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Title: CERAMIZATION IN (Ba1-XMx)Al2Si2O8 CELSIAN SOLID SOLUTIONS OF HEAVY METALS AND RECYCLING AS PIGMENTS

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Corresponding Author: Dr. Guillermo Monrós, Dr.

Corresponding Author's Institution: Jaume I University

First Author: Guillermo Monrós, Dr.

Order of Authors: Guillermo Monrós, Dr.; Carina Gargori, Dr; Sara Cerro, Dr; Natalia Fas, Graduate; Mario Llusar, Dr

Abstract: Ceramization of several heavy metals such as M=Cr, Fe, Co and Ni in celsian lattice has been studied by sintering up to 1500°C of its oxides with BaCO3, Al(OH)3 and SiO2 in order to obtain (Ba1-XMx)Al2Si2O8 solid solutions. Cr3+ enters in solid solution forming anionic vacancies up to x=0.5 (both celsian and hexacelsian coexists), Fe3+ and Co2+ only up to x=0.1 (both celsian and hexacelsian coexists) and melts at higher x values, Ni only forms solid solution at low x=0.02 coexisting hexacelsian and celsian, at higher x crystallizes NiAl2O4 spinel. But using forming glasses mineralizers such as borates increase the reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding 10wt% of glass forming agent at only 1000°C/3h of sintering temperature. Powders have been reused as ceramic pigments and leachate test is performed in order to classify the resulting solid solution in order to its landfill disposal (Council Directive 1999/31/EC on the waste landfill).

Suggested Reviewers: Jeús M Rincón Dr
CSIC, glassceramics, CSIC
rinconjma@gmail.com
Expert on ceramics

Joao Labrincha Dr
Associate Professor, Ceramics Engineering, University of Aveiro
jal@ua.pt
Expert on ceramics and wastes

Javier Alracón Dr
Dr, Inorganic Chemistry, University of Valencia
Javier.Alarcon@uv.es
Expert on ceramic pigments.
Highlights.

- Heavy metals have been immobilized in celsian (Ba$_{1-x}$M$_x$)Al$_2$Si$_2$O$_8$ solid solutions.

- Borates have been used as mineralizers obtaining monophase celsian at 1000°C/3h.

- Solid solutions act as ceramic pigments in ceramic glazes.

- Solid solutions have been evaluated by leachate test for its landfill disposal.
CERAMIZATION IN (Ba_{1-x}M_x)Al_2Si_2O_8 CELSIAN SOLID SOLUTIONS OF HEAVY METALS AND RECYCLING AS PIGMENTS

C. Gargori, S. Cerro, N. Fas, M. Llusar, G. Monró

Dpt. Of Inorganic and Organic Chemistry, Jaume I University, Castellon (Spain)

Abstract.

Ceramization of several heavy metals such as M=Cr, Fe, Co and Ni in celsian lattice has been studied by sintering up to 1500°C of its oxides with BaCO_3, Al(OH)_3 and SiO_2 in order to obtain (Ba_{1-x}M_x)Al_2Si_2O_8 solid solutions. Cr^{3+} enters in solid solution forming anionic vacancies up to x=0.5 (both celsian and hexacelsian coexist), Fe^{3+} and Co^{2+} only up to x=0.1 (both celsian and hexacelsian coexist) and melts at higher x values, Ni only forms solid solution at low x=0.02 coexisting hexacelsian and celsian, at higher x crystallizes NiAl_2O_4 spinel. But using forming glasses mineralizers such as borates increase the reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding 10wt% of glass forming agent at only 1000°C/3h of sintering temperature. Powders have been reused as ceramic pigments and leachate test is performed in order to classify the resulting solid solution in order to its landfill disposal (Council Directive 1999/31/EC on the waste landfill).

Key words: Heavy metals, Solid solution, Celsian, Ceramic pigment.

