the occurrence of $^2E \rightarrow ^4A_2$ phosphorescence. Indeed, we observed a small band about 13200 cm^{-1} which can be attributed to this transition.

4. Summary

In this paper, we have investigated the spectroscopic properties of Cr (III) in various glasses. WHITE and KNIGHT [7] suggested that Cr^{3+} ions spectra in many different glass compositions can be best interpreted if the ions are assumed to be on octahedral sites. The local environment of the transition metal ion is determined by its own bonding requirements of the glass network. The spectroscopic data for many glasses doped with Cr (III) ions seem to confirm this hypothesis.

We have found that the fluorescence band positions varied less than the positions of 4T_2 band in absorption spectra. It may be explained by larger distortion of the potential energy surfaces of this excited state. Most probably the minimum of potential energy surface of the 4T_2 state does not change with variation of glass composition due to the identical nearest oxide neighbourhood of Cr (III) ion.

The largest distortion was found for tellurite glass. It leads to the significant Stokes shift of fluorescence. So, this glass is interesting material for luminescent solar concentrators.

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Оптические свойства стекол активированных Cr(III)

Описаны спектры оптического поглощения и флуоресценции неогранических стекол активированных ионами Cr³⁺. Обсуждены свойства этих стекол для их применения в солнечных люминесцентных концентраторах.