

Crystal Chemistry and Crystal Growth of Optical Materials

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Abstract: Crystal chemistry and crystal growth are prior to any detailed investigation of a material that is expected to show interesting linear and nonlinear optical properties. Here, we report on (i) the possibility of exploring the luminescence and optical hole burning properties of Sm²⁺ in oxide lattices, and (ii) laser frequency shifting crystals showing stimulated Raman scattering (SRS) effects.

Keywords: Crystal growth · Lasers · Optical hole burning · Optical materials · Samarium · Stimulated Raman scattering

1. Introduction

Along with other (ceramic, glassy) forms of condensed matter, *single crystalline* materials were basic to fundamental studies of many properties which finally have found widespread applications in optical and other technologies: Dielectric laser and frequency converting crystals emerged from synthetic work in materials chemistry and efforts in the growth of bulk crystals. Although it is commonly recognized that knowledge on crystal growth and corresponding industrial technologies are indispensable for today's key applications, crystal growth activities in central Europe have declined over the last decade. It is therefore a basic task, even more a challenging issue for solid state chemistry and physics to support research and teaching in *crystal growth*. It was only recently that within BENEFRI a teaching program on 'Science and Technology of Advanced Materials' received funding (starting Fall, 2001) [1].

Because the group's activity in this field is rather widespread, we shall focus

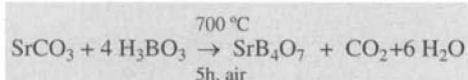
here on (i) the crystal chemistry and spectral hole burning properties of Sm²⁺ ions in oxide lattices, and (ii) the stimulated Raman scattering (SRS) properties of solids built up from molecular entities. The review covers work performed during the last five years.

Other activities of the materials chemistry and crystal growth group at Bern (fluoride laser crystals, upconversion materials, polar supramolecular materials [2]; new physical methods for the characterization of inhomogeneous polar crystals and stochastic theories for understanding polarity formation in molecular crystals [3]) have been reviewed in previous issues of CHIMIA.

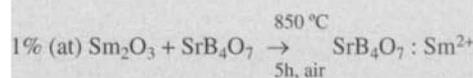
2. On the Existence and Optical Properties of Divalent Samarium in Oxide Lattices

Some of the lanthanides, *e.g.* Eu, Yb and Sm can be obtained in the *divalent* oxidation state in crystalline form. Generally, the reduction of Ln³⁺ to Ln²⁺ needs a strong reducing agent (H₂) or electrochemical means. However, Pei *et al.* have reported a ceramic preparation of Sm²⁺-doped SrB₄O₇ (tetraborate) [4]. The solid-state reaction used only Sm₂O₃, but no denotable reducing agent.

Solid state reaction:



Inclusion of Sm:



This observation is unique because it shows that in *strontium tetraborate*, Sm²⁺ can be stabilized at high temperature (850 °C) and in air. There were previous attempts to form SmO, however, using Sm metal and at reduced O₂ pressure, Ar or vacuum. A different situation is found for *halogenide* lattices. In these cases, Sm²⁺ doped crystals could be obtained using H₂ for reduction.

Interest in divalent samarium-doped materials came up after laser action in CaF₂: Sm²⁺ was demonstrated a long time ago. Single crystals of a large number of host lattices doped with Sm²⁺ were grown thereafter, in view of obtaining laser crystals or a system for fundamental optical studies. Today, recent interest is associated with high-pressure cells, where Sm²⁺ spectroscopy is used to monitor the applied pressure on a sample [5]. Other fields of interest are again laser properties, optical hole burning and applications covering luminescent pigments. For a review on Sm²⁺ in oxide lattices, see [6].