1. Introduction.

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 g/l, their toxicity depends on several factors including the dose, route of exposure, and chemical species, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals [1]. For an effective immobilization of wastes by sintering (ceramization), ceramic oxide materials such as perovskite (CaTiO_3), zirconolite CaZrTi_5O_{12}, hollanidite (Ba_{0.23}Al_{2.46}Ti_{5.54}O_{16}), pyrochlore (Ln_2Zr_2O_7 and Ln_2Ti_2O_7, Ln = rare earth metals), NASICON (Na_{1+x}Zr_{2-x}P_{3-x/2}Si_{x}O_{12}) and sphene (CaTiSiO_3), have gained tremendous interest in the eighties because of their application as the geological medium for the immobilization of radioactive wastes due to the stacking of the metal-oxygen polyhedra in their structure results in the formation of cavities and vacant interlayers capable of accommodating a large number of radioactive cations [2]. With a similar cation distribution to hollanidite Ba_{1/2,23}Al_{2/2,46}Ti_{5,54}O_{11/2} (monoclinic, point group 2/m, space group I2/m), celsian BaAl_2Si_2O_8 (monoclinic, point group 2/m, space group I2/c), is a feldspar, although its symmetry is somewhat different: the order in the Celsian is simple, each tetrahedron AlO_4 is surrounded by four SiO_4 tetrahedra and vice versa, the Ba shows an irregular configuration with 10 neighbours equidistant. This disorder induces a low symmetry and increases the kinetic barrier of nucleation, in fact the Celsian has a metastable polymorph, the Hexacelsian or hexagonal celsian composed of a double alternating sheet of tetrahedra (AlSi)O_4 [3,4]. In this communication the immobilization of several heavy metals such as M=Cr, Fe, Co, Ni in celsian system has been studied by sintering up to 1500°C of its oxides with BaCO_3, Al(OH)_3 and SiO_2 in order to obtain (Ba_{1-x}M_x)Al_2Si_2O_8 solid solutions.

2. Material and methods.

By the solid state conventional method or ceramic method (heat and beat, shake and bake) solid
solutions \((Ba_{1-x}M_x)Al_2Si_2O_8\ x=0.02, 0.1, 0.5, 1.0\) and \(M=\text{Cr, Fe, Co, Ni}\) into celsian lattice has been studied by sintering up to 1500°C the metal oxides \((\text{Cr}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Co}_3\text{O}_4\) or \(\text{NiO})\) with \(\text{BaCO}_3, \text{Al(OH)}_3\) and \(\text{SiO}_2\) (quartz) as precursors in order to immobilize the metals into the celsian crystal lattice. In the ceramic method the precursors were homogenised in a planetary mill in acetone media. When acetone was evaporated the raw powders were successively fired at 800°C, 1000°C, 1200 °C and 1500°C with a soaking time of 3 hours and with free cooling to room temperature. The as-prepared powders were homogenized manually with mortar and pestle. The resulting powders were 5 wt% glazed into a conventional ceramic glaze of the \(\text{CaO-ZnO-SiO}_2\) system for double firing stoneware (1050°C) in order to characterize its pigmenting properties.

Samples were characterized by the following techniques: a) X-Ray Diffraction (XRD) carried out on a Siemens D5000 diffractometer using \(\text{Cu K}_\alpha\) radiation, 10-70 °20 range, scan rate 0.02 °20/s, 4 s per step and 40 kV and 20 mA conditions, b) UV-Vis-NIR spectra of fired powder samples and of 5 wt% glazed samples collected using a Jasco V670 spectrometer through diffuse reflectance technique, c) \(L*a*b*\) color parameters of glazed samples measured following the CIE-L*a*b* (Commission International de l’Eclairage) colorimetric method (29) using a X-Rite SP60 spectrometer, with standard lighting D65 and 10° observer. On this method, \(L*\) is a measure of lightness (100=white, 0=black) and \(a^*\) and \(b^*\) of chroma (-\(a^*\)=green, +\(a^*\)=red, -\(b^*\)=blue, +\(b^*\)=yellow), d) Microstructure characterization of powders was carried out by Scanning Electron Microscopy (SEM), using a Leo-440i microscope supplied by LEYCA.

In the case of cobalt solid solution \(x=0.1\), two leach test were performed: (I) a weight ratio of powder:water=1:5 was stirred a room temperature during 24h simulating the conventional washing procedure of ceramic pigments before its commercialization, and (II) the as dried (a) whased powders with a weight ratio powder:water=1:16 were stirred a room temperature during 24h in order to classify the resulting solid solution for its landfill disposal (Council Directive 1999/31/EC on the waste landfill).

3. Results and discussion.

XRD evolution of crystalline phases for samples \((Ba_{1-x}M_x)Al_2Si_2O_8\ M=\text{Cr, Fe, Co, Ni}\) with temperature is shown in Table 1. Results indicate that \(\text{Cr}^{3+}\) enters in solid solution forming anionic vacancies up to \(x=0.5\) (both celsian and hexacelsian coexist), \(\text{Fe}^{3+}\) and \(\text{Co}^{2+}\) only up to \(x=0.1\) (both celsian and hexacelsian coexist) and melts at higher \(x\) values, \(\text{Ni}\) only forms solid solution at low \(x\) =0.02 coexisting hexacelsian and celsian, at higher \(x\) crystallizes \(\text{NiAl}_2\text{O}_4\) spinel. In the case of \(\text{Co}\) the XRD patterns are shown in Figure 1.a. The reactivity of the powders can be increased using forming glasses mineralizers such as borates (boric acid or sodium perborate); in the case of \(\text{Co-celsian solid solution},\) monophasic monoclinic celsian is obtained adding 10wt% of glass forming agent at only 1000°C/3h of sintering temperature as it can be observed in Figure 1.b.

Powders have been reused as ceramic pigments and leachate test is performed in order to classify the resulting solid solution in order to its landfill disposal (Council Directive 1999/31/EC on the waste landfill). Table 2 displays the visual colour and CIEL*a*b* colour parameters of powders and 5wt% glazed tablets into a double firing frit (1050°C). Samples with \(x=0.02\) and 0.1 don’t show colour showing \(L^*\) values higher than 80 except \(\text{Co}\) that show light blue colour in \(x=0.02\) and blue colour \(L^*a^*b^*=57.4/1.8/-22.4\) in \(x=0.1\). In \(x=0.5\) and \(x=1\) samples Iron and Cobalt melt, \(\text{Ni}\) powders show turquoise colour that turns in green colour in the glaze, finally \(\text{Cr}\) samples produce green coloured powders and green glazed tablets. Figure
2.a displays the UV-Vis-NIR spectra of glazed samples (of powders fired at 1500°C) and SEM micrograph of the x=0.1 corresponding powder: Co samples show bands associated to Co(II) in tetrahedral coordination (5), Fe samples show bands associated to Fe(III) in octahedral coordination (6), Cr glazed samples show Cr(III) in octahedral coordination (7) and finally Ni glazed tablets show Ni(II) in octahedral sites (7). Figure 2.b shows the UV-Vis-NIR spectra of M=Co mineralized by progressive addition of acid boric (from 0 to 10 wt%) fired at 1000°C before leachate I and SEM micrographs of 0% and 10% addition of H₃BO₃. The UV-Vis-NIR absorption increases with the addition of the mineralizer and the feature of SEM images indicates that sintering of powders is similar in 0% and 10% addition of H₃BO₃.

Table 3 shows the obtained results of leachate tests (I) and (II) for (BaₓCoₓ₋₃Al₂Si₂O₈ mineralized by progressive addition of acid boric (from 0 to 10 wt%) fired at 1000°C. In order to its landfill disposal the leaching limits of the “COUNCIL DECISION of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills” (minimum pH=6) and the Spanish “Real Decreto 849/1986 del reglamento del Dominio público Hidráulico” (pH between 5.5–9.5 and boron 10 ppm) has been considered. pH and conductivity were measured with pH-meter and conductimeter (both supplied by Crison) respectively, boron has been measured by azometine optical spectroscopy at 410 nm in a Jasco spectrometer, cobalt was measured by ethyl ether extraction of the blue complex Co(SCN)₄²⁻ by addition of NH₄SCN to the leachates. On leachate II the Microtox™ test based on Photobacter phosphoreum (Vibrio fischeri) bioluminiscence inhibition was performed. The results indicate a decrease on the screening measurement for Microtox™ test which always is lower than 25% (indicating a EC50 higher than 3000) and good inertization of cobalt (always over the detection limit by the Co(SCN)₄²⁻ assay) but the presence of boron increases with mineralizer addition and exceeds the limit of 10 ppm, then although mineralizer increase the reactivity it contravenes environmental criteria.