Basic to our studies was to discover which type of excitation could be used to distinguish Sm²⁺ from its trivalent state. Divalent Sm is isoelectronic to Eu³⁺. A comparison of *cathodoluminescence* and *photoluminescence* spectra showed that characteristic and narrow lines of the

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transitions $^5D_0 \rightarrow ^7F_{0,1,2,3}$ belonging to Sm^{2+} could be traced by photoluminescence in different types of oxide materials [7]. Correspondingly, cathodoluminescence lines of divalent Sm and broad intense bands of Sm^{3+} were observed. In the case of cathodoluminescence we have found that the ratio of divalent Sm is markedly influenced by the accelerated electrons *via* ionization of Sm^{2+} to Sm^{3+} (see Fig. 1). A clear difference between the optical behavior of the Sm^{2+} and Sm^{3+} states is shown by the excitation spectra in Fig. 2: Intense absorption around 685 nm makes Sm^{2+} interesting for flash lamp pumping. Reversible effects of optical bleaching of the Sm^{2+} luminescence [8] and optical hole burning were observed as well [9b].

Within a broad chemical study we have investigated the possibility of doping a number of oxide-type materials with Sm^{2+} . Among them were $SrSiO_3$, $SrWO_4$, $SrAl_2O_4$, $SrAl_4O_7$, $SrSO_4$, $BaSO_4$, $CaSO_4$, $CdSO_4$, BaB_2O_4 , BaB_4O_7 , CaB_4O_7 , PbB_4O_7 , CdB_4O_7 , SrB_2O_4 , $Sr_2B_2O_5$, and $Sr_3B_2O_6$. However, in all these materials only traces of Sm^{2+} could be detected by the means outlined above. All syntheses were performed in air and at high temperature. In the case of $Sr_2MgSi_2O_7$, $Ca_2MgSi_2O_7$, and $Ca_2ZnSi_2O_7$, H_2 was used for reduction. No significant doping level could be achieved for these silicate lattices.

Surprisingly, there is one exception, SrB_4O_7 , which at the given conditions showed significant solid solution formation with Sm^{2+} [9a]. Clearly, the size of Sm^{2+} (1.27 Å, CN 8) fits well into a Sr^{2+} site (1.26 Å, CN 8). Nevertheless, up to date no convincing electronic explanation could be found as to why Sm^{2+} shows only stability in crystalline SrB_4O_7 .

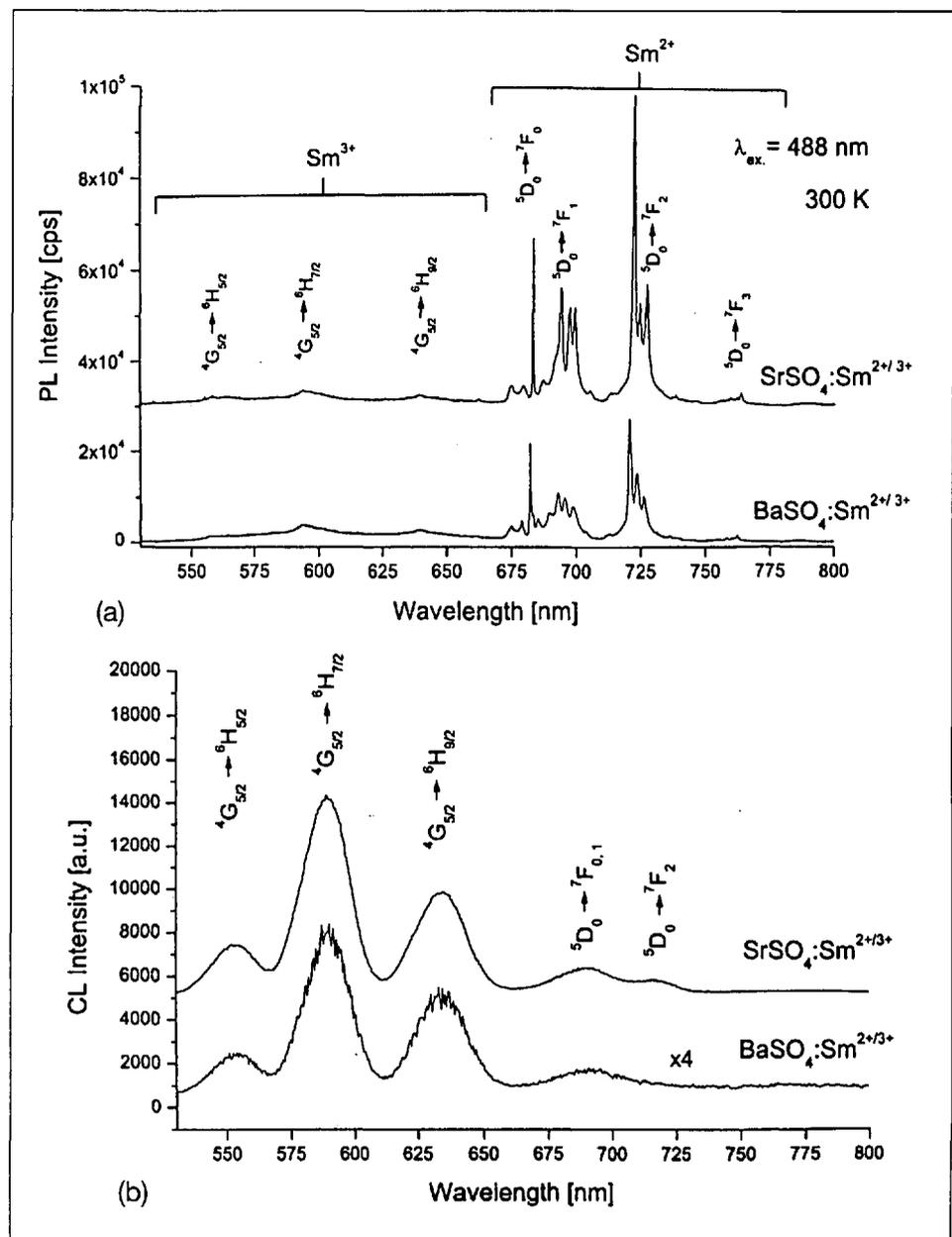


Fig. 1. Photoluminescence (a) and cathodoluminescence (b) spectra of $SrSO_4$ and $BaSO_4$ ceramic samples at 300 K [7].

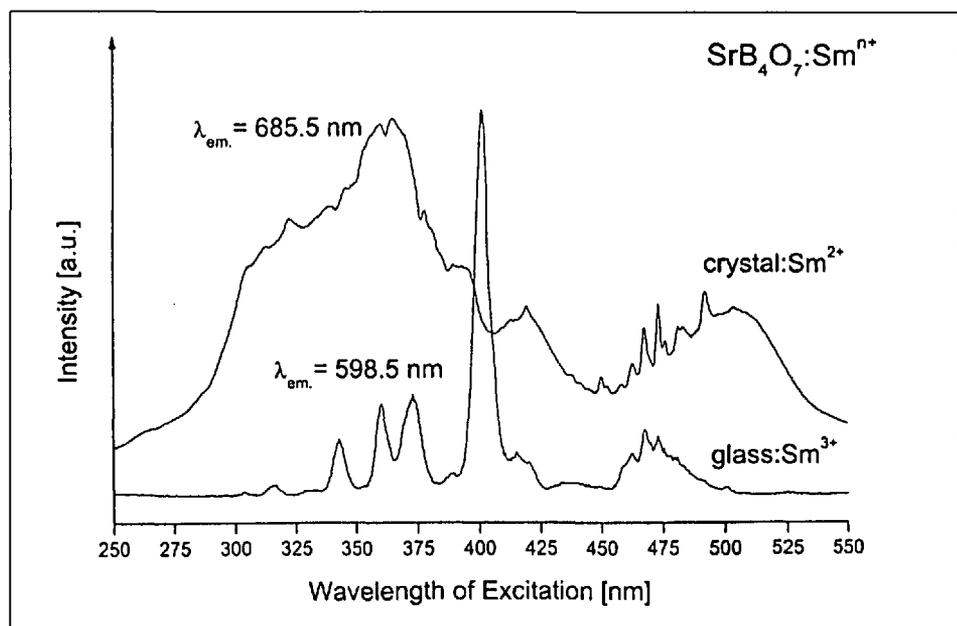
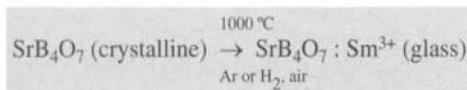


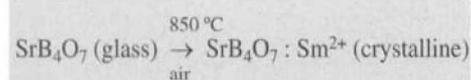
Fig. 2. Excitation spectra of Sm in SrB_4O_7 at 300 K [7].