Immobilization of several heavy metals such as M=Cr, Fe, Co and Ni in celsian lattice has been reached by sintering up to 1500°C of its oxides with BaCO₃, Al(OH)₃ and SiO₂ in order to obtain (Baₓ₋₃Mₓ)Al₂Si₂O₈ solid solutions: up to x=0.5 for Cr³⁺, Fe³⁺ and Co²⁺ only up to x=0.1 and Ni only at x=0.02. Using forming glasses mineralizers, such as borates, increase the reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding 10wt% of glass forming agent at only 1000°C/3h of sintering temperature. Powders have been reused as ceramic pigments and leachate test has been performed in order to classify the resulting solid solution in order to its landfill disposal. Co produces adequate blue pigmenting shades and both Cr and Ni, green colours in conventional double firing frit (1050°C). The addition of boron mineralizers increase the reactivity but from leachate tests, although a decrease on the screening measurement for Microtox™ test and good inertization of cobalt is detected, boron exceeds the limit of 10 ppm, then the use of boron mineralizer contravenes environmental criteria.

Acknowledgement.

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References


Figure 1. XRD patterns of samples: a) \((\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8\) \(\text{M}=\text{Co}, x=0,02\) and 0.1 powders fired at 1500°C, b) the composition (a) with additions of boric acid (wt%) fired at 1000°C. CRYSTALLINE PHASES: Q (Quartz SiO\(_2\)), U (Unidentified), F (Hexacelsian), M (Celsian BaAl\(_2\)SiO\(_3\)).
Figure 2. UV-Vis-NIR spectroscopy of glazed samples: a) \((\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8\) fired at 1500°C and SEM micrograph of the \(x=0.1\) corresponding powder, b) \(\text{M}=\text{Co}\) mineralized by progressive addition of boric acid (from 0 to 10 wt%) fired at 1000°C, SEM micrographs of 0% and 10% addition of \(\text{H}_3\text{BO}_3\).
<table>
<thead>
<tr>
<th>Sample</th>
<th>800°C/3h</th>
<th>1000°C/3h</th>
<th>1200°C/3h</th>
<th>1500°C/3h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ba_{1-x}Cr_x)Al_2Si_2O_8</td>
<td>Q,W(s)BA(w)</td>
<td>Q(s) BA(m) H(vw) CF(w)</td>
<td>Q(w) BA(m) CF(s)</td>
<td>F(s)M(m)</td>
</tr>
<tr>
<td>x=0.02</td>
<td></td>
<td>Q(w) BA(m) F(s)</td>
<td></td>
<td></td>
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<tr>
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<tr>
<td>x=1</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>(Ba_{1-x}Fe_x)Al_2Si_2O_8</td>
<td>Q,W(s)BA(w)</td>
<td>Q(s) BA(m)BS(vw)CF(w)</td>
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<td></td>
</tr>
<tr>
<td>x=0.02</td>
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<td></td>
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<td></td>
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<tr>
<td>x=0.1</td>
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<tr>
<td>x=0.5</td>
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<tr>
<td>x=1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ba_{1-x}Co_x)Al_2Si_2O_8</td>
<td>Q,W(s)BA(w)</td>
<td>Q(s) BA(m)BS(vw)CF(w)</td>
<td></td>
<td></td>
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<tr>
<td>x=0.02</td>
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<tr>
<td>x=0.1</td>
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<tr>
<td>x=0.5</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>x=1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ba_{1-x}Ni_x)Al_2Si_2O_8</td>
<td>Q,W(s)BA(w)</td>
<td>Q(s) BA(m)BS(vw)CF(w)</td>
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</tr>
<tr>
<td>x=0.02</td>
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<tr>
<td>x=0.1</td>
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<tr>
<td>x=1</td>
<td></td>
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</tbody>
</table>

**Table 1.** XRD evolution of crystalline phases for samples \((\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8\) with temperature.