Interestingly, in the glassy state we have found exclusively Sm^{3+} , whereas after recrystallisation in air, again Sm^{2+} appeared.

Glass formation:



Recrystallisation:



A sequence of optical spectra confirming the general observation is shown in Fig. 3.

For a particular case we have investigated the solid solution formation behavior ($\text{M}_{1-x}\text{Sm}_x\text{SO}_4$, $\text{M} = \text{Ba}, \text{Sr}$) at *high* and *room* temperature [10a]. Solid solution formation was performed at $\sim 600^\circ\text{C}$ using a LiCl flux and Ar/H_2 (80:20 mol %). In such crystals both Sm^{2+} and Sm^{3+} were present, however, below a doping level of one mol%. A completely different situation was found if an electrochemical approach using water at 300 K was applied.

Sm^{2+} was first prepared by electrochemical reduction followed by a precipitation reaction. Powder X-ray diffraction confirmed solid solutions for both Sr and Ba systems. Significant luminescence quenching was observed at $x_{\text{sm}} > 0.05$. Solid solutions obtained along this route were not stable at high temperature. Sm was converted into the Sm^{3+} state. This example shows that a *low*-temperature synthesis may allow incorporation of Sm^{2+} into some oxide lattices. However, Sm^{2+} is not stable in many oxide environments if exposed to high temperature. In this respect, SrB_4O_7 represents a unique case, but it is not yet understood why particularly this lattice stabilizes the Sm^{2+} state.

This is nicely seen from solid solution formation with Pb, *i.e.* $\text{Sr}_{1-x}\text{Pb}_x\text{B}_4\text{O}_7 : \text{Sm}$ [10b]: For a given level of Sm in the melt, the Sm^{2+} luminescence intensity in solid solutions continuously decreases as x increases. In the case of $\text{PbB}_4\text{O}_7 : \text{Sm}$, predominantly Sm^{3+} luminescence was observed.

3. Molecular-type Materials for Raman Laser Converters

The process of stimulated Raman scattering (SRS) allows the conversion of laser emission wavelengths of organic

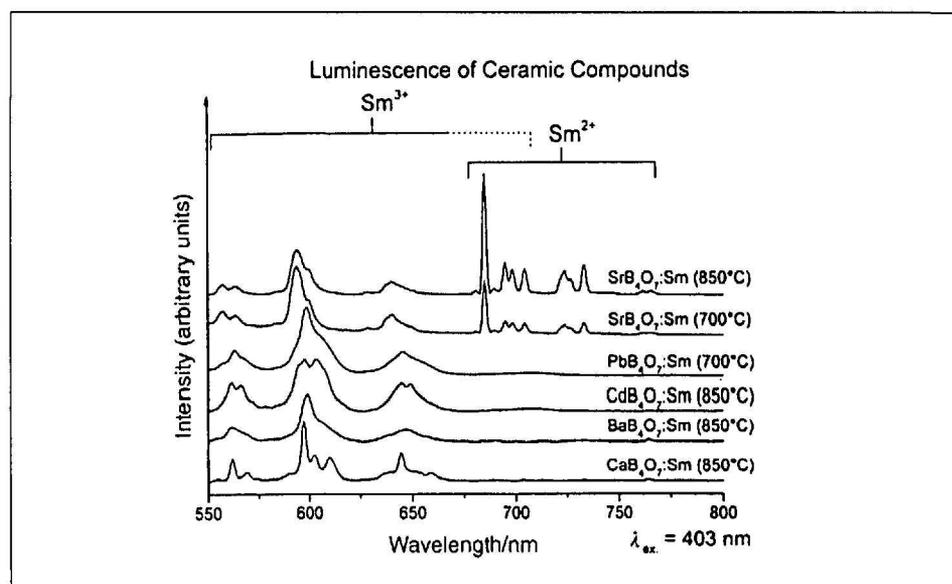


Fig. 3. Fluorescence spectra of various ceramic tetraborates at 300 K [9a].

and inorganic materials to provide suitable molecular or lattice modes which contribute to the *third* order non-linear optical susceptibility $\chi^{(3)}$. For a recent review including many references to original papers, see [11]. SRS of known materials has produced Stokes or anti-Stokes shifts in the range of about $100\text{--}3100\text{ cm}^{-1}$. Renewed interest in this field emerged because of the investigation of many SRS active crystals and demonstrations of all solid state SRS lasers.

Among materials studied are nitrates, oxides, chlorates, sulfates *etc.* and several organic crystals. Organic nonlinear optical materials used so far for frequency doubling and third harmonic generation seem to have a considerable potential for SRS applications. Because for SRS there is no need to have *acentric* materials, many of the organic crystals and polymers showing pronounced $\chi^{(3)}$ properties may be reconsidered for as yet unexplored directions in testing all solid state laser frequency converters. SRS laser systems are of interest in various fields including remote sensing of the atmosphere. In crystals showing also a $\chi^{(2)}$ effect, the combination of $\chi^{(2)} + \chi^{(3)}$ properties can give rise to diverse parametric generation phenomena. Typical SRS gain coefficients g_{SSR} of crystalline materials vary in the range of about $0.2\text{--}10\text{ [cm/GW]}$. A characteristic SRS response is shown in Fig. 4.

Sodium chlorate, NaClO_3 , has been the subject of many kind of physical investigations, dating back to the second half of the 19th century [12]. Recently,

the cubic 23 phase of NaClO_3 could be obtained from Czochralski growth using a low-temperature phase seed crystal, although sodium chlorate undergoes a phase transition from monoclinic to cubic at 230°C on cooling [13]. Crystals of optical quality, a length of $50\text{--}70\text{ mm}$ and a diameter of $5\text{--}15\text{ mm}$ were obtained. However, further improvement of the growth procedure would require temperature control better than 0.1°C . For this reason supercooled melt growth is considered the method of choice for producing large crystals free of internal stress.

The optical vibration mode $\omega_{\text{SRS}} = 936\text{ cm}^{-1}$ attributed to the ClO_3^- moiety produced efficient multiple Stokes and anti-Stokes emissions for an excitation along the (111)-axis.

An all solid state nanosecond Raman laser at $\lambda = 1.1628\text{ }\mu\text{m}$ was demonstrated using a solution-grown NaBrO_3 crystal, isomorphous to NaClO_3 [14]. The resonator contained basically three elements: the primary laser crystal, a Q-switch and the Raman active shifter (Fig. 5). A frequency doubling crystal was included to generate SRS of the $\lambda/2$ wave.

Newest developments concentrate on the preparation of Raman active inorganic glasses, providing a high density of scattering centers. First examples along this line are sodium polyphosphate glass $(\text{NaPO}_3)_x$, which may be used as ingots or in the form of fibers [15], and nitrate glasses [16].

Last but not least we should once more mention the excellent SRS properties of $\chi^{(2)} + \chi^{(3)}$, or simply $\chi^{(3)}$ active