CRystalline phases: W (Witherite \(\text{BaCO}_3\)), Q (Quartz \(\text{SiO}_2\)), BA (\(\text{Ba}_2\text{AlO}_4\)), BS (\(\text{Ba}_2\text{SiO}_4\)), BS2 (\(\text{Ba}_2\text{Si}_2\text{O}_8\)), HE (\(\alpha\)-Fe\(_2\)O\(_3\)), CO (corundum, \(\text{Al}_2\text{O}_3\)), B (Bunsenite NiO), NA (Ni\(_2\)AlO\(_4\)), MU (Mullite \(\text{Al}_2\text{Si}_3\text{O}_9\)), CR (Cristobalite SiO\(_2\)), E (\(\alpha\)-Cr\(_2\)O\(_3\)), H (Hashemite \(\text{BaCrO}_4\)), U (Unidentified, F( Hexacelsian), M (Celsian \(\text{BaAl}_2\text{Si}_2\text{O}_8\))

Peaks intensity: s(strong), m(medium), w(weak), vW(very weak).
Table 2. CIEL*a*b* measurements for powders and 5wt% glazed tiles of \((\text{Ba}_{1-x} \text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8\) samples fired at 1500ºC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x= 0.02</th>
<th>x=0.1</th>
<th>x=0.5</th>
<th>x=1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba}_{1-x} \text{Cr}_x)\text{Al}_2\text{Si}_2\text{O}_8 &amp; powder</td>
<td>88.5/-2.1/2.7 white</td>
<td>81.9/-4.6/4.9 cream</td>
<td>54.3/-4.8/4.4 dark green</td>
<td>62.3/-9.6/8.9 green</td>
</tr>
<tr>
<td></td>
<td>glazed</td>
<td>80.3/4.5/11.6 white</td>
<td>74.2/0.8/14.8 cream</td>
<td>49.3/-5.9/8.1 green</td>
</tr>
<tr>
<td>(\text{Ba}_{1-x} \text{Fe}_x)\text{Al}_2\text{Si}_2\text{O}_8 &amp; powder</td>
<td>89.2/-0.2/3.0 white</td>
<td>71.6/7.0/13.2 pink</td>
<td>melts</td>
<td>melts</td>
</tr>
<tr>
<td></td>
<td>glazed</td>
<td>81.6/5.2/10.4 white</td>
<td>79.3/6.8/13.1 light pink</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Ba}_{1-x} \text{Co}_x)\text{Al}_2\text{Si}_2\text{O}_8 &amp; powder</td>
<td>76.2/-2.4/-23.5 Light blue</td>
<td>62.4/-2.2/-29.8 blue</td>
<td>melts</td>
<td>melts</td>
</tr>
<tr>
<td></td>
<td>glazed</td>
<td>73.3/0.3/-3.4 light blue</td>
<td>57.4/1.8/-22.4 blue</td>
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<tr>
<td>(\text{Ba}_{1-x} \text{Ni}_x)\text{Al}_2\text{Si}_2\text{O}_8 &amp; powder</td>
<td>84.4/-4.1/-11.8 light blue</td>
<td>80.9/-7.0/-4.0 light blue</td>
<td>63.7/-12.5/-7.4 turquoise</td>
<td>58.4/-11.2/-4.6 green</td>
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<td>glazed</td>
<td>79.7/3.8/8.8 white</td>
<td>76.2/4.4/14.2 cream</td>
<td>59.6/-5.0/9.0 green</td>
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</table>

Table 3. Results of leachate test (I) and (II) for \((\text{Ba}_{0.9} \text{Co}_{0.1})\text{Al}_2\text{Si}_2\text{O}_8\) mineralized by progressive addition of boric acid (from 0 to 10 wt%) fired at 1000ºC.

<table>
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<tr>
<th>% (\text{H}_3\text{BO}_3) addition</th>
<th>TEST</th>
<th>pH</th>
<th>Cond. (µS)</th>
<th>B (ppm)</th>
<th>Co (ppm)</th>
<th>MICROTOX (screening)</th>
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<tbody>
<tr>
<td>0</td>
<td>I</td>
<td>12.82</td>
<td>990</td>
<td>5</td>
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<tr>
<td></td>
<td>II</td>
<td>8.63</td>
<td>316</td>
<td>3</td>
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<td>13.26%</td>
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<tr>
<td>2</td>
<td>I</td>
<td>11.22</td>
<td>3300</td>
<td>48</td>
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<td></td>
<td>II</td>
<td>8.67</td>
<td>432</td>
<td>47.9</td>
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<td>11.76%</td>
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<tr>
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<td>1386</td>
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<td>II</td>
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<td>2450</td>
<td>56</td>
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<td>8.69</td>
<td>1043</td>
<td>55.4</td>
<td>ND</td>
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(*) ND: Not Detected by Co(SCN)\(_2^+\) test.