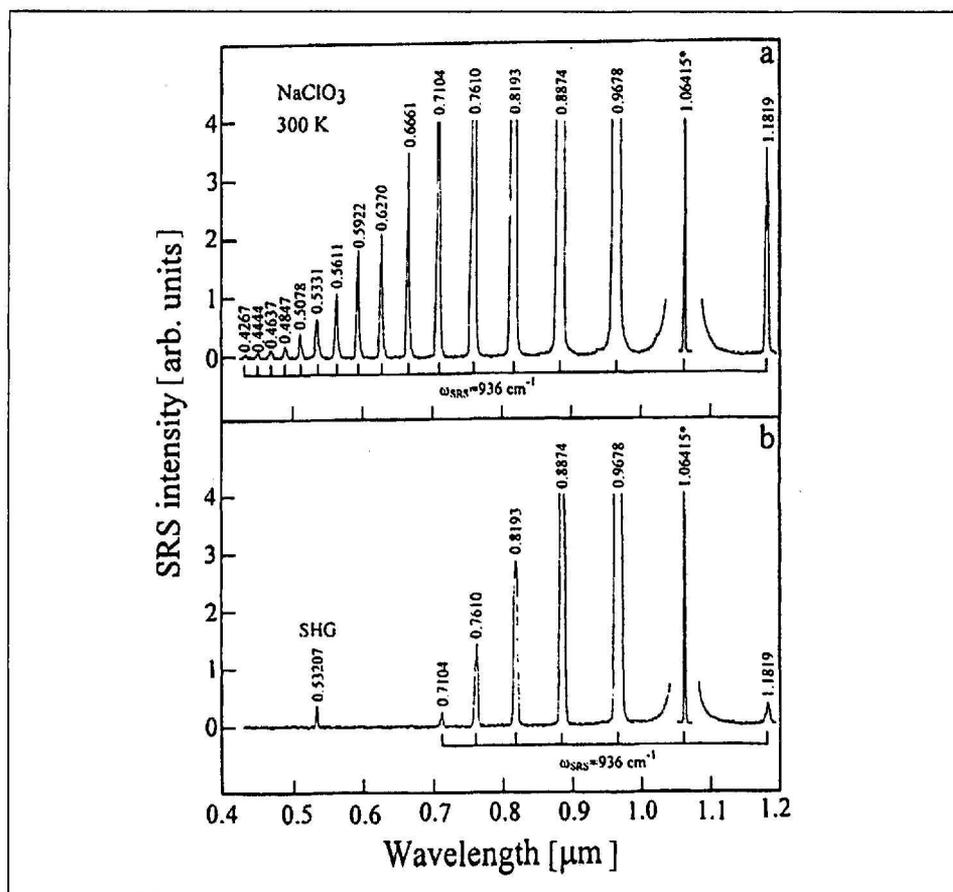


Fig. 4. SRS spectra of a NaClO_3 crystal at 300 K [13].

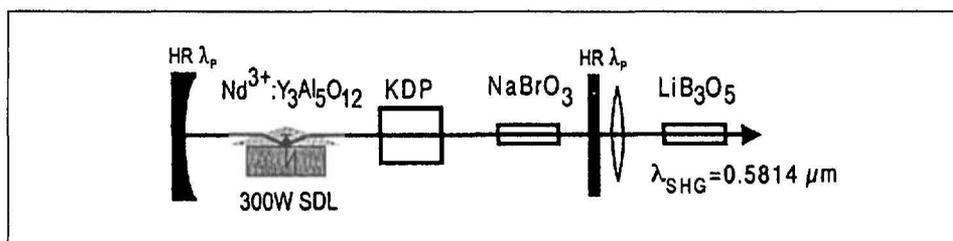


Fig. 5. Schematic view of the NaBrO_3 SRS laser set up [14].

organic crystals and polymers. A field that was opened by our activities during this year [17].

4. Conclusions

Absorption, emission and scattering properties of a particular valence state of ions or molecular entities can give access to wavelengths of interest in many fields of applications. In this respect, high-quality crystals and glasses play an important role. Although there are already systems that are considered for real-world applications, there is still more to be explored than can be reported here. Particularly, the field of SRS effects in organic crystals just started to become elaborated.

Here, crystal growth is generally facilitated because there is no real need for growing polar structures.

Ideas are around – much will, however, depend on the number of students who become interested in spending days and sometimes nights growing crystals, adjusting mirrors *etc.* for the demonstration of lasers. Although computer skills are very important in performing science nowadays, main progress in my field is nevertheless attained by people with practical skills we can be proud of.

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